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Radioactive and other environmental contamination from uranium mining and milling

1

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1.1 Introduction

Mining of uranium-bearing ores dates back to the Middle Ages in Central Europe, although the target metals were silver, gold, or copper. Pitchblende encountered was dumped as waste. Pitchblende was targeted only in the early twentieth century for its radium content, and small-scale mines were operated in England (Cornwall), Portugal, and the Erzgebirge (Ore Mountains), namely in Joachimsthal, now Jachimov in the Czech Republic. The interest in uranium for military and later energy uses sparked prospecting and exploration activities all over the world from the 1930s onward, which increased significantly in intensity as the nuclear arms race gained momentum. Exploration activities lessened after the 1960s, but mining continued to increase until the end of the 1980s. The end of the Cold War led to a significant drop in demand for uranium, while surplus military uranium was fed into the energy market, making only the most efficient mines with the highest ore grades commercially viable (OECD-NEA/IAEA, 2014). From the 1990s onward, many uranium mines all around the world were closed, and their legacies began to be addressed (OECD-NEA/IAEA, 1999). With production (mainly for military use) being the paradigm, environmental impacts and long-term safety at the sites were largely neglected. This resulted in considerable environmental legacies, not only in former Eastern Bloc countries, but also, for example, in the United States (IAEA, 2000b). Some of these legacies had already been addressed in the Western countries from the 1970s onward, following the generally increasing awareness of industrial and other environmental contamination. The size of the problem in the Eastern Bloc and former Soviet Union countries became apparent only post-1990. The majority of mines were dedicated to uranium, but some mines co-mine(d) uranium together with other metals. A notable example is Olympic Dam in Australia (OECD-NEA/IAEA, 2014), which, at current uranium prices, is mainly a copper mine. Due to the depletion of high-grade deposits that are easily accessible, mining can be expected to move to lower-grade deposits, resulting in larger waste volumes, and to deeper, more difficult-to-mine deposits.

Section 1.2 of this chapter will provide an overview of the various life-cycle stages of uranium production, together with their associated residue streams and impacts. Section 1.3 discusses life-cycle management with a view to minimizing impacts. Section 1.4 discusses the existing uranium production legacies and their management. Finally, Section 1.5 provides an overview of future trends in uranium mining and processing.

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1.2 The front end of the nuclear fuel cycle

1.2.1 Exploration of uranium resources and resulting waste streams

Exploration, at least in its more advanced stages, involves invasive techniques such as drilling and sampling. Drilling results in waste streams and other impacts that need to be managed adequately. Country-specific legislation for permission of drilling will cover many of these aspects. The drilling process, depending on the techniques used, results in drill chippings, mud, and cores that need to be managed to avoid environmental contamination and exposure of drilling rig personnel. A borehole may penetrate formations that not only contain uranium below a grade of interest, but also heavy metals and other elements of concern, such as arsenic. Drilling mud may contain additives (e.g., to adjust viscosity) and may also be contaminated by oils from the rig and other substances that may be harmful, when dispersed in the environment. The resulting chippings and contaminated drilling mud must be collected and, if necessary, disposed in a licensed facility. As a borehole may penetrate several water-bearing strata before reaching the target formation, it will have to be sealed carefully at each formation once the necessary samples have been taken and the borehole logging is complete. To avoid cross-contamination between different formations, the borehole may need to be cased temporarily during the drilling operation. If the borehole pene-trates radionuclide-bearing formations, radiation protection measures will have to be put into place to protect the crew from direct exposure to material recovered.

Certain geophysical exploration techniques can also disturb the environment. Seismics may require the drilling of boreholes for the explosives charges, and the blast itself may disturb fauna and people. The access to land with heavy vehicles may already disturb sensitive environments and leave long-lasting traces (Figure 1.1).

Figure 1.1 Traces of 1950s uranium exploration campaigns as seen in 2004 in Cañonlands National Park (Utah, USA).
Photograph: W.E. Falck.

Responsible exploration and mining companies today operate near-zero-disturbance exploration sites. In some cases, for example, in very sensitive environments such as the arctic permafrost, drilling installations are put onto elevated pads that isolate them from the environment (Wollenberg, 2011). All wastes are carefully collected and returned to adequate management or recycling facilities.

1.2.2 Uranium mining techniques and their waste streams and impacts

1.2.2.1 Mining techniques

The mining technique used at a given site depends on a wide variety of factors, such as the depth and extent of the mineralization, the host rock type, the grade of mineralization, but also on the socioeconomic and geographical settings (IAEA, 2000a). Open-cast mining is applied to shallower and more extended mineralizations, whereas underground mining is better suited to deeper and more compact ore bodies. *In situ* leaching (ISL) is gaining importance in world uranium production. Each technique results in specific waste streams and impacts.

Open-cast mines require large amounts of overburden to be removed and stored for later backfill. This kind of mining is generally viable only when the overburden consists of softer and less-cohesive geological materials. Due to the need to maintain safe slope angles, which depend on the consistency of the material, the footprint and land disturbance of open-cast mines is considerably larger than the mineralized zones. In consequence, the volume of the mine that needs to be dewatered is usually much larger than for a comparable deep mine (Figure 1.2) and can be of enormous extension. It may result in issues, such as water wells falling dry and acid mine drainage (AMD) when sulfide mineral–bearing strata become exposed to the atmosphere. It should be noted that these issues are not unique to uranium mining, but do occur in any type of open-cast mining. Continuous backfilling of mined-out parts will help to alleviate some of the problems: it helps to reduce the operational footprint of the mine, prevents aeration of sulfide-bearing strata, reduces the volume to be dewatered, and reduces the need for slope maintenance. To ensure geochemical compatibility, the overburden should be brought back into the pit in the same sequence as the natural geological layers (cf. Figure 1.7). The topsoil would be set aside for later use in recultivation (IAEA, 2010).

Underground mining results in smaller volumes to be excavated and dewatered and, hence, a smaller surface footprint of the mine (Figure 1.2). This comes at the price of higher geotechnical and workplace risks and the need to provide for ventilation against radon build-up. The layout and actual mining technique depends on the shape and location of the ore body as well as the type of host rock. For mine safety reasons, at least two shafts have to be sunk or access tunnels (inclines) dug. In practice, there may be more shafts and additional drill holes not only to provide access but also for ventilation purposes. In strong rocks, the drifts and other types of access tunnels may remain unlined, whereas in weaker rocks such "permanent" mine opening may need to be secured by linings. Liners will reduce the groundwater inflow and, hence, the amount of potentially contaminated and acidified waters to be managed. Liners

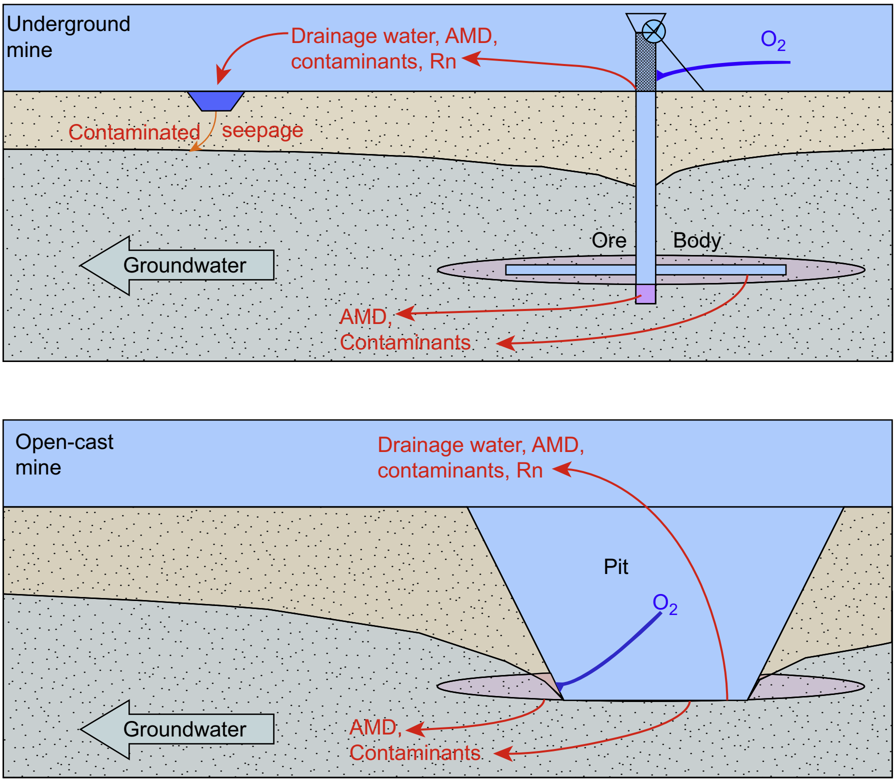

Figure 1.2 Environmental impacts associated with different types of mines. AMD, acid mine drainage.

also reduce the radon burden in the mine air and thus the amount of radon emitted from ventilation shafts. Leaving mined-out areas to collapse is a practice that becomes less and less acceptable, because of potential surface effects and because it will make groundwater management more difficult after mine closure. Backfilling the mined-out areas counteracts these issues and at the same time reduces the amount of excavated material that needs to be lifted to the surface. Backfilling and sealing off mined-out areas also reduce the radon burden in the operating part of the mine and, hence, the ventilation needs.

In both cases, in an open-cast and a deep mine, the excavated ore will be brought to the surface for further processing in an industrial plant. To reduce the amount of material to be lifted, there will be some presorting underground. A refined sorting or screening will take place before the material enters the processing plant. In modern mines, much of the ore dressing is moved underground so that only the material that will be milled has to be lifted.

The efficiency of the milling process, the reagent consumption, and the commercial viability of the mill depends on the ore grade. Ore that is considered subgrade at a given moment may be subject to heap leaching (see below) or stockpiled. Such

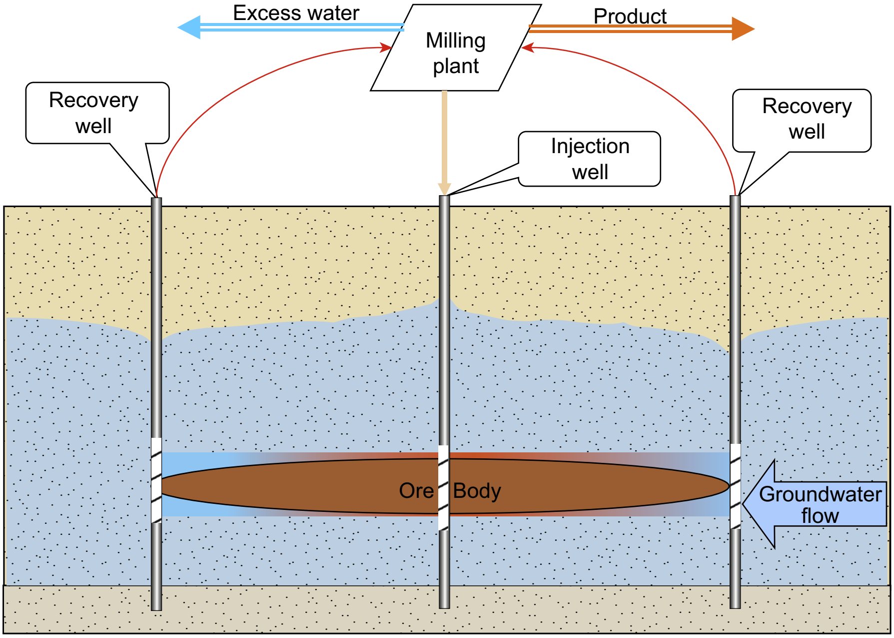

Figure 1.3 The principle of *in situ* leaching (ISL) mining.

stockpiles may become of commercial interest if the price for yellow cake increases. In some cases, however, mines were closed before the ores stockpiled on the surface became commercially viable and as a consequence have become an environmental legacy (see Section 1.4).

ISL, also called *in situ* recovery or solution mining, is a technique that is considered to have a number of advantages over conventional excavation (IAEA, 1989, 1993, 2004a; USNRC, 2001, 2003) and the number of ISL mines has increased in recent years (OECD-NEA/IAEA, 2014). The main advantage is that no overburden, barren rock, and gangue need to be removed. The technique consists of drilling a number of wells that serve as injection and recovery wells (Figure 1.3). A well screen controls the inflow of groundwater into the mine area and prevents the outflow of contaminated fluids (IAEA, 2001a) by maintaining a slight drawdown cone. Although an ISL mine results in much less groundwater drawdown than conventional mines, the leaching solutions will be difficult to remove from the formation at the decommissioning stage. Well drilling results in some waste potentially contaminated (see the section on exploration) that needs to be managed. There will also be excess water to be discharged after treatment to remove any contaminants and process chemicals (IAEA, 2002d). The lixiviant can be either acidic or alkaline solutions, sometimes with oxidizing agents added. Acid ISL mines are much more frequent than alkaline ISL operations (OECD-NEA/IAEA, 2014), as commercially viable uranium mineralizations often are associated with permeable sandstones. Uranium mineralizations in carbonaceous rocks, in which acids would attack the bulk host rock, are much less frequent

(IAEA, 2005c). ISL requires a certain permeability of the ore/host rock (which can be increased by hydraulic fracking) and accessibility of the uranium minerals within the matrix. Although ISL mines produce relatively small amounts of operational waste, their closure and remediation pose significant challenges. Contamination of aquifers, either associated with the ore or above and below the mineralized zone, has been of concern (USNRC, 2001). However, mining the mineralized zone by conventional methods is likely to have more severe overall impacts, both on site and off site. One may also note that groundwaters from ore-bearing strata may not be useable in any case for human or animal consumption, due to high natural concentrations of salinity and toxic constituents that are costly to remove.

In some mines, namely in the former GDR (Hähne & Altmann, 1993) and in the Czech Republic (Fiedler & Slezák, 1993), traditional underground mining was combined with solution mining. Here the mineralized zones were hydraulically isolated by horizontal and vertical well screens drilled from drifts underground. Internal surface areas were increased by controlled blasting. Acid was circulated through these "blocks" to leach the uranium without bringing the ore to the surface.

1.2.2.2 Mining waste types

Both deep and open-cast mines produce a considerable variety of wastes that need to be adequately managed to minimize environmental impacts and exposures.

Open-cast mining requires vast amounts of overburden to be removed. The amount generated depends on the geotechnical stability of the pit slopes. The less cohesive the material is, the more material has to be removed to arrive at sufficiently shallow slopes. It needs to be noted that under operational conditions, with continuous maintenance, slopes can be steeper than what is permissible after closure (see below). Depending on the size and depth of the pit, it may be possible to continuously backfill excavated material as it is being removed. Topsoil requires special attention to maintain its function as vegetation substrate. It is stored separately to be available for later recultivation of the pit area and spoil heaps, among other purposes.

Most open-cast mines have to manage large quantities of mine waters. Unlike in underground mines, controlling water inflow is possible only by backfilling, which will reduce the volume to be dewatered.

Underground mining results in excavated rock from sinking shafts and opening up drifts and other types of tunnels being brought to the surface. The form and consistency of the mine waste generated depends on the type of rock excavated and on the mining technique. As hoisting material to the surface is costly, modern mining aims to reduce this amount and to re-use excavated material underground. However, for a deep mine targeting a relatively small mineralized zone, this may not be feasible, as not enough underground storage space may be available.

The distinction between what is mineable ore and what is gangue depends on the available milling technology and also on the market price of yellow cake that determines the commercially viable ore grade. In consequence, subgrade ores will arise and typically are stored separately from other excavated materials, awaiting increasing market prices.

The amount of drainage water to be managed depends on the hydrogeological setting and on the permeability of the host formations. Water ingress can be reduced by casing of shafts and lining (e.g., with shotcrete) of nonproducing mine openings, as well as backfilling mined-out areas. These drainage waters come from different formations, including the mineralization itself, that will have been altered by the ingress of atmospheric oxygen. This will result in AMD so that the waters cannot be simply discharged, but need to be treated. Treatment aims at raising the pH values and at the removal of toxic or radioactive constituents as well as contamination from oils and explosive residues. The resulting treatment sludges require adequate conditioning and disposal. Some of the mine water will be reused as process water either in the mine itself or in the mill.

Radon exhalation and accumulation in the mine openings may be a workplace exposure problem. Forced ventilation will remove gaseous radionuclides (radon, thoron) from the mine, but the exhausts have to be adequately dispersed so as not to cause inadmissible exposures of the adjacent environment and its population.

A problem frequently encountered in mining areas is the unauthorized or ignorant use of mining residues. The loose material found on spoil heaps, for example, leads to its use as an aggregate in construction. When such an aggregate is used in buildings, any radionuclide content may lead to exposure to radon or even direct doses inside the buildings (USEPA, 2008; Chapter 4).

ISL mining will result mainly in wastes from drilling the array of injection and recovery wells. The processing of the pregnant solution will result in additional wastes that will be discussed in the section on milling. Protective wells that keep a depression cone in the water table around an ISL mine will have to discharge the excess water. As in other mines, these waters may be acidified due to sulfide mineral–bearing strata becoming exposed to the atmosphere after the lowering of the water table.

1.2.2.3 Mining impact pathways

Uranium mining is a practice that is controlled by both the applicable national radiation protection legislation (IAEA, 2002b) as well as mine safety and other workplace safety regulations. Impacts from industrial-type accidents are not discussed in this section, which focuses on environmental impacts. Relevant environmental impacts may arise from radionuclides (Chareyron, 2008), as well as from other constituents in mine host rocks or foreign materials introduced by the mining operation.

Liquid effluents in the form of drainage and leachates may contain elevated concentrations of radionuclides, heavy metals, and other toxic or noxious substances. These can include explosive residues, oils, fuels, and other compounds introduced by the mining operation. Mine effluents need to be treated to comply with discharge standards in force at the mine site (IAEA, 2002d). Treated effluents may be used to reduce water stress on vegetation over the depression cone and to augment affected surface water courses.

AMD generation is a major concern in the mine itself and in spoil heaps or other mine wastes, resulting in pH values as low as 2 in some cases (Nordstrom & Alpers, 1999). Although only a small fraction of the mine wastes may contain radionuclides in relevant concentrations, there may be other metals and minerals of concern. AMD results from the percolation of oxygenated surface waters through geological materials underground or in wastes that contain sulfidic minerals, such as pyrite. Although the acidity in itself would have an impact on aquatic life when discharged without prior neutralization, it also results in the dissolution of minerals that contain toxic or radioactive elements, including heavy metals and arsenic, for instance.

Radon and thoron in the mine air are due to the presence of uranium minerals in the ore and adjacent formations. The outgassing of ^{222}Rn and ^{220}Rn from stockpiled subgrade ore or other uranium-bearing rocks in mine waste heaps can be an issue, in addition to emission by the mine ventilation. The impact on the surrounding environment depends on the meteorological conditions and the topographic setting. It is possible that radon-enriched air becomes trapped in valleys due to meteorological inversion; for example, a layer of cold air is overlain by warmer air, resulting in reduced circulation and exchange and, hence, dilution (Steck, Field, & Lynch, 1999). This may result in elevated doses to the local populations.

Dust is raised by the action of wind from (uncapped) mine wastes and from the walls of open pits. Significant amounts of dust may also be raised during poorly controlled blasting operations in open pits. The dispersed dust can spread contamination by radionuclides and other toxic compounds. The dust may settle on residential and agricultural areas, leading to direct exposure or exposure through ingestion, for example, from agricultural and horticultural products. Dust washed off by rain may enter surface water courses and be further dispersed. Dust may be also leached out, with the contaminants being taken up by the vegetation or eventually reaching the groundwater table.

Erosion will affect uncovered and unvegetated spoil heaps and similar disposal sites that may have little erosion resistance. During rainfall events, fine-grained material will be washed out and may eventually reach streams. The accumulating bottom sediments can be re-eroded and further dispersed downstream, taking with them any heavy metals, radionuclides, and other contaminants. Inadequately placed heaps can also be prone to direct erosion by streams. Geochemical mining signatures can be found far downstream in surface water courses that drain catchment areas with mining activities.

Geotechnical issues occur in all mines, whether deep or open-cast, including uranium mines. If the deep mining technique involves letting collapse mined-out areas, the process of collapsing can cause small local earthquakes. Subsidence can occur over collapsed areas that may result in damage to buildings and other infrastructures. A major issue is the stability of slopes within open pits and of mine waste heaps. Slumping slopes or dams can affect areas outside the licensed mine area, damaging or destroying infrastructure and buildings. Strong and/or persistent rainfall events may compromise slope stability by increasing water contents of the geological materials beyond safe levels. The same problem can arise in open-cast mines, when groundwater levels rise. Raising porewater pressures may lead to ground instability. The collapse of slopes can lead to the dispersal of contaminants.

Carbon emissions. Mining is an energy-intensive process, and a wide variety of sources contribute to greenhouse gas (GHG) emissions. In open-cast mines, the majority of mobile machinery is powered by diesel engines running on liquid fossil fuel. Underground combustion engines in vehicles may run on liquified natural gas or may be electrically driven. Stationary machinery usually is powered by electric motors. Depending on the location of the mine, the electricity is generated locally, for example, by diesel generators, or supplied by local or regional power stations. Large mines may have dedicated power stations. The carbon balance of a uranium mine and mill (Falck, 2009) depends on the power generation technology (thermal, hydropower) and on the fuel used (oil, gas, coal, nuclear). Recent research, for example, in the context of the I^{2}Mine project (http://www.i2mine.eu), looks into capturing the carbon emitted from machinery underground.

1.2.3 Uranium ore milling, its waste streams, and associated impacts

1.2.3.1 Ore processing

Milling. The ore extracted from underground or open-pit mines is transported to the mill typically by wheeled vehicles. The ore is sorted according to the grade and subgrade pieces may be sent for stockpiling. The rocks are crushed and ground to a small and uniform particle size to increase the surface area for the following leaching process. Unless the host rock is carbonaceous, an acid solution is used, usually sulfuric acid. The sulfuric acid is brought in or produced on site, depending on the location and available transport options. Some sulfidic ores may not require the addition of acid. An oxidizing agent, such as peroxide, may be added to help break down certain uranium minerals. The resulting slurry is stirred in reaction tanks. After a sufficient reaction time, the slurry is transferred into a settling tank and the supernatant solution containing inter alia the uranium is removed. The remaining solids are washed to further remove dissolved uranium. They are a fine suspension of particles and will be run through thickeners to remove the water for re-use. These residual solid materials are the so-called mill tailings and are disposed of in tailings management facilities.

There are different processes for recovering the uranium from the “pregnant” leaching solution. Sodium chloride, ammonium chloride, or ammonium sulfate are used as stripping solutions, or a nonaqueous liquid extraction process is used. Uranium is precipitated from the highly concentrated stripping solutions by the addition of ammonia, resulting in ammonium di-uranate (“yellow cake”). The choice of stripping process depends on the types and concentrations of other (heavy) metals dissolved by the leaching, with the intention of making the process as uranium specific as possible. There are also processes using solid ion exchangers to concentrate the uranium. The concentration processes result in waste solutions from which the unwanted metals are removed by neutralization/precipitation. The precipitates are disposed of together with the tailings, while the solutions may be re-used.

The uranium di-uranate slurry is concentrated in filter presses and then dried before packaging (usually in drums) for shipping as yellow cake to the enrichment (if applicable) and fuel fabrication process.

Potential impacts from milling plants include leaking tanks and pipework, dust generation, and radon emanation. In comparison with similar mills for other types of ore, uranium mills tend to be well maintained, as at least parts of them are “controlled practices” in a radiation protection sense.

Heap leaching. For low-grade ores, the process described above may not be sufficiently energy and materials efficient. Such ores may be put onto so-called leaching pads, that is, shallow ponds with drainage systems beneath. Acid or alkaline leaching solutions are continuously sprinkled over the heaps of subgrade ore, collected, and then sprinkled over the ore again until a sufficiently high uranium concentration is reached. The pregnant heap-leaching solution is processed into yellow cake, as described before.

ISL. *In situ* leaching combines mining and milling into one continuous process. Depending on the uranium concentrations achieved, the leaching solution is processed for uranium recovery or is recirculated and a certain portion split off for processing. The uranium is removed from the pregnant circulation fluid as described above. The barren leaching solution is returned to the ISL field for re-use. The ISL technique uses a range of chemicals to enhance the solubility of uranium underground and to adjust the pH of solutions (CO_2, NaOH, NH_4, H_2SO_4, HCl, Na_2CO_3), to precipitate the uranium ($BaCl_2$), to adjust the redox state (H_2S, Na_2S, H_2O_2), and to regenerate ion exchange resins used to recover the uranium (NaCl). As with any industrial plant, there is the risk of pipe and tank ruptures and other kinds of spills that could have impacts on the environment or pose health and safety risks (USEPA, 2008; Appendix III).

1.2.3.2 Processing wastes

Mill tailings are the residual slurries from the wet processing and are the main wastes from conventional ore milling. They contain, inter alia, the nuclides ^{230}Th and ^{226}Ra, which are typically not removed by the milling process (IAEA, 2004b). They are disposed of in tailings management facilities that may also receive other waste streams, such as neutralization slurries. The different wastes may be mixed or emplaced at different locations within a tailings pond. The water content of tailings depends on the thickening process and technology. Thickening is an energy-intensive step and is usually limited as much as possible. The mode of conveyance from the mill to the disposal site is another consideration when deciding on the water content: slurries can be easily pumped, whereas paste-like tailings need to be transported by conveyer belts.

A major long-term issue is the slow settling and dewatering of the tailings due to the colloidal nature of the finely ground particles. As the natural dewatering can take years or even decades, large volumes of ponds are needed, and decant water will need to be managed over long periods of time. Dewatering can be accelerated, for instance by wick drainages, but this is done mainly in a remediation context (see below). Re-cognizing this problem, industry has moved toward the so-called paste technology, that is, further thickened tailings (Dudgeon & Waite, 1999). Further dewatering leads to a disposal technique called “dry stacking”. These tailings cannot be pumped, but have to be transported to the management facility by conveyer belts. Low water-content tailings pose fewer engineering risks, such as dam failure (Luppnow, 2013). An added incentive is the recuperation of process water, which is encouraged for resources conservation reasons and may even be essential in arid environments with limited water supply (Figure 1.4). The main stream of tailings would have much of the acid–alkali-leachable constituents removed. However, the sludges from the stripping process will contain all non-uranium heavy metals and radionuclides.

It should be noted that such tailings arise from all wet milling processes for metal ores. They usually contain all (heavy) metals and radionuclides from the original ore, minus the target metal(s). As only the uranium will have been removed, the amount of radioactivity in them may still be considerable. Although the milling process does not increase the concentrations by weight compared to the original ore, it may have changed the mineralogical and chemical form, making constituents of concern more mobile. Modern ore processing tries to minimize the volume of waste streams (IAEA, 1999) and to render contaminants less mobile.

Decant waters from the tailings pond may contain radionuclides, (heavy) metals, and other toxic compounds, although the neutralization with limestone and the stripping process will have precipitated a considerable fraction of them. Operating tailings ponds are uncovered, and any atmospheric precipitation will add to the water balance. The decant water may also still be acidic, depending on the effectiveness of the neutralization step and whether there are any sulfide-bearing minerals left in the tailings (Metzler & Ritchey, 2011). As a consequence, decant water almost always has to be treated before being released into the environment. The resulting treatment sludges are returned to the tailings pond. While the treatment of the decant waters is part of the mill operation, it may pose considerable organizational and stewardship challenges after its closure. The use of passive treatment systems, such as constructed wetlands, has been proposed as a low-technology solution, but still requires the adequate management of the biomass that has accumulated the radionuclides and heavy metals (IAEA, 2004c).

Figure 1.4 Dry stacking of tailings in Arlit (Niger).
Photograph: W.E. Falck.

Auxiliary processes, such as the on-site production of sulfuric acid, will result in liquid and solid wastes. For the solid wastes, either dedicated impoundments are constructed, or they are disposed of in the tailings ponds. If the mine is close by, waste streams of similar types and disposal requirements may be combined.

Gaseous wastes, such as ventilation air, are normally released directly into the environment. They may need to be filtered to remove dust particles that can act as vectors for radioactivity. The resulting filter cakes need to be disposed of adequately in compliance with radiation protection and other environmental impact legislation. A discussion of the use of the atmosphere as a repository for oxidized carbon (CO_2, CO) and other GHG discharges is beyond the scope of this book.

1.2.3.3 Impact pathways from milling residues

As uranium ore milling is a controlled practice from a radiation protection perspective, workplace exposures are not discussed in this section, nor are industrial-type accidents that may occur during operation.

Geotechnical issues. Tailings are difficult-to-manage materials, owing to their high water content and uniform grain-size distribution (Figure 1.5). Unless paste technology or dry stacking (see above) is used, freshly deposited tailings are not stable and have to be retained in an engineered pond that relies on the stability of the surrounding dams (IAEA, 2004b). A breach of a dam, for example, due to erosion or ground instability, can have catastrophic effects (Azam & Li, 2010; http://www.wise-uranium.org/mdaf.html), such as flash floods and mud flows downstream. Tailings ponds may also overflow when the water management system breaks down or its capacity is exceeded due to persistent rainfall. Apart from the immediate physical

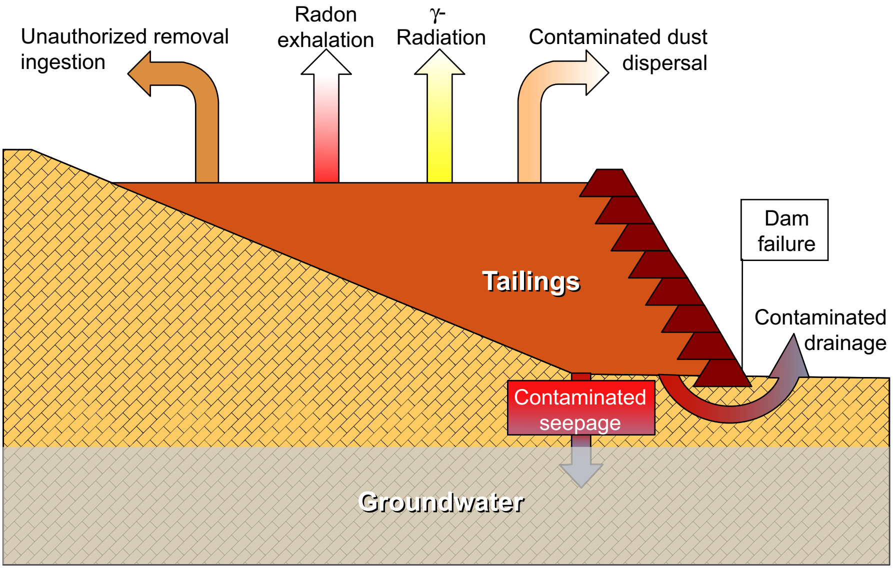

Figure 1.5 Potential environmental impacts from uranium mill tailings.

impacts, long-term problems will arise from any tailings mass dispersed into the surrounding environment. The tailings will be difficult to recover because of their amount and consistency. Long-term contamination of (agricultural) soils, contamination of groundwater due to infiltration of leachates, generation of contaminated dusts that can be inhaled and ingested, and direct exposure will be the results (Moncur, Ptacek, Blowes, & Jambor, 2005).

Dust. Particularly during the dry season, uncovered tailings may dry out sufficiently to give rise to dust dispersal. The dust may settle on surrounding fields and plants, opening up pathways for direct exposure by contact and for ingestion. Contaminants may be leached from the dust by atmospheric precipitation and may reach groundwaters. The dust may also be washed into surface water courses and may accumulate in bottom sediments, from where it may be eroded again and further dispersed.

Uncollected and untreated drainage will reach surface water courses and groundwaters. The drainage can have very low pH values, due to incomplete neutralization at the end of the milling process or due to secondary acidification by the oxidation of sulfur-bearing minerals (acid drainage) in the tailings. Acid drainage will promote the dissolution and migration of radionuclides and heavy metals. These contaminated waters may be ingested directly or used for irrigation purposes. Low-pH discharges into surface waters can also have an adverse impact on aquatic life.

Ventilation discharge points of the milling plant have to be selected so that a sufficient dilution by dispersion is ensured to prevent the local population from receiving impermissible doses from it. Uncovered tailings ponds may release radon and thoron, if the tailings still contain radionuclides of the relevant decay chain. Under quiet weather conditions, radon may accumulate in valleys or other topographical depressions, in which the ponds often are located, resulting in exposures further down-valley (Steck et al., 1999).

Residues, such as tailings, are attractive as aggregates for the preparation of concrete and there are various examples of unauthorized removal of such materials for construction purposes (USEPA, 2008; Chapter 4). This may result in direct exposures from walls or floors/ceilings and radon accumulation in homes. In other instances, tailings material and mining residues have been used to ameliorate garden soils, resulting in contaminants being ingested through food plants (Marks, Denham, Cross, & Kennedy, 1984).

1.3 Uranium mining and milling (UMM) legacy sites and their remediation

1.3.1 The scope of the issue

Since some mines and mills may have been in operation for many decades, sometimes with different operating companies, it is often not so easy to distinguish between sites that are part of the current operation and legacy sites. Although waste and residue management facilities that have been operated in the more distant past may not fulfill modern requirements with respect to environmental safety and thus may require remediation, they are part of the current operation (IAEA, 1997b). Therefore, the current operator is legally and financially responsible for their maintenance and eventual remediation. On the other hand, there are many uranium mining sites worldwide that technically have become “orphaned”, as the mine operator, often a state-owned company, has ceased to exist, particularly after the fall of the Iron Curtain in 1989. In most cases, the respective government has assumed responsibility for such sites. This does not necessarily mean that the government has the financial resources and technical capability for their remediation. Particularly in the former Eastern Bloc countries, such sites posed a threat to the environment and to the surrounding population (IAEA, 2005b; Jacubick, Kurylchyk, Voitsekhovich, & Waggitt, 2008), but also are of concern in the United States, with its many abandoned mines (USEPA, 2008; Chapter 5). International aid programs under the auspices of the European Union (EU) and the IAEA have helped to assess the extent of the problems and to implement solutions. In the United States, the Uranium Mine Tailing Radiation Control Act (UMTRCA, 1978) provided for the management of the uranium-mining legacies in this country.

To enumerate these sites is very difficult, as many of them have been mere experimental diggings and exist in most countries with uranium-bearing host rocks (OECD-NEA/IAEA, 1999). The multitude of such sites, not only in the Eastern Bloc countries, but also in the United States and various Western European countries, has necessitated a prioritization of actions based on risk assessments.

1.3.2 The objectives and limitations of remediation

The IAEA Safety Glossary (2007) defines remediation as “any measure that may be carried out to reduce the radiation exposure from existing contamination of land areas through actions applied to the contamination itself (the source) or to the exposure pathways to humans. Complete removal of the contamination is not implied. The often read terms rehabilitation and restoration may be taken to imply that the conditions that prevailed before the contamination can be achieved again, which is not normally the case (e.g., owing to the effects of the remedial action) and should not be used”. Remediation is an intervention. In radiation protection, an intervention is any action intended to reduce or avert exposure, or to reduce or avert the likelihood of exposure to sources that are not part of a controlled practice or are out of control as a consequence of an accident. The analogous applies to nonradiological contamination.

The goal of remediation is the timely and progressive reduction of hazard and eventually, if possible, the removal of regulatory control from the mining or milling site without restrictions (“free release”). Remedial measures should do more good than harm and should provide optimized arrangements for protection to maximize the net benefit to society. However, there are situations in which the removal of control from the area cannot practicably be achieved; in such cases, at least the unacceptable risks to human health and the environment should be removed while the sites remain under institutional control, that is, stewardship (see Section 1.4). The objective of remedial actions is to reduce the doses to exposed individuals or groups of individuals, to avert doses to individuals or groups of individuals that are likely to arise in the future, and to prevent or reduce environmental impacts from the radionuclides (and other contaminants) present in the contaminated area. These objectives will be achieved by either removing a hazard, for example, the source of contamination, or by modifying or interrupting the pathway of exposure, that is, by risk reduction. However, radiological contamination may often be of far less concern at uranium mining and milling (UMM) sites than other types of hazards.

1.3.3 Remediation strategies and techniques

A diverse portfolio of remediation strategies and techniques is available today that can be applied to uranium mining and milling sites (Figure 1.6). The baseline option against which other options are compared with respect to feasibility, effectiveness, cost, as well as public and regulatory acceptance is always monitored non-intervention (IAEA, 2006a; USEPA, 1999b, 2007a, 2007b). This option is based on the resilience of the surrounding environment against impacts from such sites. Sites that have been reasonably stable over several decades are likely to remain so and may not need immediate invasive attention. However, their likely long-term risk will have to be assessed.

Isolation. Many remediation techniques, on the other hand, aim to improve the resistance of the sites against the actions of the surrounding environment. Capping of mine wastes and tailings ponds reduces the ingress of precipitation and thus reduces the vector of contamination. It also reduces materials loss due to erosion and suppresses radon exhalation. Underground *in situ* barriers will reduce the spread of contaminants in to groundwaters. They may be needed around open-pit mines or to prevent downstream contamination from unlined tailings ponds. Permeable reactive barriers serve a similar purpose (Blowes, Bain, Jeen, & Hughes, 2008; Csövári, Földing, Csicsák, & Frucht, 2008; USEPA, 1999a), sometimes as part of a pump-and-treat scheme for contaminated groundwaters. Tailings ponds often release draining waters for decades due to the slow dewatering of the stacked material. Thus, the water has to be collected in engineered draining systems and treated before release. Low-technology solutions such as phyto-treatment plants have been tried out, but are not reliable under all conditions. A disposal route for the separated radionuclides and other contaminants has to be available. The engineering features that provide for isolation (e.g., dams, caps, liners) have to be maintained periodically to ensure their effectiveness, which provides particular stewardship challenges (see below).

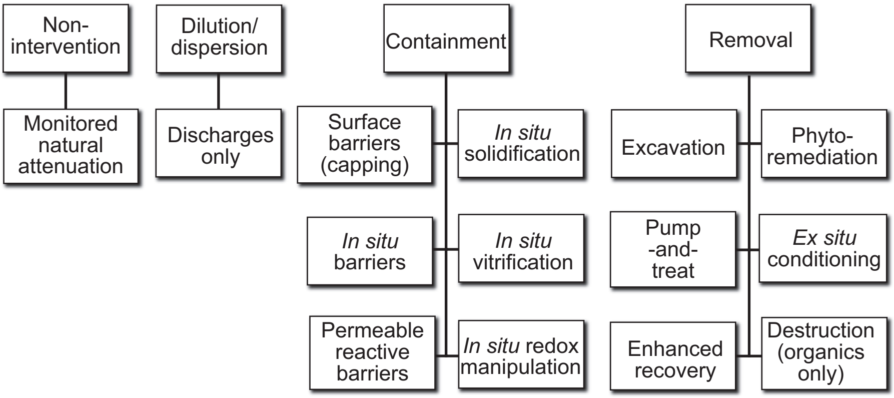

Figure 1.6 Conceptualization of remediation strategies.

Relocation. Excavation and relocation of mine waste or tailings would be undertaken only under rare circumstances due to the large volumes involved. For instance, the Lichtenberg open pit of the Wismut operation in Saxony (Germany) was backfilled with materials from various surrounding waste heaps (Figure 1.7). Another example of such a large-scale relocation operation is the tailings pond upstream from Moab (Utah, USA) (http://www.moabtailings.org) that is under the threat of erosion from

Figure 1.7 (a–c) Backfilling the open-pit mine Lichtenberg with material from various mine waste dumps. The waste material was selected such that the original geological sequence was reconstituted as far as possible.
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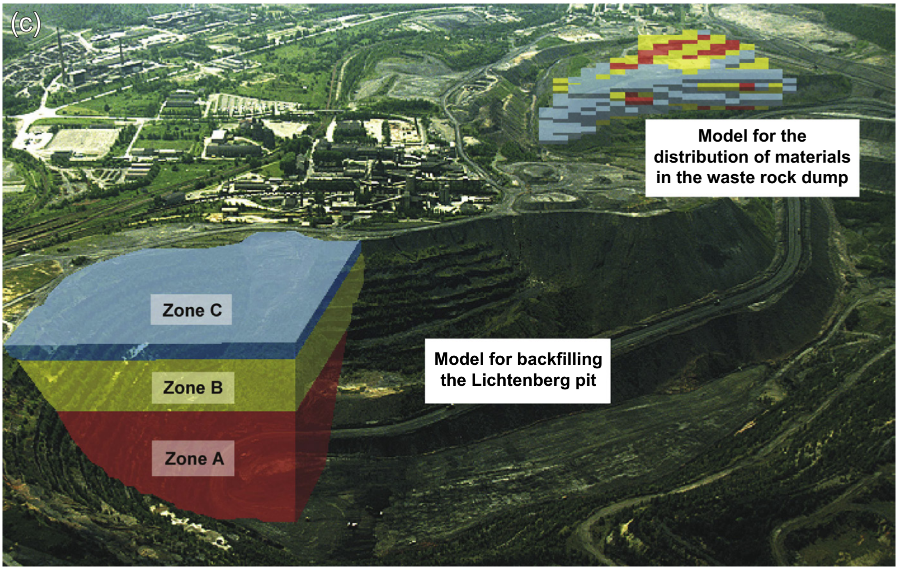

Figure 1.7 Continued.

the Colorado River. At many operations, smaller waste heaps and tailings ponds have been excavated and merged into larger ones, to reduce the number of sites for which institutional control stewardship activities are needed.

Reworking. Considering that extraction techniques were often less efficient in the past than they are today, the reworking of old tailings or below-grade ore dumps can be of economic interest, and they can form part of a remediation program or even its incentive. Whether it is a viable option depends on the specific local circumstances and the availability of a processing plant for the materials. The commercial viability may be further improved by the presence of other metals of interest that can be extracted. It is also important that the resulting residues are easier and safer to dispose of with reduced probability of remobilization of toxic constituents than the original residues.

1.3.4 Nontechnical considerations

The choice of remediation strategy and technology and associated stewardship programs is determined not only by technical and economic considerations, but also by their respective public acceptance (IAEA, 2002a). The granting of a “social license” (Thomson & Boutilier, 2011) for particular remediation projects will involve deliberations with respect to the envisaged future land use, residual risks, visual aspects of the sites, regulatory acceptability of the proposed technology, long-term liabilities/stewardship needs, and collateral impacts of the remediation process (Falck et al., 2014b; IAEA, 2006b). There have been cases in the past in which stakeholders (the public; political decision makers) objected to the continuation of uranium production as part of the remediation process. In consequence, solutions that are desirable from a technological or economic point of view may not necessarily find the required acceptance.

1.4 Life-cycle management of UMM sites

1.4.1 A change of paradigms

Uranium mining and milling projects, in line with the development in other areas of the raw materials industry, increasingly adopt a life-cycle management approach (Figure 1.8).

This means a move away from the "end-of-the-pipe" treatment of environmental and socioeconomic impacts (Falck, 2009). Life-cycle planning facilitates decommissioning and reduces the need for remediation (IAEA, 2009). Decommissioning and remediation costs are fully internalized, and hopefully few or no unresolved problems are left to future generations. Life-Cycle (Impact) Assessments also help to internalize noneconomic costs, which will result in less material being mined, less waste to be managed, and hence lower impacts downstream in the processes. A life-cycle perspective will also change the approach to facility design and operation. Facilities, particularly those for the management of residues, will be designed with their decommissioning and long-term stewardship in mind. In this way, these future challenges will already be considered at the design stage, rather than faced only at the closure stage. Overall, this should lead to lower long-term impacts.

1.4.2 Mining residues

In the management of mining and milling residues, one needs to distinguish the operational phase and the post-closure phase of the life cycle of mines and mills. In each phase, different objectives, criteria, and sets of technical parameters will guide the selection of management solutions (OECD-NEA/IAEA, 2002). The operational phase is characterized by continuous care and maintenance; in contrast, the post-closure phase solutions have to be selected that render the residues safe with a minimum of maintenance. In the past, these paradigms often have not been followed, resulting in legacy sites that may require remediation (see Section 1.4).

Overburden and barren rock is stored or disposed of at locations that minimize transport distances and according to the availability of land. The latter may not be a very constraining factor in remote, sparsely populated areas. There, a location that minimizes the risk from leaching-out contaminants may be chosen, avoiding zones of fractured bedrock or selecting areas with less pervious geological formations. A bottom liner may be needed to collect acid drainage and prevent it from seeping into surface and groundwaters. Such liners typically consist of compacted clay. Geomembranes may also be used. A gravel drainage or geotextile

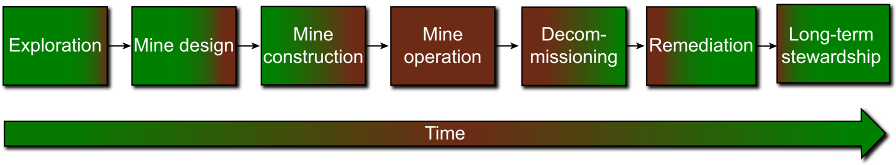

Figure 1.8 Life-cycle management approach for uranium mining and milling facilities.

layer above the liners will facilitate the collection of seepage waters for proper management. In practice, liners under spoil heaps do not seem to have been used very often in the past. Constraining factors include the cost of and availability of suitable lining materials, such as dense clays. The clays used have to be tested for their geochemical compatibility with the drainage waters, as these may degrade their beneficial properties.

The grading of slopes usually is chosen so as to minimize the footprint of the site. However, one may need to optimize between the cost of stacking higher and the footprint. The load-bearing capacity of the underlying geological strata may be a limiting factor for stacking height, as could be esthetic requirements. The grade of the slope is normally the one that develops naturally for a given type of material, moisture content, and compaction rate. Erosion tends to flatten these slopes, so that spoil heaps have to be maintained periodically to re-establish the desired angle. Once a decision has been made that no further mine waste will go into a particular facility, the slopes are graded to be comparable to those of the natural surroundings (IAEA, 2002b).

Erosion, acid drainage, and dust can have significant impacts, but they can be controlled by covering and vegetating inactive areas of spoil heaps. Covers and vegetation reduce the amount of rainwater infiltration and oxygen ingress. For the same reason, covers enhance the geotechnical stability of the slope. Covers can also be designed to trap radon and thoron and thus allow these to decay before they reach the atmosphere. The design of the covers has to be adapted to the surrounding ecosystems, its soil profile, and vegetation type. The cover design may range from a simple layer of rubble in arid areas to a complex sequence of layers that mimic the soil in the surrounding ecosystem (IAEA, 2006b). Periodic monitoring and maintenance ensure the integrity of cover and vegetation (IAEA, 2002c). The roots of trees and other plants can penetrate the covers and compromise their function, and therefore need to be removed. Likewise, burrowing animals, such as rabbits, can enhance the erosion of covers and need to be controlled. Layers of rubble are elements of cover design intended to discourage roots from penetrating and animals from building burrows. The effects of human penetration, accidental or intentional, may also need to be repaired. In areas of active disposal, the construction of such covers is not practical, but a cover with geotextiles that can be taken up before a new layer of waste is deposited may reduce the impacts noted above.

Subgrade ore that is retained for a time when its milling may become commercially viable needs to be stored under conditions that prevent auto-leaching by acid drainage formation. In other words, it needs to be covered, and bottom liners to collect contaminated drainage must be constructed. Alternatively the storage site may be designed as a heap-leaching facility (either with or without the addition of lixiviants), where the uranium-enriched drainage is collected and added to the milling process stream. The leached residues would be transferred to a spoil heap or co-disposed with the mill tailings. Subgrade ore that has not been milled by the time that a mine and mill are destined for closure may require special treatment to prevent impacts from auto-leaching. A capping, at least, needs to be put in place.

1.4.3 Mill tailings

Since waste management is an unproductive activity from a commercial point of view, operators understandably seek the least costly option for constructing tailings ponds that is in compliance with the applicable mining and civil engineering regulations (IAEA, 2004b). The use of natural depressions as sites for tailings ponds is an obvious choice. In hilly and mountainous terrains, often a valley was chosen and blocked off with a dam, behind which the tailings were emplaced. Sometimes small lakes are used for this purpose (subaqueous tailings disposal) or a mined-out pit. The rationale was that the temperature-induced stratification of a deep lake, with cold waters remaining at the bottom, would prevent any radionuclides and other constituents from entering the biosphere. A water layer above an active tailings pond would also delay radon escape until it decays (Courbet et al., 2013).

Where such landscape features are not available, above-ground tailings ponds surrounded by dams (“turkey nests”) have to be built. An infrequently used option is backfilling the tailings into underground mines. Paste tailings conditioned with binders would be most suitable for this (Moran, Christoffersen, Gillow, & Hay, 2013). Although the resulting backfill mass would have a low permeability and, therefore, low leachability, the addition of binders would be detrimental for the materials and energy balance of mining and milling operation. There are also concerns that the ^{226}Ra content could lead to enhanced radon concentrations in the mine air (Clausen & Archibald, 1983). For other tailings, the drainage waters would need to be managed adequately to prevent later impact on the flooding waters, once the mine is closed out.

Tailing ponds present a considerable engineering and long-term management challenge (IAEA, 2004b). Suitable dam materials and the construction of the retaining dams are important cost factors. Similar to hydropower and irrigation pond dams, these dams are in permanent contact with water and therefore need to be water-proofed. To distribute investments over time, dams are often built in stages and heightened according to operational needs. Different strategies to increase the height and minimize the use of additional building materials are used. Thus it is possible to built a new dam partly over the impounded tailings, if their dewatering has progressed sufficiently (Figure 1.5). An important factor to consider is the load-bearing capacity of the underlying strata. Dams also need to be keyed well into the sole and flanks of the valley to prevent them from being pushed out of place by the tailings mass. Injection curtains may be needed to prevent the flow of porewaters around the dam and through the surrounding rocks, thus compromising the keying-in of the dams. Like all earth dams, tailings dams are vulnerable to earthquakes. The engineered structures of tailings dams require constant monitoring and maintenance to ensure their integrity (IAEA, 2002c).

In the past, tailings ponds were typically built without bottom liners, using the permeability of the underlying ground to aid the dewatering. This means that untreated drainage waters entered the subsurface and reached the groundwater. Today, tailings ponds are constructed with liners and (bottom) drainage systems to collect the drainage water for treatment. A variant to this is the “pervious surround” system developed in Canada (Donald, Welch, Holl, & Landine, 1997). Here the tailings are dewatered and mixed with lime to achieve a permeability lower than that of the surrounding rocks.

This reduces the leaching-out of the material, albeit at the expense of an increased energy and materials footprint.

Naturally Occurring Radioactive Material (NORM)-containing tailings other than uranium mill tailings, for example, phosphogypsum, have been and still are being discharged into the sea, although this practice is being discouraged (IAEA, 2003).

1.4.4 Decommissioning of mines and mills

It has been common practice in mining, for centuries, to abandon the site, often including the surface structures, without any particular measures to decommission it. This has often resulted in orphan and legacy sites. The reason is that after the ore had been exhausted, the mining companies often ran into financial difficulties, and resources for an orderly closure were no longer available. Today, before a mine license is granted, some form of financial security, for example, bonds deposited, is usually required that will cover decommissioning and remediation costs (IAEA, 2006b). In practice, in many non-uranium mining examples, the objectives and purposes of remediation were not very well understood or acknowledged by either the operators or the licensing authorities, and the financial instruments were insufficient, allowing only for cosmetic actions such as revegetation. For modern uranium mining and milling projects, a full life-cycle management plan will be developed before any mining commences. The "polluter pays principle" is applied analogously to mine sites. Stepwise decommissioning of mined-out areas and filled waste management facilities distributes the cost and work over the operational time of the mine and mill, rather than accumulating it at the end of the lifetime (Falck et al., 2009; IAEA, 2009).

The orderly closure of both underground and open-cast mines aims at making safe the mine works themselves, as well as the residue management facilities (IAEA, 1994, 1995, 2010). The objective is to prevent uncontrolled ground movements, such as subsidence, and to ensure the slope stability of pits, waste rock dumps, and tailings ponds. Necessary measures may include backfilling and sealing of shafts and other underground mine workings. Before open mine works are closed, normally all materials potentially hazardous to the groundwater, such as oils, transformer fluids, and explosives, have to be removed and brought to the surface for orderly recycling or disposal. Slopes may need to be re-graded to a shallower inclination so as to reduce the risk of erosional losses of stability. Waste rock dumps are best covered and re-vegetated as soon as they are not needed anymore in the operation. This reduces end-of-operation remediation costs and can make use of existing mine infrastructure and personnel. Sealing and backfilling of mined-out areas has the objective to reduce groundwater circulation after flooding, thus reducing the leaching of hazardous substances and the AMD generation potential (IAEA, 1997a). Strategic sealing and backfilling during operation also reduces the radon load in the mine air and thus the ventilation needs and above-ground impacts.

Most mine operations are below the local groundwater table and require constant pumping to keep the mine dry. Over the years, this will have resulted in a considerable depression cone in the surrounding aquifers, particularly in the case of open-cast mines. Flooding of the mines has to proceed in a controlled way that allows the re-establishment of the pre-mining water table. Letting a mine flood in an uncontrolled way can have severe impacts on the surrounding hydrological regime. It may result in locally reversed groundwater flows and drying up of local rivers. It can also lead to AMD generation and dispersal. Uncontrolled flooding can also compromise the geotechnical stability of underground and open-cast mines due to an uncontrolled re-equilibration of stresses. The controlled flooding, particularly of open-cast mines, is a process that may take many years.

The closure, decommissioning, and remediation of ISL mines pose specific problems. The hydraulic regime established for the mine has to be maintained and operated as a pump-and-treat remediation facility; that is, the acidic leaching solution has to be neutralized and then re-injected into the ground (USNRC, 2007, 2009). This means that the uranium recovery plant will have to operate for several years beyond the commercially viable point. There has to be a disposal or market route for any metals (including uranium) removed during the neutralization step. The sale of the recovered metals can contribute to covering the decommissioning and remediation costs. Of particular concern are hydraulic shortcuts among several aquifers, some of which may be used for drinking water abstraction. Although the host rock may not have been suitable for drinking water production in any case, differences in hydraulic head may lead to cross-contamination into aquifers without mineralizations along inadequately sealed boreholes. This is not a problem specifically associated with ISL systems, however. The shafts of deep mines may also penetrate several aquifers and need to be sealed when the mine is decommissioned and flooded.

Above-ground structures of the mine and mill need to be decontaminated, if necessary, before they can be demolished and removed. Decontamination will ensure that most of the materials can be recycled or re-used. Whether foundations and similar structures have to be removed depends on the planned future land-use for the site. In some cases, infilling may be sufficient. When designing new facilities, decommissioning needs can already be taken into account. This will facilitate the eventual decommissioning.

Remediation of mining and milling facilities often is a long-lasting process and may require a variety of installations to handle and treat materials (IAEA, 1998). The careful integration of decommissioning and remediation will often facilitate both processes (IAEA, 2009). During decommissioning only those plants, structures, and buildings will be removed that are not needed anymore. Conversely, certain installations of the mine and the mill can be used for managing wastes and residues that arise out of remediation and decommissioning activities. These typically include sorting, water treatment, and conditioning plants. Certain buildings and infrastructure, such as the power and water supply, will be retained until the remainder of the project is completed. This integration will reduce the decommissioning and remediation costs by creating synergies (Falck et al., 2009).

1.4.5 Long-term management (stewardship) of UMM sites

Any man-made structure above ground has significant amounts of potential energy stored in it. The second law of thermodynamics mandates that this energy be dissipated unless more energy is spent on maintaining the status quo. In other words, such structures require maintenance forever (IAEA, 2006b). When designing waste disposal sites it is therefore wise to minimize the amount of potential energy stored in them, for instance, by going underground (Figure 1.9).

The classical engineering paradigm in waste disposal is to design structures to contain wastes. This inevitably introduces chemical and physical potentials into the environment, as the structures are made from alien materials and the wastes themselves are alien materials (Figure 1.10). UMM residues management not only is an engineering task, but requires a good understanding of the long-term geological, geochemical, and hydrological processes in the host geology. Adaptation to the local situation will help

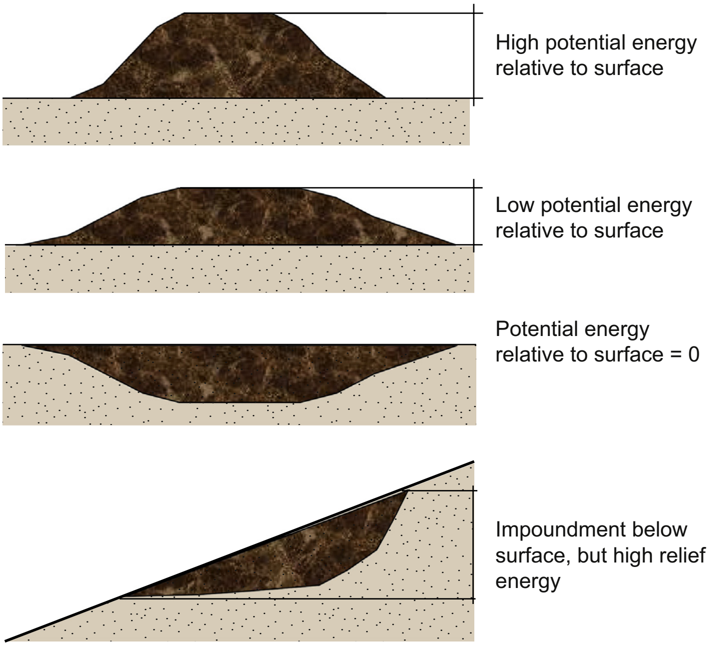

Figure 1.9 The paradigm of engineering with nature, not against it.
From IAEA (2006b) with permission.

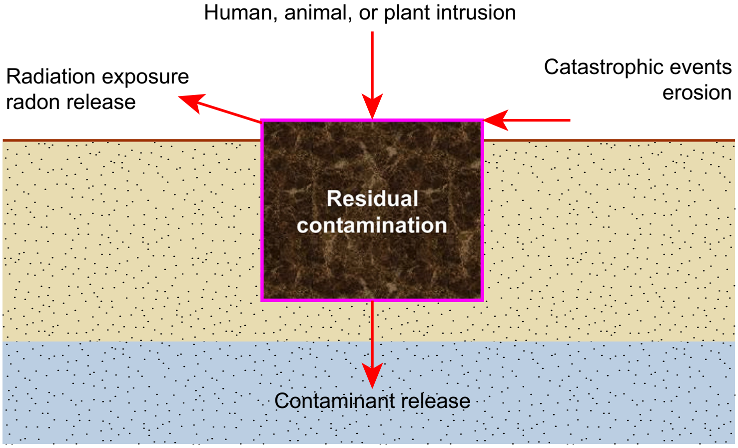

Figure 1.10 Long-term stewardship challenges.
Modified from IAEA (2006b), with permission.

to extend the time horizon over which the various potentials will be dissipated, perhaps well beyond a time horizon over which active maintenance can reasonably be expected.

Modern approaches to mining, including uranium mining, are based on a full life-cycle approach. In this, plans are made for the long-term management and long-term safety of such sites right from early days of project development. This allows, for instance, introduction of long-term stable engineering solutions, thus preventing costly re-engineering and remedial actions. Assessing all material flows over the life cycle will help to reduce the amount of materials moved around, which will also result in cost savings. Modern mining process engineering under development (see, e.g., the I^{2}Mine project, http://www.i2mine.eu) aims to reduce the amount of unwanted materials brought to the surface with a view to reducing the amount of material requiring long-term management. A life-cycle energy and material flow assessment will also help to reduce the overall impact of UMM operations.

Given that any engineered surface structure, such as tailings ponds or (covered) residue heaps, will require periodic monitoring, surveillance, and maintenance after their closure and after active UMM has ceased (IAEA, 2002; Kreyssig, Sporbert, & Eulenberger, 2008), the question arises as to who will be responsible for these. The same question arises for (near-)surface radioactive or hazardous waste repositories and has been debated extensively in this context (OECD-NEA, 2007). Looking back in history, it is rather unlikely that a certain government structure or other institution will survive beyond a 100-year time frame. There are notable exceptions, in which institutions and their infrastructure actively survived for hundreds of years, such as the Christian Church, the Academie Française, the British Monarchy, and others. There are also many counter examples for institutions that persisted for centuries and then have disappeared, particularly over the past 50 years or so. One can note that there is always a special spiritual relationship between the public and the institution and perhaps also its physical infrastructure (OECD-NEA, 2007). However, it is nearly impossible to deliberately create such spiritual long-term relationships; they develop, or do not develop, naturally. Reflecting on these difficulties, organizations such as the OECD-NEA (OECD-NEA, 2010) and the IAEA (IAEA, 2006b) came to the conclusion that, rather than focusing on lengthy time scales, it is better to focus on a horizon of two to three generations (=30–60 years), rather than on “archaeological” (=1000 + years) or even “geological” (=10,000 + years) time horizons.

1.5 Future trends

1.5.1 Impacts as a function of the resource type

Uranium mining, in line with other metal mining, is likely to move toward lower ore grades and deeper deposits, as the richer and shallower deposits have been mined out. The majority of uranium mineralizations that have been mined in the past and that are currently mined are associated with sandstones, although considerable mineralizations may be also found in more difficult-to-mine hard rocks. Projections on the likelihood of discovering rich deposits vary (OECD-NEA/IAEA, 2012), but it cannot be ruled out that rich deposits are found, considering the relatively low prospecting expenditure since the late 1970s, compared to that for oil and gas, for instance (Falck, 2009).

Such deposits, however, would be at greater depth than those mined currently. Lower ore grades mean that more material has to be moved and processed, which in turn results in potentially greater impacts, as impacts are related to the amount of material mined. For these reasons, the construction of new open-cast mines is becoming less likely in the future. Therefore, the associated large-scale impacts due to the need for managing large volumes of overburden will become less. Mine operators will balance the economic, operational, and other advantages or disadvantages of bringing materials to the surface against using them as backfill underground. Life-cycle impact analyses increasingly will inform the decision-making processes (Falck, 2011).

1.5.2 Improved deep mining operations

Not bringing mined-out material to the surface improves the energy balance of the operation, but may have certain operational disadvantages, as intermediate storage volumina have to be found underground. Use of tailings as backfill would obviate the need for surface tailings ponds, but has higher energy requirements due to longer transport routes, the need for more complex modes of conveyance, and certain conditioning needs. These are issues that arise not only in the uranium mining industry, but in any type of mining industry. They are currently the subject of various national and international research projects, including the European Commission 7th Framework project I^{2}Mine (http://www.i2mine.eu). This project investigates the implications of having to mine deeper and in harder rocks. The energetic requirements for mining and milling hard rocks are certainly higher than for other types of rock, such as sandstones. The project also aims at developing techniques and procedures for moving at least part of the milling process underground. In consequence, the mining and milling residues will remain underground. It is anticipated that the development toward less visible mines will be honored by stakeholders with an easier process to obtain the "social license to operate" (Falck et al., 2014a). In any case, licensing of uranium mines remains a challenge (IAEA, 2001b).

To reduce exposure of the miners to the harsh environment in deep mines, modern mines are likely to be more remotely operated whenever possible. In some modern uranium mines (e.g., Cigar Lake in Canada), this development is already taking place, due to the high dose rates received otherwise by miners.

1.5.3 Increasing importance of in situ *leaching (ISL) operations*

Nearly two-thirds of the uranium produced now is produced from ISL mine operations (OECD-NEA/IAEA, 2014). This trend is likely to continue, as long as mineralizations in porous host rocks can be mined. ISL is not feasible where the uranium minerals form a constituent of a largely impermeable rock matrix. In matrices, such as granites, even permeability-enhancing techniques, such as fracking, would not provide sufficient access to the uranium minerals that need to be dissolved. Otherwise, given diligent process control by the operator and adequate regulatory oversight, ISL has the potential for low-impact mining (NRC, 2009). From a resource use–efficiency perspective remains the concern that the percentage of uranium recoverable from the formation by ISL is smaller than when using traditional mining techniques. This is a problem that is also faced by other mining industries that use ISL, namely, the copper mining industry, and research and development efforts are being made to improve the effectiveness of the process.

1.5.4 Changing paradigms in the mining industry as a whole

Not the least by facing increasing difficulties to obtain the social licensing, the mining industry aims to avoid the mistakes of the past that have created long-term liabilities (Waggit, 2011). The construction of surface repositories for mining and milling residues probably can never be completely avoided, but the amount of material disposed of in these repositories can be kept to a minimum and the materials can be made more inert. A full life-cycle approach to designing and managing mines and mills will help to reduce the need for stewardship after the end of the operation. Although mining and environmental legislation do exist in many countries, regulatory oversight and the enforcement of legislation often leaves much to be desired, particularly in some less-developed countries. Many uranium mining companies operate globally and thus are under the scrutiny of globally operating environmental NGOs as well. European Union regulations stipulate that mining companies that have their legal seat in the EU have to comply at their overseas operations with EU standards and regulations. Large mining companies also subscribe to voluntary standards of environmental and social conduct, for example, through the International Council on Mining and Metals (ICMM) (http://www.icmm.com). Of concern, however, are the many so-called “junior” mining companies that often operate only one mine with a short lifespan. For them, there is little incentive to comply with voluntary codes of conduct and good practice. Such mines still have the potential to become “orphaned” at some stage, although the license to operate may have been coupled with deposits for remediation.

As has been noted above, a fully comprehensive life-cycle management approach becomes increasingly the planning guideline in the mining industry, including the uranium mining industry. This leads to the anticipation of (environmental, societal) problems before they actually manifest themselves, rather than their remediation. The improved internalization of life-cycle costs of producing uranium will lead to less cost that has to be borne indirectly, for example, through tax payers’ money being used for legacy management. Avoiding sources of impact will also avoid the associated impacts, the costs of which are usually impossible to internalize in retrospect.

1.6 Sources of further information

Probably the largest body on technical and regulatory guidance for uranium mining can be found in the various publications produced by the International Atomic Energy Agency (IAEA), namely, in their Nuclear Fuel Cycle and Materials, Waste Technology, and Waste Safety Sections, respectively (http://www.iaea.org). Many of the more recent and important publications are listed in the references section below.

Together with the OECD–Nuclear Energy Agency (http://www.oecd-nea.org), the IAEA also produces the so-called “Red Book” on uranium resources and demand that details the various uranium production activities in their Member

States (OECD-NEA/IAEA, 2012). The work is supported by the so-called "Uranium Group" of experts from the respective countries.

To facilitate the exchange of knowledge among practitioners, regulators, and other interested stakeholders, the IAEA set up a network of experts under the name ENVIRONET (Fernandes & Carson, 2011).

The International Mine Water Association (http://www.imwa.info) brings together many important players in mining, consulting, and research, some of whom have a uranium mining background.

A comprehensive resource on uranium mining projects worldwide is the Web site of the privately operated World Information Service on Energy—Uranium Project (http://www.uranium-wise.org).

Recognizing its legacy of UMM sites, the United States passed, in 1978, the so-called Uranium Mill Tailings Radiation Control Act (UMTRCA), resulting in the UMTRA project (see, e.g., http://www.nrc.gov/reading-rm/doc-collections/fact-sheets/mill-tailings.html). Since then, a large body of remediation experience, mainly in arid areas, has been accumulated.

One of the most daunting tasks in terms of remediation was faced in Germany by the states of Saxony and Thuringia, following the decision in 1989 to abandon uranium mining. The state-owned successor company (http://www.wismut.de/en/) to the former mining company has accumulated a wealth of experience in the area of remediation.

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Note: extensive use was made of IAEA reports because they summarize the current state of knowledge at the time of their writing, including many case studies, contain many further references, and are easily accessible through the Internet.

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Radioactive contamination and other environmental impacts of waste from nuclear and conventional power plants, medical and other industrial sources

2

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2.1 Introduction: radioactively contaminated sites and other environmental impacts from nuclear and radioactive installations

The use of radioactive materials for a variety of purposes has resulted in contamination of sites (i.e. land areas, including structures, soils, rocks, surface and ground waters, etc.) worldwide. The radionuclides involved may have been produced for a variety of reasons, including research, industry, medicine or warfare (the last item, although predominant in some countries, is beyond the scope of this chapter). In terms of radiological impacts on the environment, the airborne, liquid-borne and solid wastes from fuel cycle facilities, especially nuclear power plants (NPPs), are prevailing over impacts from other industrial activities.

The affected sites can range from small localized areas in urban environments (e.g. a radium factory located downtown in the early 1900s) to larger areas encompassing many tens or hundreds of square kilometres (e.g. in case of such accidents as Chernobyl or Fukushima). Figure 2.1 shows an abandoned building in the Chernobyl exclusion zone. The source of the radioactive contamination may come from a known activity at the site, and the radionuclides involved may be known. Records may provide information about the radionuclides involved and their likely fate. Alternatively, a chance discovery may have revealed the presence of contamination, with no other information available. In case of a severe accident, the types, amounts and physical–chemical characteristics of effluents are unknown a priori. It could be that the site is populated and that immediate steps must be taken to control damage, or that people are relocated and there is sufficient time to undertake investigations and take remedial action.

These and other differences mean that each contaminated site must be treated as a unique situation, taking into account its own particular circumstances.

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Figure 2.1 Abandoned apartment building in the contaminated area near Chernobyl.

2.2 Environmental impacts from nuclear power plant radioactive effluents

Nuclear energy has long been recognized as a leading energy source that produces minimal pollution to the environment. As of December 31, 2013 there were 434 commercial nuclear power reactors operating in the world and 72 units under construction (IAEA, 2014). Although it is known that commercial NPPs release small amounts of radioactivity into the environment, there is still some potential for these releases to contaminate the environment. In addition, recent events at several NPPs in the United States involving unplanned releases, especially tritium, have led to increased scrutiny on monitoring and evaluating releases.

Many of the radioactive isotopes that are released are in the form of gaseous or liquid effluents and solid radioactive waste conditioned by the plant (Harris, 2011). Three categories of radioactive by-products are produced during routine operation of a commercial reactor: fission products, neutron activation products and tritium. Fission products are created as a result of the radioactive decay of the nuclear fuel and out-leakage to reactor systems. Although there is a large quantity of fission products formed, many have little impact on the radioactive releases to the environment because of their extremely short half-lives, small quantities or biological insignificance. Gaseous fission products important to these releases include noble gases (krypton and xenon), iodine and tritium. Other fission products may appear in the gaseous effluents as particulates (mostly Cs and Sr radioisotopes).

Activation products are formed by neutron interactions with oxygen in water and air, with nitrogen and argon in air, and with impurity corrosion elements. Like fission products, many of the neutron activation products produced are insignificant in reactor effluents because of their short half-lives or small quantities. Relevant gaseous activation products include ^{13}N, ^{14}C, ^{16}N and ^{41}Ar. Among airborne corrosion products ^{60}Co is generally predominant, with others including ^{51}Cr, ^{58}Co and ^{59}Fe. The same isotopes appear in liquid and solid wastes.

Figure 2.2 Stack at G1 reactor being dismantled.

Tritium is produced as a result of both nuclear fission (ternary fission) and neutron activation of deuterium. A significant source of tritium is the interaction of high-energy neutrons with boron. Boron is used in PWRs for shim control (as boric acid) and in BWRs as a burnable poison. Tritium is also formed from the interaction of neutrons with ^{6}Li (as lithium hydroxide in water treatment).

Each NPP has its own waste-processing facilities to properly treat the gas and liquid wastes generated during operation. The waste treatment process includes filtering, clean-up, storage, decay and dilution, depending on the characteristics of the wastes and its radioactivity. When the radioactivity of the waste has diminished to a very low level, it would be released to the environment on condition that it would not exceed the permissible limit. The gaseous waste is released to the environment after treatment, usually via the stack. Figure 2.2 shows the dismantling of the G1 reactor stack at Marcoule, France. The liquid waste after treatment is diluted with other effluents from the plant before being discharged to the sea or a watercourse.

Typically, the radioactive emissions from operating NPPs result in insignificant doses to the general population. The annual doses estimated for critical groups used for licensing and effluent control of NPPs are, in most countries, constrained by an annual dose limit of 200–300 μSv, but actual doses are generally much lower. Table 18 in USCEAR (2008) provides dose data for NPP radioactive releases in 1998–2002, normalized to energy generation. The collective dose due to airborne releases is estimated at 0.22 person-Sv/GW-a, and for liquid releases, 0.05 person-Sv/GW-a.

In addition to washout of radioactive particulates and vapours discharged to the atmosphere, and deposition of liquid-borne radionuclides, the potential principal sources of radioactive contamination of land on an NPP site are as follows (Hill, Steeds, & Slade, 2001):

- Leakage from surface or underground pipes carrying liquid radioactive effluents;
- Leakage from effluent storage tanks;
- Leakage from spent fuel storage ponds;
- Radionuclide migration from old waste storage facilities, particularly those underground (vaults, pits, silos).

The main contaminants from all of these sources are fission and activation products, i.e. beta- and gamma-emitting radionuclides such as ^{137}Cs, ^{60}Co and tritium. For NPPs in normal operation, environmental contamination from alpha emitters is usually negligible.

At operational power stations, contamination is of concern because of the health risks that it can present to individuals working on the site, its potential to move off-site to pollute surface waters or groundwater, and, when off-site, its potential to present health risks to the general public.

Some radionuclides also accumulate in flora and fauna.

A review of epidemiological studies of cancer in populations near nuclear facilities showed that in all scientific reports analysing NPPs, a cause-and-effect relationship between cancer risk and radiation exposure could not be found.

2.3 Environmental impacts from coal power plant radioactive effluents and solid waste

Over the past few decades, the general public has become increasingly wary of nuclear power because of concern about radiation releases from normal plant operations, plant accidents and nuclear waste. Except for a few nuclear accidents, releases have been found to be almost undetectable in comparison with natural background radiation. Partly because of these concerns about radioactivity and the cost of containing it, the public and many electric utilities have preferred coal combustion as a power source. This preference is surprising for two reasons. First, coal combustion produces carbon dioxide and other greenhouse gases that are suspected to cause climatic warming, and it is a source of sulphur oxides and nitrogen oxides, which are harmful to human health. Second, although not as well known, releases from coal combustion contain naturally occurring radioactive materials – mainly, uranium and thorium. This factor suggests that coal combustion can be more hazardous to health than nuclear power, and that it may add to the background radiation burden even more than does nuclear power. It is likely that if radiation emissions from coal plants were regulated as for NPPs, their capital and operating costs would increase, making coal-fired power less economically competitive.

Trace quantities of uranium in coal range from less than 1 part per million (ppm) in some samples to around 10 ppm in others. Generally, the amount of thorium contained in coal is greater than the amount of uranium. Using these data, the releases of radioactive materials in a typical plant can be calculated. Assuming that coal contains uranium and thorium concentrations of 1.3 ppm and 3.2 ppm, respectively, each typical plant releases 5.2 t of uranium and 12.8 t of thorium in a given year (Gabbard, 1993). UNSCEAR (2008) gives a range of 5–300 Bq/kg for radioactive concentrations in coal. The main sources of radiation released from coal combustion include not only uranium and thorium but also daughter products produced by the decay of these isotopes, such as radium, radon, polonium, bismuth and lead. Although not a decay product, naturally occurring radioactive ^{40}K is also a significant contributor. Collective doses to the population arise through inhalation of radioactivity during the passage of the cloud containing fly ash emitted from the stack, but the use of coal combustion residues in buildings and other constructions is an important contributor to public doses.

The conventional combustion of coal in coal-fired power plants results in the generation of bottom ash, which is collected at the bottom of power plant boilers, and fly ash, which is collected before being discharged from the stack. Fine particles, or fly ash, are also emitted from the stack. Flue gas desulphurization, which is commonly being implemented on coal-fired power plants, results in additional residues in the form of sludge or dry solids. Volatile radionuclides, such as ^{210}Pb and ^{210}Po, accumulate in the fly ash and on the smaller particles emitted via the stack (IAEA, 2003b).

All studies of potential health hazards associated with the release of radioactive elements from coal combustion conclude that the perturbation of natural background dose levels is almost negligible. However, because the half-lives of radioactive ^{40}K, uranium and thorium are practically infinite in terms of human lifetimes, the accumulation of these species in the biosphere is directly proportional to the length of time that a quantity of coal is burned (Gabbard, 1993). In addition the use of coal combustion residues in building construction and in other biosphere applications requires attention.

The investigators in a detailed study of the environmental impacts of coal-fired plants in India report the following conclusions (Pandit, 2011). ‘The calculated effective dose rates in air varied from 0.31 to 1.61 mSv/y, with an average value of 0.68 mSv/y. In areas with normal background radiation, the average annual external effective dose rate from the terrestrial radionuclides is 0.46 mSv/y. The main contributions to radium equivalent activity and external hazard index are ^{232}Th and ^{226}Ra for fly ash and bottom ash, and hence when these are used as additives in building materials, the concentration of natural radionuclides should be monitored’.

2.4 Solid radioactive wastes from nuclear power plants

Based on physical–chemical characteristics, solid radioactive wastes from NPP operation typically fall into three broad categories, the solid organic waste groups, the solid inorganic waste groups and the wet solid waste groups. The solid organic group consists of contaminated clothing, rubber gloves, oil clothing, contaminated paper and wood trunks. This group may contain 40–50% in volume of total solid waste generated. The inorganic group consisting of contaminated equipment, such as scrap metals and reactor components, constitutes about 30–50% and the wet solid group lies between 24% and ~10%. The bulk of the wet solid waste comes from evaporator concentrates; some fraction of the wet solids waste also results from inputs of resins. Other wet solids include the sludge, filter concentrates, oil solvents and adsorbents. Some waste resulting from NPP decommissioning has special features.

2.4.1 Solid waste generation from nuclear power plants

There are traditionally three types of solid nuclear wastes classified in terms of its radioactivity: low-, intermediate- and high-level waste. A recent revision by the

IAEA (2009) of the waste classifications added two new classes between low-level waste and exempt waste. The IAEA classification consists of the following:

- *Exempt waste (EW)*: contains such a low concentration of radionuclides that it can be excluded from regulatory control because radiological hazards are negligible.
- *Very-short-lived-waste (VSLW)*: can be stored for decay over a limited period of up to a few years and subsequently cleared of regulatory control as non-radioactive waste.
- *Very-low-level-waste (VLLW)*: does not need a high level of containment and isolation and therefore is suitable for disposal in near-surface landfill-type facilities with limited regulatory control. Figure 2.3 shows the VLLW repository at El Cabril, Spain.
- *Low-level waste* (*LLW*): contains limited amounts of long-lived radionuclides. This classification covers a very wide range of radioactive waste, from waste that does not require any shielding for handling or transportation up to activity levels that require more robust containment and isolation periods of up to a few hundred years. There are a range of disposal options, from simple near-surface facilities to more complex engineered facilities. LLW may include short-lived radionuclides at higher levels of activity concentration, and also long-lived radionuclides, but only at relatively low levels of activity concentration.
- *Intermediate-level waste (ILW)*: contains increased quantities of long-lived radionuclides and needs an increase in the containment and isolation barriers compared to LLW. Long-lived radionuclides such as alpha emitters will not decay to a level of activity during the time for which institutional controls can be relied upon. Therefore, ILW requires disposal at greater depths of tens to hundreds of metres. In some countries, LLW and ILW are combined as LILW.
- *High-level waste (HLW)*: has high levels of activity that generate significant quantities of heat by radioactive decay that need to be considered in the design of a disposal facility. Disposal in stable geological formations usually several hundreds of metres below the surface is recognized as the most appropriate option for HLW.

The used fuel assemblies taken out from the reactor (spent fuel) during the refuelling outage are regarded as HLW. The HLW contains highly radioactive fission products and radionuclides with long-lived radioactivity. The spent fuels would be stored and cooled in the reactor spent fuel pool for several years to allow for the radioactive

Figure 2.3 El Cabril very-low-level waste repository in Spain.

decay of its nuclides and removal of the residual heat. The spent fuels would then be arranged for either reprocessing or direct deep underground burial as HLW.

According to the IAEA (undated) the generation of electricity from a typical 1000-MWe nuclear power station, which would supply the needs of a city the size of Amsterdam, produces approximately 300 m^3 of low- and intermediate-level waste per year and some 30 t of high-level solid packed waste per year. By way of comparison, a 1000-MWe coal plant produces some 300,000 t of ash alone per year, containing among other things radioactive material and heavy metals which end up in landfill sites and in the atmosphere.

The waste arising from decommissioning is often different from the waste generated during normal operations of the facility. These differences may include its chemical, physical and radiological characteristics, and the general amounts or volumes. Owing to these specific characteristics, some of the waste could require special considerations for the selection of specific management options. In terms of volumes, the rule-of-thumb is that for an NPP the decommissioning waste volumes are about the same order of magnitude as operational waste produced over the entire service life of the plant. However, this statement should be taken cautiously, since a number of factors may increase (or decrease) the amounts of decommissioning waste significantly. Currently, 5,000–10,000 m^3 of LILW arisings are a realistic order of magnitude for the full dismantling of a commercial NPP: however, active waste minimization policies can push these figures further down. Conversely, the amounts of HLW resulting from NPP decommissioning are small, mostly consisting of activated reactor internals (and spent fuel, which is normally not considered decommissioning waste).

A comprehensive discussion of ‘problematic’ factors for certain decommissioning waste is available in IAEA (2006). Some examples are as follows:

1. Inactive (non-radioactive) solids and liquids are generated during the decommissioning of nuclear facilities, and generally compose the largest part of the waste. Typically, non-radioactive solid materials include items such as piping, pumps, tanks, duct work, concrete rubble, structural equipment, electrical equipment and soil. A large proportion of this waste can be eligible for clearance as exempt waste or treatment as VLLW.
2. Waste may also be considered problematic because it is hazardous because of its inherent toxicity. These types of material represent a potential hazard to human health or the environment when improperly treated, stored or disposed of. A list of chemicals and toxic materials that may result from decommissioning of nuclear facilities includes the following (IAEA, 2006):

    a. Beryllium
    b. Sodium and its alloys
    c. Cadmium
    d. Mercury
    e. Lead
    f. Decontamination solvents
    g. Asbestos
    h. Polychlorinated byphenyls

During its permanence in radiological areas, hazardous waste may become radioactively contaminated (mixed waste, a particularly difficult-to-handle category of radioactive waste). More detail is given below about the commonest type of hazardous materials, i.e. asbestos. Asbestos is no longer widely used commercially, but it can still be found in many older plants. You may find asbestos wrapped around older hot water pipes and boilers, or used to tape together sections of heating ducts. You may also find asbestos in cement, flooring and ceiling materials. When large amounts of asbestos fibres are inhaled, they can become lodged in the lungs. This can cause scarring and inflammation. In the longer term, it could increase the risk of getting a variety of diseases such as lung cancer or mesothelioma. Asbestos poses a health risk when it is disturbed, fraying, or crumbling and fibres are released in the air.

3. Some decommissioning waste is unusually large (e.g. reactor vessels or steam generators). These components are optimally removed in one piece, and serve as self-containers for transport and disposal, assuming all openings, access ways, and so forth are properly sealed. Low-density grout can be used to stabilize internal contamination. The dimensions of these components need to be considered when designing a repository, and need to address proper sizing of entrances, vaults and handling areas, as well as transportation and equipment capacities. The safety assessment for disposing large components that are neither conditioned nor packaged needs to address water penetration and mobilization of radionuclides (IAEA, 2007).

2.4.2 Transport of nuclear materials from nuclear power plants

Nuclear and radioactive materials are widely transported within and between countries. These practices have been regulated for decades under the aegis of the IAEA (2012). The handling and transport of such materials (e.g. spent nuclear fuel) can give rise to exposures of members of the public, such as pedestrians and passengers. Normally, transports occur without loss or damage to the package and dispersion of radioactive substances. In fact, mishaps and incidents do happen in the transport of nuclear and radiological materials, but their consequences are limited by built-in safety features of the package together with specific transport arrangements.

Road, rail and sea transport are all commonly used for the transport of nuclear fuel cycle material. The available data indicate that exposures under normal conditions of transport are low. The following data are from UNSCEAR (2008). In Germany, the highest conservatively estimated annual dose to members of the public due to nuclear fuel shipments is typically less than 0.1 mSv. In France, shipments of waste at a storage facility are estimated to give rise to a maximum annual dose of 0.12 mSv. More recent estimates have predicted annual doses of less than 0.002 mSv to critical groups. Figure 2.4 shows the transport of a large steam generator from a decommissioning project.

2.4.3 Disposal of solid waste arising from nuclear power plants

The term ‘disposal’ refers to the emplacement of radioactive waste into a facility or a location with no intention of retrieving the waste. The ability of the chosen disposal method to isolate the waste from the human environment should be commensurate with the hazard and the longevity of the waste. Near-surface disposal is an option

Figure 2.4 Transport of steam generator.

used for disposing of radioactive waste containing short-lived radionuclides, which would decay to radiologically insignificant levels within a time period ranging from a few decades to 300–500 years (^{137}Cs, ^{90}Sr) and acceptably low concentrations of long-lived radionuclides. Near-surface repositories fall into two main categories: (1) facilities consisting of disposal units located either above (e.g. mounds) or below (e.g. trenches or pits) the original ground surface and (2) rock cavity facilities.

Near-surface disposal has been practiced in a number of countries for decades, with a wide variation in sites, in types and amounts of waste and in facility design. The safety of a repository and the public's confidence in it can be enhanced by, or depend partly upon, appropriate post-closure institutional controls (which include active controls, such as monitoring, surveillance and remedial work, and passive controls, such as control of land use and record keeping). The duration of controls will depend on factors such as characteristics of the waste, institutional issues, economics, site features and facility design.

The safety assessment of near-surface repositories should involve consideration of the impacts both during operation and in the post-closure phase. Potential radiological impacts following closure of the repository may arise from gradual processes, such as degradation of barriers, and from discrete events that may affect the isolation of the waste. The potential for inadvertent human intrusion can be assumed to be negligible while active institutional controls are considered to be fully effective, but may increase afterwards.

By contrast, geological disposal consists of a facility constructed in tunnels, vaults or silos in a particular geological formation (e.g. in terms of its long-term stability and its hydro-geological proper ties) a few hundred metres below ground level. Such a facility could be designed to receive HLW, including spent fuel if it is to be treated as waste.

No releases of radionuclides, or only very minor releases, may be expected during the normal operation of a radioactive waste disposal facility, and hence there will not be any significant doses to members of the public. Even in an accident involving the breach of a waste package on the site of a disposal facility, releases are unlikely to have any radiological consequences outside the facility.

The safety criteria for the protection of people and the environment after closure of a disposal facility are as follows (IAEA, 2011):

> *'(a) The dose limit for members of the public for doses from all planned exposure situations is an effective dose of 1 mSv in a year.*
>
> *(b) To comply with this dose limit, a disposal facility (considered as a single source) is so designed that the calculated dose or risk to the representative person who might be exposed in the future as a result of possible natural processes affecting the disposal facility does not exceed a dose constraint of 0.3 mSv in a year or a risk constraint of the order of 10^{-5} per year.*
>
> *(c) In relation to the effects of inadvertent human intrusion after closure, if such intrusion is expected to lead to an annual dose of less than 1 mSv to those living around the site, then efforts to reduce the probability of intrusion or to limit its consequences are not warranted. If human intrusion were expected to lead to a possible annual dose of more than 20 mSv to those living around the site, then alternative options for waste disposal are to be considered: for example, disposal of the waste below the surface, or separation of the radionuclide content giving rise to the higher dose.*
>
> *(d) If annual doses in the range 1–20 mSv are indicated, then reasonable efforts are warranted at the stage of development of the facility to reduce the probability of intrusion or to limit its consequences by means of optimization of the facility's design'.*

Differences between operational and decommissioning waste need to be addressed during the source term assessment (the near-field analysis), which is an important component of the site-specific safety assessment for a disposal facility. Typically, safety assessments for decommissioning waste should address the following waste characteristics: increased content of mobilization agents, such as surfactants and chelating compounds from the use of chemical decontaminants; greater waste heterogeneity; higher potential for non-uniform distribution of activity; and large component size, often with void spaces (IAEA, 2007).

2.5 Solid radioactive wastes from facilities for medical, research or industrial purposes

Radioactive materials are extensively used in industrial and research activities for medical, agricultural and environmental applications, and in various other areas. During the production and use of these materials, radioactive waste will inevitably arise; this must be managed with particular care, owing to its inherent radiological, biological, chemical and physical hazards. Producers and users of radioactive materials must be sure that a waste management strategy exists before any waste is generated. A well-developed strategy should consider the entire sequence of waste management operations, from the waste production until disposal, including all regulatory, socio-political and economic issues (holistic approach).

2.5.1 Solid waste generated at medical and industrial facilities

The amount of radioactive waste produced in different countries varies widely, depending on the scale of the applications and the range of activity associated with particular nuclear materials. The associated activities and practices in different Member States may be grouped into five classes in accordance with the extent of the use of radioactive materials (IAEA, 2001). Note that NPP and fuel cycle waste are produced by class D and E countries and are dealt with elsewhere in this chapter.

Class A includes countries in which practices are represented by the application of a few sealed radiation sources used in industry and limited quantities of predominantly short-lived radioisotopes used in the field of medicine. The resulting waste can be a few spent sealed sources and small amounts of low-level solid waste.

In a typical class A country, the situation with waste arisings can be characterized by the following:

- Short-lived waste that will decay and be disposed of as non-radioactive waste;
- A few spent sealed sources with long half-lives or relatively high activity levels, which usually are returned to the original suppliers;
- Small quantities of waste containing weak beta-emitting radionuclides (^{3}H, ^{14}C) in concentrations allowing dilution and discharge;
- Very small quantities of solid waste.

Class B encompasses countries in which radioactive materials are used in various applications, including a wide use of sealed sources for medical, industrial and agricultural purposes, as well as unsealed sources used, for example, in radiochemistry, radiobiology, diagnostic and therapeutic applications in medicine or for industrial radiography. The radionuclides used may include both short- and long-lived. The waste generated consists primarily of spent radiation sources and various medical and biological wastes containing appreciable concentrations of short-lived radionuclides, along with lesser amounts of long-lived ones. Most radionuclides in this waste decay rapidly, permitting the waste to be handled as non-radioactive waste. The remainder will need to be treated, conditioned and stored as radioactive waste. In general, the types of waste generated by class B countries will be essentially the same as those produced by class A countries, except that the volumes will be notably greater and may require the establishment of a central waste operating facility.

2.5.2 Solid waste generated at research facilities

Class C as defined in IAEA (2001) includes countries in which, in addition to the activities mentioned for class B countries, research reactors are in operation. These reactors may also be used for radioisotope production. The waste generated (in addition to waste similar to that of class A and B countries) includes spent fuel elements, spent ion exchange resins, liquid waste from radioisotope production, items with induced activity and decommissioning waste. Management of these wastes usually requires the establishment of a centralized waste processing, storage and disposal facility, which in many cases will be associated with a research reactor site. Typical waste arisings for class C countries are shown in Table IX of IAEA (2011). Typically, solids (compatible) are in the range of 20–80 m^3/a; solids (non-compatible; trash, sealed sources, radium needles, etc.) 5–10 m^3/a; solid biomedical waste 0.1–0.2 m^3/a; ion exchange resins 0.5–1 m^3/a; total 100–200 m^3/a at a concentration range of 10^4–10^{10} Bq/m^3.

A specific feature of research reactors (and research facilities at large) is the ubiquitous appearance of variable unique waste. Research reactors, by definition, are experimental facilities intended for investigation of new processes or new materials, or behaviour of existing materials in specific conditions. Therefore, radioactive wastes generated during such operations may have unusual radionuclide and chemical compositions when compared with those from NPPs. Such waste may require special and rather complicated technologies for treatment and conditioning. Compliance with waste acceptance criteria for disposal may require special consideration.

Radiation sources represent a considerable part of the non-nuclear applications. The irradiation ‘market’ is huge. At the end of their service life, spent radiation sources become a waste to manage and dispose of. The following is a summary of products/activities demonstrating that everyone will, in some way, benefit from the industrial technology; IAEA (2014) provides a complete list:

- Food irradiation is the process of exposing food to ionizing radiation to destroy microorganisms, bacteria, viruses or insects that might be present in the food. Further applications include sprout inhibition, delay of ripening, increase of juice yield and improvement of rehydration.
- The sterile insect technique is a method of biological control, whereby overwhelming numbers of sterile insects are released.
- The radiation sterilization of products used in medical care is a fully accepted process. Radiation sterilized disposables such as surgical gloves, surgeon gowns, syringes, sponges, bandages, and also implants and catheters are standard hospital products.
- Hospitals and blood banks irradiate blood products to prevent transfusion-associated graft-versus-host-disease.
- Calibration systems use high-activity radiation sources to produce radiation fields of known intensity for calibration of radiation monitoring equipment and dosimeters.
- Research irradiators are used to expose biologic and non-biologic materials to radiation to evaluate the response of target materials to various doses.

2.5.3 Management and disposal of radioactive materials

The risk of health effects to people from the disposal of VLLW or LLW from the non-nuclear industry is very low. The demonstration of these low risks is through the study of possible ways in which people could receive a radiation dose from the radioactivity present in the waste, called ‘potential exposure scenarios’. Theoretical scenarios used in the assessment of environmental doses from radioactive waste management and disposal include the following (DOE, 2012):

- Combustion of waste at incinerators, and discharge of radioactivity to air and water;
- Disposal of ash and incinerator residues from incinerators to landfill, and dispersal of radioactivity into the environment via leachate;

- Use of some incinerator residues (e.g. in construction) or recycling of these residues (e.g. in the chemical industry);
- Inadvertent excavation of a site used for VLLW or LLW after closure and loss of institutional control.

Predictive models are used to assess potential exposure scenarios resulting from disposal practices. In the case of discharges into the air from incinerators, the models are used to calculate the concentration of radioactivity in air, and deposition on land, as a function of distance from the stack. This enables calculation of potential exposures from inhalation, and from consuming contaminated food and water. In the case of landfill disposals, the models are used to calculate the amount of radioactivity that may arise in leachate as a function of time, and then the concentrations in drinking water or food.

Once theoretical concentrations of radioactivity have been calculated for the surface of land, in air, and in drinking water and food, assumptions are made about the habits of potentially exposed people (i.e. where they spend their time on contaminated land, and air, and how much locally grown food and water they consume).

Due to the conservatisms built into the models, it is highly unlikely that people actually receive the assessed doses. It is also unlikely that all the possible exposure pathways would apply to a single group of people. The latest assessments of worker and public doses from LLW and VLLW disposal to incinerators and to landfill are all less than 10 μSv per annum.

Management and disposal options for spent radiation sources include more scenarios (e.g. the return to the manufacturer or borehole disposal).

2.6 Environmental impacts from nuclear and radiological accidents

Figure 2.5 shows the various environmental impacts from nuclear and radiological accidents. It should be observed that the relative significance of pathways leading to human exposures and environmental contamination is highly variable, depending on such factors as radionuclide amounts and mixture, their physical and chemical features, environmental parameters (rivers, lakes, hydrogeology, prevailing winds, etc.), demography, living habits and many others. Therefore the environmental impacts of each accident should be dealt with specifically.

2.6.1 Nuclear accidents

IAEA uses the International Nuclear and Radiological Event Scale (INES) to assess the severity of nuclear accidents according to their impacts. This scale was introduced to enable prompt communication of safety-related information in case of nuclear accidents. The scale is logarithmic, and each increasing level represents an accident some 10 times more severe than the previous level. For the purposes of this chapter, only levels 5, 6 and 7 are considered, as events of a lower category can hardly cause any serious environmental impacts off-site.

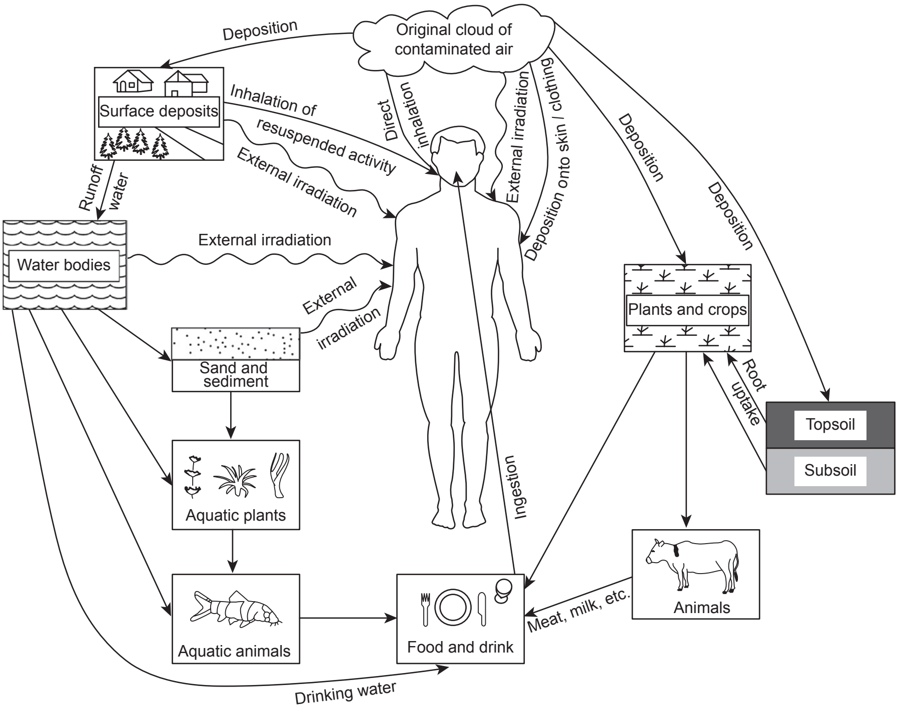

Figure 2.5 Main environmental pathways of human radiation exposure.

Level 7 represents major accidents described by a major release of radioactive material with widespread health and environmental effects, requiring implementation of planned and extended countermeasures. A major accident is an event resulting in an environmental release corresponding to more than several tens of thousands of TBq of ^{131}I. This corresponds to a large fraction of the core inventory of a power reactor. With such a release, stochastic health effects over a wide area, perhaps involving more than one country, are expected, and there is a possibility of deterministic health effects. Long-term environmental consequences are also likely, and it is very likely that protective action such as sheltering and evacuation will be judged necessary to prevent or limit health effects on members of the public. There have been two level 7 accidents up to now, namely, the Chernobyl and Fukushima accidents.

Level 6 represents a serious accident described by an impact on people and environment with significant release of radioactive material likely to require implementation of planned countermeasures. A serious accident is an event resulting in an environmental release corresponding to the order of thousands to tens of thousands of TBq of ^{131}I. With such a release, it is very likely that protective action such as sheltering and evacuation will be judged necessary to prevent or limit health effects on members of the public. Only one accident classified on this level has occurred up to now, namely, the Kyshtym accident (Russia, 1957).

Level 5 represents accidents with wider consequences. Their impacts on people and environment are described by limited release of radioactive material likely requiring implementation of some planned countermeasures. Their impacts on radiological barriers and control are described by severe damage to the reactor core and hence release of large quantities of radioactive material, with a high probability of significant public exposure, possibly arising from a major criticality accident or fire. The terminology of 'Accidents with wider consequences' is used for events resulting in an environmental release of the order of hundreds to thousands of TBq of ^{131}I, The Windscale fire (United Kingdom, 1957) and the Three Mile Island accident (United States, 1979), fall under scale 5.

A summary of radioactive releases and environmental contamination caused by the Fukushima accident is provided below (IRSN, 2012). Radioactive releases into the air, still considered provisional, were estimated as follows (selected radionuclides):

- Releases of radioactive noble gases: 6550 PBq (petabecquerels = 10^{15} Bq) (the same order of magnitude as at Chernobyl) composed mainly of ^{133}Xe (half-life of 5.3 d);
- Releases of radioactive iodine: 408 PBq (about 10 times less than the Chernobyl accident), including 197 PBq of ^{131}I (half-life of 8 d);
- Releases of radioactive caesium: 58 PBq (about three times less than at Chernobyl), including 21 PBq of ^{137}Cs (half-life of 30 y), and 28 PBq of ^{134}Cs (half-life of 2.1 y).

Plutonium released during the accident (attested by its isotopic composition) was detected in the deposits formed in the northwest of the Fukushima plant, but at very low levels, difficult to distinguish from the fallout in the atmosphere produced by nuclear weapons testing.

Over the course of the air contamination events, a portion of the radionuclides dispersed into the air in the form of very fine particles (aerosols) or soluble gases (a portion of the radioactive iodine) settled onto the ground surfaces, forming radioactive surface deposits. The sources of these deposits are two complementary processes, as follows:

Dry deposits are formed on surfaces that come into contact with the contaminated air, due to air turbulence. The size of these dry deposits depends on, in particular, the concentration of radionuclides in the air at the ground level and the duration of air contamination.

Wet deposits are formed on land areas where precipitation (rain or snow) was produced during the dispersion of the radioactive plume. They resulted from the transport of radioactive particles or soluble gases (e.g. iodine) by water droplets through the air. The distribution of contamination on ground surfaces with wet deposits is highly variable locally, because of the water flow from rain (or melting snow) on the surface or infiltration into the soil.

These deposits led to a contamination of land that has remained after the dissipation of the air contamination caused by the accidental releases. The deposits have had two consequences:

- A permanent increase in the ambient dose rate due to gamma radiation emitted by the radionuclides contained in the deposits, which progressively decreases over time as a function of the radioactive decay of the radionuclides making up the initial deposit;
- Contamination of agricultural products, more or less immediate and more or less long lasting.

Inside the 20-km zone (zone of emergency evacuated at the time of the accident), surface activities in ^{137}Cs measured in the soil samples vary between less than 30 and 15,000 kBq/m^2, a difference of a factor of 500 between the extreme values.

In the planned evacuation zone which started 22 April, 2011 more than 20 km northwest of the plant, the surface activities in ^{134}Cs and ^{137}Cs vary between <60 and 8000 kBq/m^2. Out of some 100 sampling points in this zone, three have a measured surface activity exceeding 3000 kBq/m^2 in ^{137}Cs.

Beyond these two zones, cumulative surface activities in ^{134}Cs and ^{137}Cs do not exceed 600 kBq/m^2, except in a limited section between 20 and 30 km to the southwest.

Contamination levels being equal, the surface areas involved in Japan are clearly smaller than those of the contaminated land around Chernobyl, which can be explained by the fact that a large portion of the releases from the Fukushima accident dispersed over the Pacific. In Japan there are approximately 600 km^2 of land with a ^{137}Cs deposit greater than 600,000 Bq/m^2 (including the part within the 20-km zone), compared to 13,000 km^2 around Chernobyl, representing 20 times less surface area. However, in addition to the 80,000 people evacuated from the 20-km zone, the population living in these areas is around 70,000, which together represents more than half of the population in the most contaminated areas around Chernobyl (270,000 people in the areas with ^{137}Cs deposits >555,000 Bq/m^2).

By interpreting the results of measurements published in Japan, IRSN was able to determine the overall quantity of ^{137}Cs released into seawater. The value thus obtained is estimated at 27×10^{15} Bq. This is the largest one-off injection of artificial radionuclides into the marine environment ever observed. However, the estimation of these releases still lacks precision.

The active sea dilution effect tended to reduce the impact of the accident on coastal waters. Contaminated waters were carried swiftly eastwards, towards the centre of the Pacific Ocean, where they continued to be diluted. Radioactive pollution in the sea caused by the Fukushima accident has also had an impact on marine species.

Waste amounts resulting from environmental remediation of contaminated sites can be huge. The actual volume of waste will depend on the type of area and the clean-up process used. For example, if a 5-cm layer of soil and sod were removed, about 50,000 m^3 of waste could arise from each square kilometre (km^2). However, the volume (but not the weight) to be transported will be greater than this. owing to a reduction in the density of the removed material during handling. Furthermore, additional organic waste would be produced, the volume of which will depend on the types of crop being grown. It is estimated that in certain cases an additional 50,000 m^3 of organic waste could be generated per square kilometre; however, the volume of the organic waste would reduce sharply as the plant material decomposed (IAEA, 1992).

2.6.2 Loss of radiation sources

Radiation sources are hundreds of thousands worldwide and ubiquitous; they have been exported and operated in a number of countries, including a few that may not necessarily possess adequate infrastructure for the cradle-to-grave management of radiation sources. This has resulted in a few cases in which radiation sources have been improperly managed after the end of their operational life and eventually have caused significant health impacts to the general public. These cases can be viewed as poorly planned decommissioning projects. Tables 3 and 4 in Ortiz (2000) give a list of fatalities and major injuries resulting from loss of source control. These tables also include accidents involving large-scale contamination of the environment. As both tables show, mobile radiography sources are the most important contributor to this type of accident, accounting for the largest number of accidents and the largest number of fatalities and severe injuries. In many of these accidents, the source was dropped at the radiography site, and was picked up by a construction worker who was not associated with the use of the source and therefore not aware of the potential hazard. Accidents have also occurred when sources have fallen out of unlocked exposure devices during transportation and have resulted in the exposure of several members of the public. The 'source in the pocket' scenario has led to fatalities and to high localized radiation doses to limbs, resulting in major surgery. The second contributor to severe accidents is medical teletherapy sources. Their high activity gives the potential for irradiating a large number of people and their physical and chemical form (thousands of pellets in the case of ^{60}Co, or salt in the case or ^{137}Cs) can lead to large-scale contamination, as in Goiania (Brazil) and Ciudad Juárez (Mexico). Sources involved in these accidents were either in the therapy device or in the transport container waiting for disposal or transfer.

In many cases, teletherapy sources were purchased before regulatory control was in place, and no provisions were made for their return or disposal. This has resulted in disused sources being stored on the premises of hospitals and clinics that were no longer in operation. IAEA missions of assistance to some countries have detected sources that were often readily accessible, with no warning labels. It can therefore be assumed that worldwide there are a considerable number of teletherapy sources waiting for a decision on source disposal or transfer, and that the security conditions of these sources are uncertain. Given their high initial activity and the half-life of the radionuclides, even sources that are 20–25 years old may still have a dangerous activity of 1–4 TBq.

An increasing number of accidents involving the melting of radioactive sources have raised concern about sources found in scrap metal. The Mexico case involving a teletherapy source is an example of disastrous consequences, both in human exposure and in financial cost.

2.7 Future trends

Table 17 of UNSCEAR (2008) clearly shows the constant reduction of effluents from NPPs over several decades. Using PWRs as references, it can be seen that:

- Noble gases decreased continually from around 500 (1970–1974) to 10 (1998–2002) TBq/GW-a
- ^{131}I airborne decreased continually from around 0.003 (1970–1974) to 0.0003 (1998–2002) TBq/GW-a

- Airborne particulates decreased continually from around 0.02 (1970–1974) to 0.000,03 (1998–2002) TBq/GW-a
- Liquid radionuclides decreased continually from around 0.2 (1970–1974) to 0.01 (1998–2002) TBq/GW-a

Similar trends are exhibited by other reactor types. The downward trend is partly due to more efficient fuel fabrication practices reflected in enhanced fuel leak-tightness and smaller amounts of fission products in the reactor systems, partly to better maintenance programmes, and also to filtration of all release pathways and growing use of effluent retention techniques (e.g. charcoal beds to delay the discharge of noble gases in BWRs).

One example of such successful developments is as follows. As regulatory, insurance, and peer pressures increase, the push to further reduce already low levels of radioactive effluent from liquid radioactive waste (LRW) processing at NPPs continues. Today it is incumbent on each plant to achieve both low absolute numbers and a trend of improvement.

Ion exchange, long the preferred processing method, is at a technological peak with regard to such improvements. Although it has been tweaked and optimized, the chief drawback of ion exchange – the fact that it forms a chemical barrier between the plant and the Monitor Tank – cannot be overcome. This chemical barrier is highly dependent on water chemistry, which may change daily in LRW. Several plants have turned to reverse osmosis technology to further reduce radioactive effluents. Membrane systems provide a physical barrier that remains constant, irrespective of the quality and chemistry of influent water. These systems, benefiting from continued improvement and refinement, are well suited to provide a leap forward in LRW processing performance (Gunderson, 2008).

It is to be noted that airborne and liquid tritium releases do not follow the same downward trend, with some reactors even showing a trend upwards. This can be due to factors such as extended lifetimes of most reactors and the trend to recycle bigger amounts of liquid volumes, both factors resulting in higher in-plant tritium build-up.

Regarding the trend towards (solid) waste minimization, the focus on radioactive waste is part of the overall societal approach towards reducing any type of waste, thereby contributing to lower environmental impact and sustainable development. The pyramid in Figure 2.6 shows strategic priorities in waste minimization. To provide just one example relevant to this chapter, it is a modern trend to melt contaminated metals resulting from the operation and decommissioning of NPPs, rather than to dispose of them with no treatment. Metal melting decontaminates the surfaces, reduces the volumes, concentrates a large part of the radionuclides in the slag, and often allows the unconditional release of the ingots.

The following components are usually considered in the planning and implementation of complex, significant waste minimization projects (IAEA, 2003a):

- Waste minimization strategy;
- Minimization of radioactive waste arisings (waste avoidance, matching Prevention and Minimization in the pyramid of Figure 2.6); and
- Minimization of the volume of waste that has been generated and requires disposal.

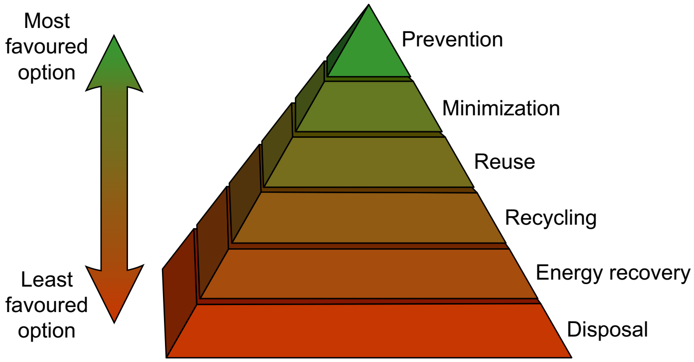

Figure 2.6 Waste hierarchy.

Until recently, waste managers' efforts were concentrated mostly on the minimization of nuclear facilities' operational liquid waste generation and the reduction of the volumes of conditioned waste for disposal. Deep evaporation of liquid waste with subsequent calcination of the evaporator concentrate and packaging of the calcinate in high-integrity containers has been routinely used at some NPPs in Europe.

A new approach to liquid waste minimization has brought the wide use of various selective sorbents and special filtration procedures for the separation of radioactive components from liquid waste. The methods include reuse of the purified water and the advanced processing of sorbents and filtration materials. In some NPPs, the liquid waste to be conditioned has been practically eliminated, and the trend towards this approach is increasing. Instead of large volumes of conditioned low-activity liquid waste, substantially smaller volumes of higher-activity conditioned liquid waste, sorbents and filtration materials remain for disposal. Most of the volume of solid waste from an NPP is VLLW and LILW.

Typically, most solid waste consists of protective clothing, mops, wipes and other incinerable materials. Despite its high-volume reduction factor, incineration has not become very popular because of problems with ash conditioning and secondary waste generation, mainly from complicated exhaust air filtration systems. In addition, incinerator ash is often classified as hazardous material and therefore may be subject to non-nuclear regulation.

Currently, the most advanced regulatory positions require that the NPP operator minimize radioactive contamination by using structure, system and component designs and operational procedures that limit leakage and/or control the spread of contamination within the facility and to the environment. The design and operational procedures should provide for the early detection of leaks, thus allowing prompt assessment to support a timely and appropriate response. In this way, the impact of legacy waste on decommissioning/environmental remediation is minimized.

To what extent minimization should be effected is a matter of optimization. This implies that other competing concerns such as the implication to safety systems and the overall cost should be considered. Minimization of contamination includes the following (USNRC, 2008):

Figure 2.7 Environmental remediation at a nuclear site.

- Minimization of leaks and spills and provision of containment;
- Prompt detection of leakage;
- Avoidance of the release of contamination from undetected leaks;
- Measures for reducing the need to decontaminate equipment and structures;
- Periodic review of operational practices;
- Development of a conceptual site model development.

Figure 2.7 shows a detail of environmental remediation following the discovery of soil contamination at a nuclear site. Finally, as far as the environmental impact from lost sources is concerned, the simple knowledge of the incidents that have occurred should lead to straightforward regulatory actions. Since governmental resources are limited, priorities need to be assigned. The first priority should be the verification that sources in industrial radiography, irradiators and medical teletherapy are under control. In developing countries, the small number of irradiators and medical teletherapy facilities should make this control relatively straightforward, but the general infrastructure can be poor. The control of industrial radiography sources is, however, complicated by the fact that mobile sources may be lost any time during operation or transport. The majority of mobile radiography devices house sources of ^{192}Ir. Since ^{192}Ir has a relatively short half-life, sources older than 2 years will not pose a significant threat and therefore priority should focus on ^{137}Cs and ^{60}Co sources.

Over the last 10–15 years, the IAEA has launched numerous campaigns aimed at identification, collection in one centralized place, conditioning and safe storage (or return to the manufacturer) radiation sources within a number of countries.

2.8 Sources of further information

In addition to the references listed below, the reader is encouraged to consult the documents and reports issued by the National Academies Press. They cover the whole realm of environmental impacts of radioactive substances in a comprehensive manner. The website http://search.nap.edu/napsearch.php?term=radioactive+waste gives access to more than 500 publications in the field of radioactive waste.

The IAEA has an impressive collection of books in the field addressed in this chapter. Enter http://www-pub.iaea.org/books/ and search with keywords (or Google). For OECD/Nuclear Energy Agency publications, enter http://www.oecd-nea.org/pub/ and use Radioactive Waste Management as the subject.

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Radionuclide behaviour in the natural environment: an overview

3

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3.1 Introduction

The aim of this chapter is to give an overview of the behaviour of artificial radionuclides (RNs) and naturally occurring radioactive material (NORM) in the environment. Focus is placed on those processes that are relevant to contaminated sites and surface repositories for radioactive wastes. Knowledge of typical chemical properties and speciation of RNs under given geochemical conditions is a prerequisite to understanding their environmental relevance as well as for planning remediation measures. Also examined are the most relevant processes to consider when assessing by modelling the potential RN migration from such sites.

3.2 Description of the radionuclides (RNs) of interest

3.2.1 Natural radioelements

Ten naturally occurring so-called radioelements, radioactive elements with no stable isotope, are presently known to exist in the earth's crust. These are mainly of primordial origin such as Th, U and RNs generated in their decay chain (e.g. Ra, Rn, Po). In addition, about 60 radioactive nuclides of elements also having stable isotopes occur in nature. These are again primordial nuclides (e.g. ^{40}K, ^{87}Rb) or nuclides that are continuously generated by the impact of cosmic radiation (e.g. ^{14}C, ^{3}H, ^{7}Be) or as members of natural decay chains (e.g. ^{210}Pb). In total, our earth bears a gross activity of about 10^{26} Bq, orders of magnitude higher than human-made radioactivity. These elements are naturally present at trace concentrations in any material on earth, at various concentrations, and contribute to the natural radioactivity which is in average at 2.4 mSv/year.

However, mining activities (coal, oil, gas, metal ores, phosphate, etc.), the technical application of natural radioelements (e.g. thorium in magnesium based alloys, welding wires, gas caps, etc.), treatment of drinking water and waste water, power generation by coal burning and the exploitation of geothermal energy may enhance the concentration of natural radioelements in residues and wastes to much higher levels as compared to that in the original material the usual background (Merkel & Hoyer, 2012). Indeed, many ores of economic interest display low initial concentrations of the target elements. Their exploitation therefore requires efficient separation and concentration

Environmental Remediation and Restoration of Contaminated Nuclear and NORM Sites.
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processing. Often, this subsequently leads to the enrichment of radioactive elements assigned as NORM or technologically enhanced NORM (TE-NORM) in mine tailings. These comprise, for instance, uranium and thorium and their progenies, e.g. in REE mine tailings, phosphate ores, spills from oil production or in uranium mine tailings, etc. As an example, Figure 3.1 illustrates the decay chain of ^{238}U in the U-ore.

NORM RNs that are most relevant with regard to their chemical and radiological toxicity are uranium isotopes $^{238/235/234}$U, thorium isotopes $^{232/228}$Th and a number of decay chain members, e.g. $^{226,\,228}$Ra, ^{222}Rn, ^{210}Pb and ^{210}Po. Those nuclides are considered potentially hazardous and are characterized by the very specific chemical properties of their compounds being either easily or poorly water soluble, existing as gaseous (Rn) or volatile (Po, Pb) species and exhibiting different decay modes. Most of those isotopes are alpha emitters and exhibit significant radiotoxicity (Figure 3.2).

3.2.2 Artificial radioelements

Development of nuclear energy since the mid-twentieth century has led to the production of numerous artificial RNs. Although natural radioactivity is dispersed and diluted, man-made radioactive material generated for instance in nuclear power plants can reach very high specific activities and thus high radiotoxicities. After being discharged from the reactor core, the fuel contains about 4 mass% fission products consisting mainly of isotopes of elements 34 (Se) up to 64 (Gd) (see Figure 3.3). For fission reactors using thermal neutrons, a bimodal fission mass yields distribution that occurs with maxima at masses around 90 (e.g. ^{90}Sr, ^{99}Tc, etc.) and 130 (e.g. ^{131}I, ^{133}Ba, ^{135}Cs, ^{137}Cs, etc.). The transuranium elements Np, Pu, Am, Cm, and, in very

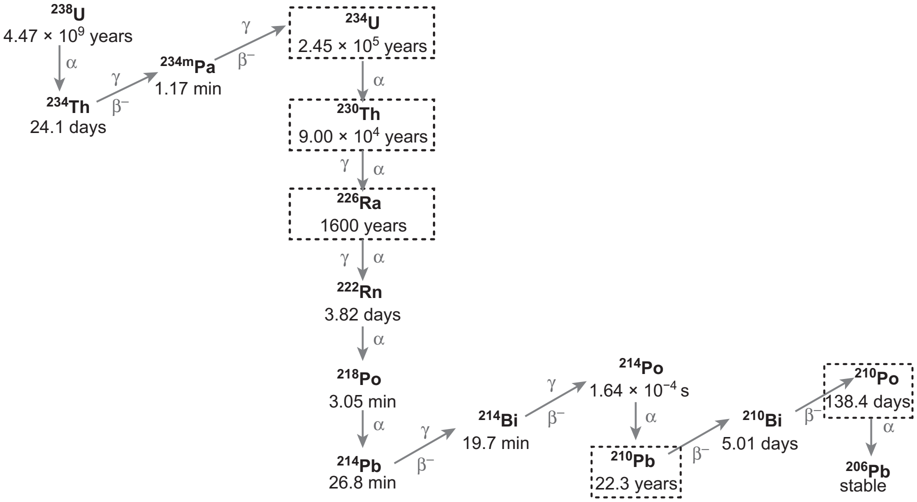


Figure 3.1 ^{238}U decay chain clearly illustrates that mining U will lead to accumulate radioactive decay products of ^{238}U in mine tailings with partly significantly enhanced specific radioactivity. Dotted squared radionuclides are those responsible for most of the ingestion dose in the long term, requiring them thus to be accounted for in any remediation strategy.

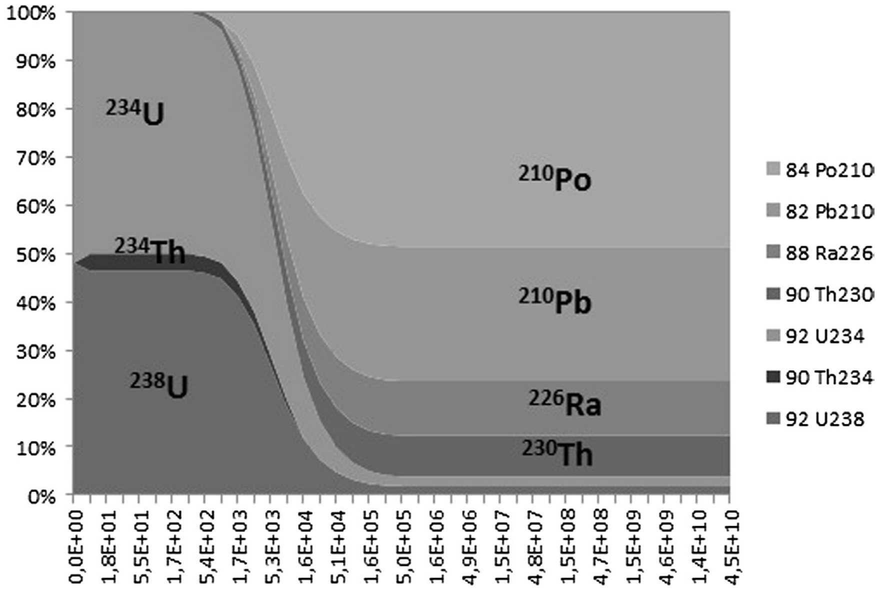


Figure 3.2 Relative radiotoxicity by ingestion of ^{238}U and daughters elements up to 4.5×10^{10} years. This figure illustrates the significant influence of ^{234}U for shorter time, and Po and Pb for longer time.

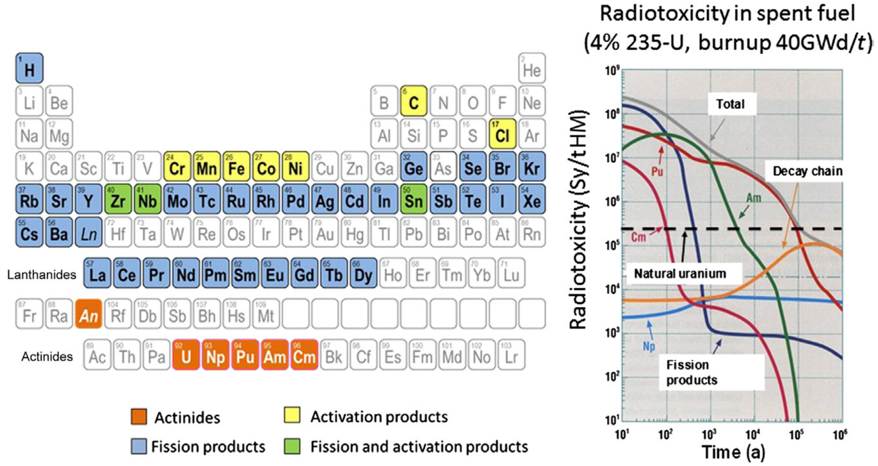


Figure 3.3 (*Left side*): Radionuclides contained in spent nuclear UO_2 fuel. Elements are marked in grey that are constituents of spent nuclear fuel as radioelement or radioisotope. Nuclides may be generated by nuclear fission, neutron activation reactions or as a consequence of neutron capture processes. (*Right side*): Radiotoxicity contributions from various spent nuclear fuel constituents over time, relative to the radiotoxicity of the natural uranium amount required to produce 1 ton of nuclear UO_2 fuel.

Poinssot and Geckeis (2012).

low trace amounts Cf, Bk, Es and Fm, are generated by neutron capture reactions from U. Pu represents the main transuranium element fraction (c. 1%), whereas the other so-called minor actinides amount to ~0.1 mass%. In addition, radioisotopes are generated in claddings of fuel elements by neutron capture reactions. Roughly 70% of the worldwide inventory of spent nuclear fuels is temporarily stored in pool or dry casks, whereas the remaining 30% has been reprocessed to recycle U and Pu and condition the ultimate waste in nuclear glass. Low and intermediate waste are stored in near-surface facilities, whereas high-level, heat-producing waste such as spent fuel or vitrified reprocessing waste is planned to be isolated from the biosphere in deep geological repositories. In normal operation, all of those RNs are permanently confined from the biosphere, thanks to a robust in-depth safety defence and multiple and redundant barriers. However, major nuclear accidents, such as Kychtym (1957), Chernobyl (1986) and Fukushima (2011), or minor leakage incidents lead to the release in the environment of artificial RNs, and to local contamination of the environment. In case of nuclear power plant accidents, mainly the relatively short-lived fission products ^{131}I, ^{137}Cs and ^{90}Sr contribute to radiological doses to the local population, as revealed by the consequences of the nuclear accidents of Chernobyl and Fukushima. Significant amounts of waste RNs have already been released to the environment from, for example, the Hanford site and Rocky Flats in the United States and at the Mayak complex in the former USSR. Those sites require now and in the future considerable efforts to ensure appropriate remediation measures. Finally, a main source of anthropogenic RN release that has already taken place is atmospheric nuclear weapon tests. During the 1950s and 1960s about 2×10^{18} Bq of the fission products ^{90}Sr, ^{137}Cs and the actinide isotopes ^{239,240,241}Pu have been distributed all over the world, exceeding the amounts of those nuclides emitted by nuclear accidents. The RN level in environmental compartments due to nuclear fallout is, however, rather low because of the strong dispersion.

In the following section of this chapter, general behaviour will be described, with a specific focus on the actinides since they represent most of the long-term radiotoxicity of radioactive waste, a fortiori of most of the contaminated sites and NORM waste.

3.3 RN migration: presentation of the different governing processes

3.3.1 Main characteristics of the relevant environments to consider

NORM containing waste and low- and intermediate-level radioactive waste are classically either stored on their production site or in a dedicated shallow repository. As in contaminated sites, similar parameters can influence RN behaviour, as follows:

- Interaction with oxygen and carbon dioxide in air, climate and weather (i.e. seasonal changes in temperature, precipitation, long-term potential climate evolution) have a significant effect on weathering of NORM matrices and leaching of RNs from wastes and contaminated areas. Chemical processes in the ecosphere are hence characterized by relatively rapid variations, and very often local chemical equilibria are not attained and reaction kinetics needs to be considered. Hydrologic regimes may also strongly evolve with time and influence the site properties, for instance water table rapid change. Surfacial environments are strongly exposed to the biosphere. Bio- and ecochemical interactions including microbiology are thus of highest relevance for understanding the behaviour of RNs and their behaviour in the food chain. Furthermore, besides abiotic processes biological material will strongly influence the local redox balance. Microbes and the local accumulation of detrital organic material may locally create strongly reducing conditions, which are strongly affecting the mobility of some RNs.

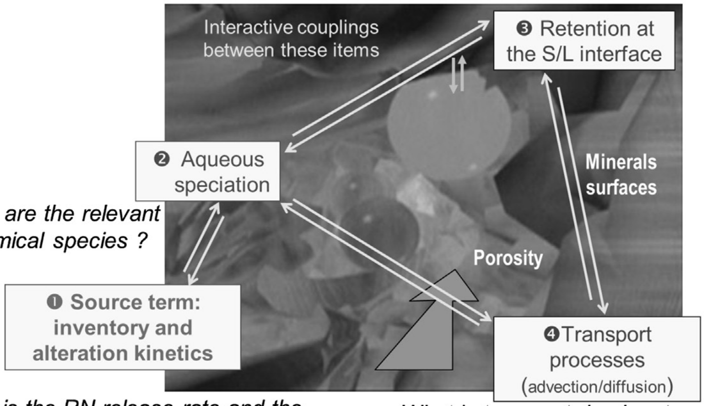
- Except in case of flooded areas, soil and subsoil layers usually are unsaturated, which means that pores are only partly filled with porewater and partly in contact with the gas phase. This zone is characterized by intermittent leaching of the soil by precipitates down to the water table, representing the boundary between saturated and unsaturated zone. The location of the water table is frequently modified by the precipitation regime.

3.3.2 Description of the main geochemical processes affecting RNs

Understanding the fate of RNs in surface storage facilities or contaminated sites needs to address and describe several processes that will govern the subsequent RN mobility (Figure 3.4):

- RNs can initially be present in different chemical forms: trapped in minerals, coprecipitated in secondary solid phases, adsorbed to mineral surfaces or organic matter. In any case, RN mobilization requires RN dissolution or desorption at a given rate from their initial sites to the aqueous phase. This is referred to as the *source term*.
- When released in the aqueous phase, RNs will undergo chemical reactions with the other chemical species depending on pH, Eh, ionic strength, presence of complexing ligands, and

What is the significance of retention, which depends on nature of minerals ?



What are the relevant chemical species ?

What is the RN release rate and the total inventory ?

What is transport-dominant process and its significance (medium-dependent)?

Figure 3.4 Schematic representation of the main processes governing the RNs migration in the environment.

Poinssot and Geckeis (2012).

so forth. The final chemical form of the RN in the system is referred to as the *chemical speciation*. It determines the overall RN reactivity, mobility, bioavailability and toxicity. Solubility of solid phases in ground- or porewater delimits the maximum quantity of RNs in the mobile aqueous phase. Speciation can also be influenced by micro-organisms or biomolecules that are present in the environment.

- Within pores of soil, landfill or sealings of a storage site, RNs will undergo interactions with mineral surfaces. Solid–water interface reactions may contribute significantly to RN retention. Retention can be of either chemical or physical nature with a broad variability in binding strengths, depending on the individual RN and mineral surface. For polyvalent cations, such as most actinide ions but also lead and polonium, sorption strongly hinders migration.
- Finally, transport processes can move RNs away from the source and potentially into the food chain. Transport can take place by advective flow or by diffusion driven by concentration gradients. Furthermore, small colloidal particles can also be transported in the aqueous phase and act as vectors for RNs. All of these processes play obviously a significant role in the overall RN migration, and their relative contribution differs from one environment to the other. Volatile RNs, especially radon, are transported by the gas phase. Decay products of radon attach to aerosols and thus can be transferred via the gas phase.

Furthermore, different chemical and physical processes can be strongly coupled. Estimating the significance of RNs migration from storage or contaminated sites hence requires answering the four following generic questions:

- What is the total inventory and the RN release rate (source term)?
- What are the relevant chemical species (speciation)?
- What is the significance of retention that depends on the chemical environment and the nature of mineral surfaces (retention)?
- What is the dominant transport process (medium-dependent)?

The following sections of this chapter will successively address these four topics.

3.4 The RN source term

Assessing the potential impact of storage or contaminated sites requires a comprehensive set of data on RN inventory and the estimated release rate.

3.4.1 The RN inventory

Together with other data, the RN inventory represents key information that defines the risk potential of a site. Although, in the case of storage site, the amounts of RN are more or less accurately known, this is not so much the case for contaminated sites. In this case, characterization is a prerequisite:

- The overall elementary composition can be analysed in selected representative samples using modern analytical tools available in dedicated analytical laboratories, such as inductively coupled plasma-mass spectrometry or -atomic mass spectroscopy.
- For the most relevant nuclides, the isotopic composition is accessible through classical nuclear spectroscopies or, more specifically, through complex isotopic measurements.

- The chemical environment of RN is of cardinal importance, as it influences significantly the release potential. In the case of contaminated sites, knowledge of the RN location in specific mineral phases should be known, as it will likely not be homogeneously distributed. This is of special importance for NORM residual waste. Special emphasis has to be placed on reducing environments, as they often contribute to trap redox-sensitive elements, such as actinides (Campbell et al., 2012). In the case of low- and intermediate-level nuclear waste, the presence of, for example, complexing decontamination agents is of importance, as these agents may induce enhanced dissolution in the case of water access.

As detailed inventory information often are not available, respective data need to be estimated from a limited set of analytical data. Depending on the complexity of site and waste composition, this issue can be a very demanding goal. Geostatistic approaches are strongly recommended to derive both a representative and a conservative set of data which account for the intrinsic heterogeneity of a site (Chiles et al., 2005; D'Or, Demougeot-Renard, & Garcia, 2009; Desnoyers, 2010; Guastaldi & Allessandro Del Frate, 2012).

3.4.2 *The RN release rate*

Assessing the global impact of any site requires information or assumptions on the potential RN release. Several cases can be encountered:

- In the most favourable case, it is possible to derive robust and reliable information about the RN solid speciation, that is, get information about the relevant chemical environment of the RN in a given site: incorporated in a host solid phase, precipitated in an RN-bearing phase, sorbed on mineral or organic material surfaces. In this case, it should be possible to derive a relevant release rate of the RN from the initial material towards the aqueous phase as a function of the different chemical parameters, either by dedicated experimental studies or based on the data available in the literature (e.g. mineral dissolution kinetic rate, solubility-controlled alteration rate, desorption kinetic rate). Theoretically, this model can be purely deterministic, which considers the different chemical reactions and reaction rates and which ensures the relevance of its application in a very large chemical domain (Poinssot & Gin, 2012). More frequently, not enough data are available to derive a consistent model, and only an empirical model describing the evolution of the release rate within a limited range defined by the different experimental points is accessible. In such a case, one can only interpolate within this initial domain, and no extrapolation is justified.
- In other cases, RN is bound to the initial contaminated material through different competitive processes that cannot easily be described. An empirical approach that aims to experimentally relate the RN release rate to the main chemical parameters should be developed. It can be based both on representative static (batch experiments) and on dynamic experiments (column or diffusion cells).
- Furthermore, RN releases into groundwater or soil porewater are often strongly coupled to weathering rates of the host mineral. For mine tailings containing sulphidic phases, those rates may become rather fast, as they frequently undergo oxidation when in contact with oxygen and water as described by the next reaction (Descostes, Vitorge, & Beaucaire, 2004):

$$2\mathrm{FeS_2(s)} + 7\mathrm{O_2(g)} + 2\mathrm{H_2O(l)} \Leftrightarrow 2\mathrm{Fe^{2+}(aq)} + 4\mathrm{SO_4{}^{2-}(aq)} + 4\mathrm{H^+(aq)}$$

In such cases, low pH conditions are established, mineral phases dissolve and toxic trace metal ions as well as RNs can be released rapidly at relatively high concentrations.

- Finally, RN release rates may also not be accessible at all, due to the complexity of the site, the lack of time or money, and other factors. In this case, although assumptions can always be used to try to limit the conservativeness, a safety assessment approach will ultimately have to consider the worst case, which is the instantaneous and complete release of the whole RN inventory in the aqueous phase. Of note, it does not mean that all RN instantaneously migrates, since additional processes as precipitation or sorption can significantly hinder the migration (discussed in the following sections).

Finally, RN release rate is a key parameter, as it determines the incoming flux of RN within the natural environment. However, it can represent a very demanding goal that requires an effort that is not always accessible within the given time frame and budget. As a general manner, focussing R&D on this issue should be a top priority either (1) when the geochemical environment is favourable to migration (e.g. oxidizing conditions, high permeability, existing colloidal transport) or (2) when the absence of robust data compels the RN source term to be modelled as an instant release.

3.4.3 Specific case of gaseous or volatile RNs

Radiological dose exposure to the population by radon Rn emanating from NORM deposits is less controlled by geochemical parameters. As a noble gas, chemical interactions are of less relevance for environmental Rn behaviour. Rn release rates are strongly related to the grain size of the tailing material and the open pore space of the tailing (Attallah, Awwad, & Aly, 2012).

RN may also be transported in the atmosphere via solid particles, gases or aerosols. In this case, they may enter the environment by dry or wet deposition. Respective releases can be minimized by sealing the site or the waste, covering it with an impermeable layer such as bituminen geomembrane or clay, or by using sprinklers to keep tailings wet (Sahu et al., 2014). These remediation approaches are often used for mine tailings and NORM.

3.5 RN speciation and precipitation

3.5.1 Assessing the RN speciation

Once the RN release from the initial material in the geochemical system, they first chemically react with the neighbouring elements that are present in the aqueous phase. The main reactions to consider are generally as follows:

- **Redox reactions**, that is, an exchange of electrons between the different oxidizing and reducing species. This is of prime importance, since it strongly influences, in many cases, the mobility, solubility, toxicity, bioavailability of the RN (e.g. U, Pu, Se, Tc, I). It is particularly relevant for the actinides. These reactions can often be relatively slow, and equilibrium may not be reached depending on the comparison between the relative chemical reaction time and transport time; for instance, uranium captured as poorly soluble tetravalent species in genuine rock is transferred under oxidizing conditions into soluble $U(VI)O_2^{2+}$ species (Figure 3.5). Very often, redox reactions are controlled by microbial activities.

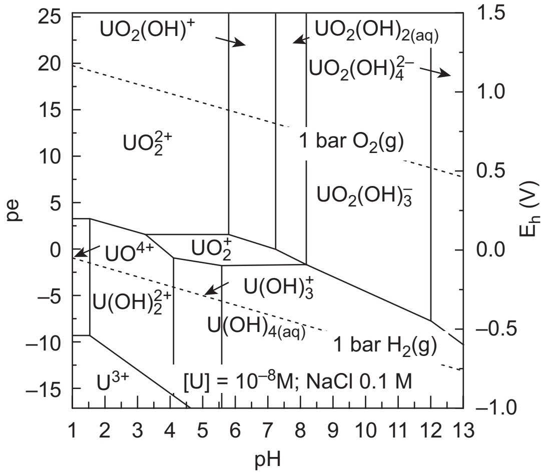


Figure 3.5 pe–pH diagrams describing predominance of uranium redox states under different environmental conditions.

Altmaier and Vercouter (2012).

- **Hydrolysis reactions**, that is, reaction with hydroxide ions, which is of particular significance for the actinides. Indeed, the actinides are known to form several complexes with the hydroxides. Furthermore, hydroxo complexes can aggregate and create polynuclear species that can evolve up to new solid phases when the concentration is high enough.
- Formation of **aqueous complexes** with the other ions. Relevant aqueous complexes to consider depend on the RN and the chemical species present in the aqueous phase. It is hence not possible, in this chapter, to draw a general map of the relevant aqueous species. Synthetic information can be found in Table A.1 and A.2 in the Appendix, and the it is recommended that the reader read dedicated scientific publications. Regarding the actinides, carbonates, phosphate and fluorides are known to significantly react and to form multispecies aqueous complexes.

Except the redox reactions, which can be slow, complexation reactions in homogeneous aqueous solution are relatively fast and can be considered as instantaneous. Equilibrium thermodynamic approaches are therefore relevant.

3.5.2 Key issue of assessing solubility limitations

RNs, like any aqueous ions, can potentially precipitate either in a pure solid phase or as a co-precipitate in another solid phase. Both reactions can be described by a solubility product. Precipitation is classically described by the solubility product, and the saturation index Ω provides a measure whether or not a solid is precipitating. Ω is the ratio of the ionic product Q_s and the solubility product K_s as given below:

$$n_1.A_1 + n_2.A_2 + \ldots \rightarrow (A_{1,n1}A_{2,n2}\ldots)_{\text{solid}}$$

$$\Omega = \frac{Q_s}{K_s} = \frac{\prod_i (A_i)^{n_i}}{\prod_i (A_i)_{\text{eq}}{}^{n_i}}$$

where (A_i) stands for the activity of the species A_i, $(A_i)_{\text{eq}}$ the activity of the species A_i when equilibrium is reached and n_i is the stoichiometric coefficient of the precipitation reaction.

The solubility limit is a key parameter determining the maximum RN concentration in porewater, which can be mobile. In a very simple simulation approach, solubility can be considered as the conservative RN aqueous concentration by assuming that its concentration is controlled by an equilibrium with a solid phase. The solubility limit can significantly vary between highly soluble species such as $^{36}Cl^-$ and relatively immobile elements such as some actinides.

Furthermore, as described above, the redox state has a strong influence on solubility limits of various RN such as the actinides but also technetium, polonium and ^{79}Se, for example. Oxidized actinides, for instance, are forming oxo-cations that strongly reduce the formal charge of the metal cation and thus reduce the affinity to hydroxide ions as compared to, for example, the reduced tetravalent cations. This leads to a solubility limit that is roughly two to three orders of magnitude higher for the oxidized than for the reduced forms. Figure 3.6 depicts the evolution with pH of some actinides solubility.

This sensitivity to redox conditions has a strong influence on the migration behaviour. Actinides and other redox-sensitive elements are usually rather mobile in oxidizing conditions and more strongly immobilized in reducing environments. This means that any locally reducing environment in a given site may act as an efficient RN trap. It should be noted that such mechanisms are responsible for the formation of numerous uranium ores in subsurface environments.

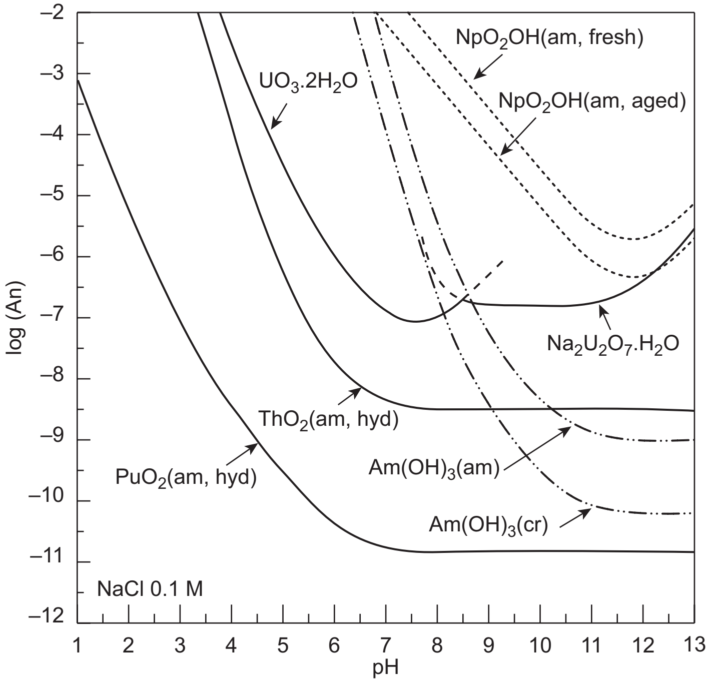


Figure 3.6 Evolution of the actinides solubility as a function of pH. (Altmaier & Vercouter, 2012).

3.5.3 Modelling the RN speciation in a complex environment

Simulating the speciation and approaching the actual speciation of the RN and the key elements is usually an important task for any serious assessment of the potential RN migration from a NORM or contaminated site. Such simulation can be performed by using geochemical software (e.g. EQ3/6, PHREEQC (Parkhurst & Appelo, 1999), Geochemist Workbench). However, the user has to be aware that such tools are basically mathematical solver designed to solve a large set of differential equations describing the different thermodynamic equilibria. The relevance of the results does not depend mainly on the mathematical solving but rather on the quality and exhaustivity of the database that is used (Nitzsche, Meinrath, & Merkel, 2000). An important and long-lasting issue can therefore be to obtain a relevant database that includes not only the usual reference data but potentially some additional thermodynamic data that have either to be derived from the available literature or to be estimated thanks to chemical analogy. Finally, the reader has to remember that, in many cases, it is more relevant, for a chemical reaction that is thought to be important, to use a rough estimation of thermodynamic data than not to include the reaction in the modelling due to the lack of reliable data.

In view of assessing the potential migration of RN on a contaminated site or (TE) NORM storage, detailing all the chemical forms of any elements can be an exhaustive task and may not always be relevant. Expert assessments are often needed to estimate when sufficient knowledge is available to reliably assess the long-term impact. For instance, it will always be mandatory to determine what is the redox state of redox-sensitive elements, since it strongly influences the reactivity, mobility and toxicity of the pollutants. However, it will likely not be necessary in a first approach to know all of the existing aqueous complexes.

3.6 RN retention at the solid–liquid interface

3.6.1 Origin and significance of retention processes

Mineral surfaces are strongly interactive with aqueous species via different mechanisms:

- The potential existence of permanent surface charges is compensated electrostatically by aqueous counter-ions. Such a mechanism is widely observed in clay minerals that often present negatively charged surfaces due to the presence of isomorphic substitutions, for example, $Al^{3+} \leftrightarrow Si^{4+}$. It is intrinsically independent on pH.
- The existence of pH-dependent charges that are created by the amphoteric properties of the broken bonds at the mineral surfaces. They are basically protonated at low pH favouring the interactions with anions, whereas they are deprotonated at high pH favouring the interactions with cations.
- The existence of low-energy interactions as hydrogen bonds that are highly reversible and play little role in retention properties.

All these mechanisms can potentially occur for any of the aqueous ions, resulting in a competition between them and the sorption of the ions with the highest affinity. Sorption can therefore be influenced by any evolution of the aqueous chemistry, such as ionic strength, pH, Eh and trace composition. As an illustration, the pH-dependent sorption behaviour of $U(VI)O_2^{2+}$ in the presence of montmorillonite is shown in Figure 3.7. Although pH-independent electrostatic ion exchange processes play a role at low pH, pH-dependent formation of inner-sphere surface complexes at broken edge sites dominates sorption at higher pH. The decrease in sorption at pH>7 is due to formation of weakly sorbing hydroxo and carbonato complexes of $U(VI)O_2^{2+}$ in the aqueous phase.

Such interactions lead to an apparent trapping of part of the aqueous ions by minerals, which is classically described by the distribution coefficient K_d, which is defined as the ratio between the sorbed and the aqueous concentrations of a given element:

$$K_d[\mathrm{L/kg}] = \frac{(\mathrm{RN})_{\mathrm{sorbed}}[\mathrm{mol/kg}]}{(\mathrm{RN})_{\mathrm{equilibrium\ in\ solution}}[\mathrm{mol/L}]}$$

By definition, K_d represents the distribution of the elements between the free solution and the mineral surfaces at equilibrium. The distribution ratio R_d is also classically used and is defined in the same way, except that equilibrium may not be reached. Retention usually changes with the chemical conditions as follows:

- with pH: it usually increases with pH for cations and decreases for anions;
- with the RN concentration: it usually decreases with the increasing RN concentration (progressive saturation of the sorption site);
- with the ionic strength: it usually decreases with the increasing ionic strength (increase of competition).

Retention is particularly significant in clay minerals, due both to their strong surface area and to their chemical flexibility, which is favourable to retention. Since retention is linked to the interactions on a limited number of sites, the behaviour of a given RN will

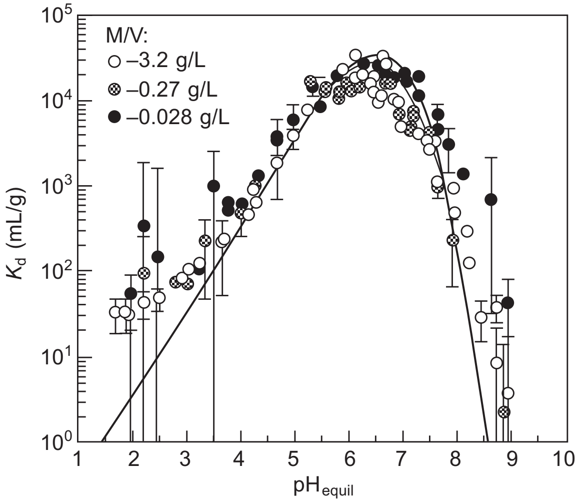


Figure 3.7 pH dependent sorption of UO_2^{2+} onto montmorillonite: low sorption coefficients are observed at low pH; formation of anionic $UO_2(OH)_x^{(x-2)-}$ are responsible for decreasing sorption at high pH.

Marques, Baeyens, and Beaucaire (2012).

be dependent not only on its capacity to interact with the mineral surfaces but also on the behaviour of the other chemical elements that are present in the system. In such cases, the overall sorption will be the result of the competitive interactions of the different aqueous species. Any simplification needed for simulation purposes has to be carefully chosen so as to avoid significant bias. Representative distribution coefficients are given in Table 3.1.

Retention is most often reversible, and sorbed RN can easily be desorbed if the chemical environment is modified. However, this may not be true for specific system in which the RN–mineral surface interactions are strong enough to be irreversible:

- because the nature of the bonding is more chemical than purely electrostatic, or
- because the RN migrates within the mineral and is hence difficult to desorb. That is the case for instance of Cs sorption on illite mineral.

3.6.2 From sorption to incorporation and coprecipitation

A wide range of mineralization reactions are also of relevance, notably in the course of mineral phase transformations. Cemented waste corrosion, for instance, produces new mineral phases such as calcium silicate hydrates (CSH), calcium aluminates (e.g. AFm) and calcite. Various cationic (actinide ions, Ra^{2+}) (Tits, Ijima, Wieland, & Kamai, 2009; Gaona, Kulik, Macé, & Wieland, 2012) and anionic RN (e.g. $^{129}I^-$) (Aimoz et al., 2012) have been shown to be incorporated in the crystal structure of those phases (Pointeau, Coreau, & Reiller, 2008).

Barite is known as a very significant sink for Ra in TENORM sites. Ra is not only incorporated during neoformation of $BaSO_4$ by coprecipitation and solid-solution

Table 3.1 **Representative sorption values of trace radionuclides (RNs) for different representative minerals at neutral pH under classical groundwater conditions**

Mineral	RN	Representative Log K_d (m^3/kg)	References
Smectite	Cs	0.1	ANDRA (2005)
	Tc	30	
	U(VI)	10–100	
	U(IV)	100	
	Pa(V)	10	
	Th(IV)	3	
	Pu(IV)	1	
	Actinides(III)	12	
Illite	Cs	100	Poinssot, Bradbury, and Baeyens (1999)
	Am	10	Bradbury and Baeyens (2009)
	Np	0.01	Bradbury and Baeyens (2009)
	Th	10–100	Bradbury and Baeyens (2009)
	U(VI)	100	Bradbury and Baeyens (2009)
	Pa(V)	100	Bradbury and Baeyens (2009)

formation, but apparently is also incorporated in part when in contact in a barite suspension being at or close to macroscopic equilibrium with aqueous solution (Klinkenberg, Brandt, Breuer, & Bosbach, 2014). Model approaches to describe the interplay of adsorption, entrapment, and solid-solution formation of trace elements and RNs have recently been proposed in the literature (Heberling et al., 2014; Thien, Kulik, & Curti, 2014).

3.6.3 Influence of retention on overall migration

Retention is mostly a reversible process. It therefore does not lead to a definitive trapping of the RN. RN incorporation into mineral matrices can lead to strong retention; but, even there, slow release still is possible by recrystallization or matrix dissolution reactions. In any case, RN migration is strongly delayed, since a very significant part of the initial aqueous RNs is sorbed at the mineral surface. They will be released when the RN aqueous concentration will decrease and would hence be able to migrate. Retention is therefore frequently referred to as a retardation process. Its impact on a purely diffusive transport process can in a first approximation be assessed via the retardation factor, which is defined as

$$R = 1 + \frac{\rho_d K_d}{\omega}$$

where ρ_d is the rock density (kg/L), K_d is the distribution coefficient (L/kg) and ω is the porosity. It can easily be demonstrated that when sorption is reversible, the characteristic diffusion time of a given species τ_{RN} is linked to the characteristic diffusion time of water τ_{water} thanks to the relation:

$$\tau_{RN} = R.\tau_{water}$$

Retardation in diffusion is hence directly proportional to the significance of the sorption, which is clearly a key process controlling the overall migration efficiency.

3.6.4 Specific behaviour of anions close to mineral surfaces

Clay minerals that are ubiquitous in the natural environment present with permanent negative surface charges as described below. In addition to the sorption of cations, these charges also lead to the repelling of anions, which cannot hence access the whole porosity. The presence of negative charges on clay mineral surfaces leads therefore to a decrease in anion migration due to a decrease in accessible porosity and apparent diffusion coefficient, which is referred to as anionic exclusion. The diminution is roughly within one order of magnitude by comparison to uncharged species. It is of specific relevance, since anions are classically not sorbed at all, and anionic exclusion is, in many cases, the sole effective retardation process. It explains why anionic RN are often, in diffusion-controlled environments, the main contributor to the long-term impact.

3.6.5 Potential influence of colloidal species, in particular, natural organic material

It is now generally accepted that mobile inorganic or organic particles or colloids are ubiquitous in most groundwater, and that these solid materials have the potential to facilitate chemical transport of contaminants (Kersting, 2012). Colloids are defined as small particles with diameters less than 1 µm, which are found in natural water. They can be composed of either inorganic minerals such as clays or organic material resulting from the breakdown of plants and animals. In the case of a permeable environment, they are transported along the waterflow. As a result of their small size and low settling velocity, colloids can remain suspended via Brownian motion and be transported with groundwater. Due to their large surface area per unit mass, colloids can adsorb significant quantities of contaminants. They can hence play a significant role in the RNs migration.

Transuranic elements such as Pu can also form nanocolloids (Kim, 1991). These transuranic oxides are called intrinsic colloids or sometimes eigencolloids. Intrinsic colloids can form when the concentration of the actinide ions in solution exceeds the solubility product for the formation of a solid phase.

The significance of colloidal transport was demonstrated earlier for the Pu migration in the Nevada Test Site, although similar observations have since been reported at many other places. Kersting et al. (1999) documented the unexpected appearance of low levels of Pu (2.3×10^{-2} Bq) in addition to Cs, Co, Eu and even Am, in the colloidal fraction of groundwater samples collected 1300 m downgradient from its source of origin. This work showed that Co, Cs, Eu, Pu and Am were transported with colloids for significant distances through fractured rhyolitic rock.

In conclusion, colloidal transport can be very significant in any permeable environment and has to be accounted for. For that purpose, the first step is to achieve an accurate and representative characterization of undisturbed sampled colloids, which is often a difficult task. Although the interactions of RN with such colloids can often be derived from literature data on similar colloid types, additional experimental data may be required when colloids are very specific.

3.7 RN transport processes

Surface environments are characterized by a significant coupling with meteorological and climate variations, which leads to fluctuation in the water table level. Above the water table level, porosity is partially filled with water and a gas phase and determines the unsaturated zone, whereas the deeper environments are characterized only by the presence of water in the porosity, which is referred to as the saturated zone (Figure 3.8).

3.7.1 Transport in saturated environment

Within the saturated zone, two types of transport processes can be distinguished:

- The displacement of the water molecules under the influence of hydraulic charge, which is described by the Darcy's law, which relates the flow velocity *U* to the permeability *K* and the hydraulic charge gradient H:

$$\langle U \rangle = K.\mathrm{grad}.\langle H \rangle$$

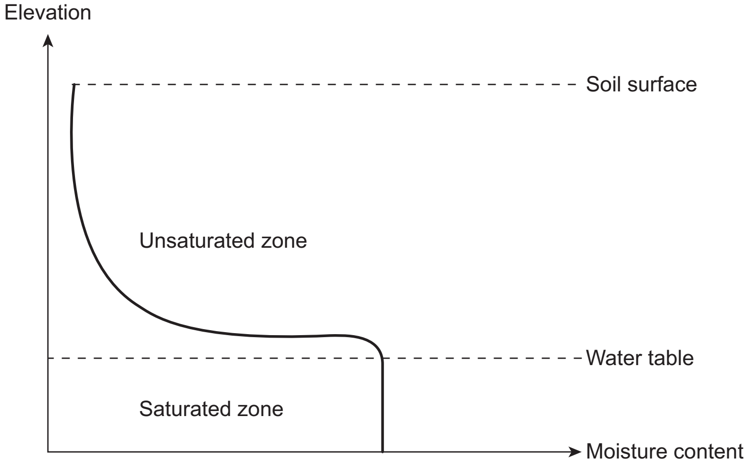


Figure 3.8 Evolution of the water content θ as a function of depth in a typical soil profile. Ledoux, Goblet, and Bruel (2012).

Table 3.2 **Representative permeability and porosity values for different types of rocks**

Medium	Value of K (m/s)	Porosity (%)
Coarse gravel	10^{-1} to 10^{-2}	Up to 80
Sands and gravel	10^{-2} to 10^{-5}	15 to 45
Fine sands, silts, loess	10^{-5} to 10^{-9}	10 to 50
Limestones	10^{-5} to 10^{-9}	0.5 to 15
Clay	10^{-9} to 10^{-13}	20 to 60
Shales	10^{-9} to 10^{-13}	0.5 to 8
Unaltered crystalline rock	10^{-9} to 10^{-13}	0.02 to 2

Ledoux et al. (2012).

- The permeability can be easily characterized by dedicated experiments on small samples and depicts large variations between 10^{-13} m/s for the clay formation up to 10^{-2} m/s for coarse gravels as shown in Table 3.2.
- In porous rocks such as those present in the natural environment, the complexity of the porosity leads to the introduction of some kind of diffusion process that describes the diversity of the migration pathway in terms of factors such as length and section, This process is often referred to as dispersion and is described with Fick's law as classical diffusion.
- Displacement of the aqueous ions within the water phase under the influence of the concentration gradient. This process, which is referred to as Fickian diffusion, is described by Fick's law, which relates the concentration evolution with time to the concentration gradient, thanks to a diffusion coefficient:

$$\frac{\partial C}{\partial t} = D_e . \nabla C$$

In porous media, the free water diffusion coefficient D_0 has to be corrected from the effect of the porosity and hence defines the efficient diffusion coefficient D_e as

$$D_\mathrm{e} = \omega . D_0 . \frac{\delta}{\tau^2}$$

where ω stands for the porosity, δ for the tortuosity and τ for the constrictivity of the rock. The diffusion coefficient can experimentally be measured, thanks to diffusion cells that also allow assessment of the porosity when stimulating the transient phase.

In reality, both advection and diffusion processes are occurring at the same time and are dependent on the site conditions; both can influence the global migration, or one can dominate the other. Basically, RN migration in a low-permeability saturated environment (e.g. clay-rich formation) will be governed by diffusion, whereas RN migration in a high-permeability environment will be mainly governed by advection. In between, both processes will have to be accounted for. Comparing the respective characteristic transport time of both processes, thanks to the Peclet number, is therefore an efficient and rapid approach to roughly assessing the dominant migration regime and adapting simulation methodology.

$$P_\mathrm{e} = \frac{qL}{\omega D}$$

P_e measures the relative importance of advection and dispersion, a large P_e (much larger than 1) implies that the diffusion process is not relevant, whereas a small P_e suggests the opposite.

3.7.2 Transport in an unsaturated environment

Migration process in an unsaturated medium is more complex due to the existence of both a liquid and a gaseous phase that interact together. Basically, the main equations have to be adapted in the unsaturated medium to account for the specificity of the interaction between water and air within the pore space (Carrera, Ayora, Saaltink, & Dentz, 2012).

- First, Darcy's law is modified by the fact that the permeability K is no longer a constant but becomes dependent on the water content θ or moisture, which is defines as

$$\theta = \frac{\mathit{volume\ of\ water}}{\mathit{total\ volume\ of\ rock}}$$

  The expression for K must be experimentally determined, and varies from low values for dry soils to the maximum value at saturation.

- Second, the variation of the moisture content $\mathrm{d}\theta$ is linked to the variation in piezometric head $\mathrm{d}h$ through the expression of the capillary pressure ψ (Pa) as a function of the moisture content, where the capillary pressure is defined as

$$\psi = p_\mathrm{air} - p$$

$$\frac{\partial\theta}{\partial t} = -\rho g \left(\frac{\partial\theta}{\partial\psi}\right) . \left(\frac{\partial h}{\partial t}\right)$$

From that set of equations, one can derive the well-known Richard's equation, which describes the water flow in an unsaturated medium.

$$div.(K(\theta).\,\mathrm{grad}(h)) = -\rho g\left(\frac{\partial\theta}{\partial\psi}\right).\left(\frac{\partial h}{\partial t}\right)$$

This equation generally has to be solved numerically because of the high level of non-linearity and the dependency on θ of its parameters. Transport in such an environment is hence more complex to simulate both numerically and for defining the flow path. From a practical point of view, specific data may be required to describe the evolution of permeability with the water content.

3.7.3 Atmospheric release

Volatile RNs (as Rn) or volatile elements (as Se) can be released in gaseous form and be dispersed in this form in the environment. This mainly concerns atoms that are present within the porosity, in particular due to recoil from the parent decay or if the parent atom is initially sorbed. Therefore, releases of radon from a residue repository to the atmosphere can take place by the following series of processes:

- **Emanation:** radon atoms formed from the decay of radium escape from the grains (mainly because of recoil) into the interstitial space between the grains. This is characterized by the dimensionless emanation coefficient *E*. This coefficient depends mainly on the grain size of the materials, moisture content and mineralogy. *E* generally lies within 0.1–0.3 (Ishimori, Lange, Martin, Mayya, & Phaneuf, 2013).
- **Transport:** diffusion and advective flow cause the movement of the emanated radon atoms through the residue or soil profile to the ground surface. Diffusion processes may be significant and are characterized by a specific Rn diffusion coefficient.
- **Exhalation:** radon atoms that have been transported to the ground surface and then exhaled to the atmosphere. This release is referred to as radon exhalation, and is characterized by the exhalation flux density (Bq/m^2/s).

Assessing the mobility and release of Rn requires the experimental characterization of the emanation coefficient, the diffusion coefficient and the radium activity concentration in the material.

Furthermore, some RN may be released through attachment to aerosol particles and be released thereby. It is specifically relevant for Po.

3.8 Coupling of chemical and transport processes: towards an efficient simulation approach

Two main families of models can be distinguished depending on their applications (IAEA, 2012); these are simple screening models or more exhaustive and detailed assessment models. Both are able to simulate either point source contamination (such as a stack of effluent discharge) or area source (such as mine tailings).

3.8.1 Simple screening models

These models are classically used in the preliminary stages to assess the feasibility of a given storage or remediation project, or to check potential compliance with regulatory conditions. They are very simple models based on conservative assumptions. They aim, therefore, to overestimate RN concentrations and the associated doses and risks. They are also used to assess the significance of the work to be performed to assess the safety case and meet the safety standards. Within this category falls the very simple box model, which allows deriving a rough estimate of the significance of the migration and understand much better the dynamic of the system. Such a model does not consider an explicit simulation of geometry of the system (no 2D or 3D mesh) but rather identifies the different type of environment and their links. Each type of environment is hence described as a single box in which chemistry can explicitly be modelled, and only the mass transfer between boxes is considered. Such an operational approach most often allows giving orders of magnitude of the different processes and is very useful to guide a subsequent, more detailed simulation.

3.8.2 Realistic assessment models

These models are designed to assess, as accurately as possible, radioelement concentrations and radiation doses resulting from a defined scenario for a given project. They therefore need to be detailed enough to correctly capture the actual behaviour of the RNs in the system. However, different levels of simplifications are possible and need to be selected depending on the complexity of the site and the objectives to achieve. Theoretically, transport and chemistry have to be considered simultaneously in such models, as they could interact together; for example. porosity may evolve induced by the chemical reactions as precipitation or dissolution. It therefore requires solving chemistry and transport in each point of a 2D or 3D mesh model for each time step. Such models are hence, in most cases, very demanding goals for complex sites and require long simulation time and a very good knowledge of the overall system.

In this context, the simulation approach can, in many cases, be simplified by decoupling transport and chemistry in the simulation, which is relevant when the intensity of the coupling between chemistry and transport is low enough. This is the case when no strong temporal or spatial gradients or change of chemical conditions occur in the system. In such a case, the evolutions of the chemical processes are rather continuous and linear, which allows a simplified modelling approach. Such a case is often referred as a **light coupling situation** and does not require implementing a full transport–chemistry coupling. Speciation can be simplified and calculated independently as well as the sorption, which can directly be introduced as a constant global retardation process. Such an approach is obviously the most used one and is relevant as long as the chemical and hydrological conditions are constant enough all along the spatial and temporal domains.

3.8.3 Use of a dedicated software simulation tool

Due to the ubiquity of NORM, many simulation tools have been developed internally for home applications or by academic teams for scientific interests, or for commercial purposes, for example, COMPLY and CAP88 (both developed by the

US Environmental Protection Agency, respectively), USEPA (1989) and USEPA (1992), PC-CREAM (funded by the European Union, Simmonds, Lawson, & Mayall, 1995), CROM, RESRAD-ONSITE or OFFSITE (developed by Argonne National Laboratory for the US Department of Energy, http://www.evs.anl.gov/resrad); AMBER (developed by AMPHOS21, Spain). In addition to these dedicated tools, more general and scientific simulation tools can also be used for the development of very detailed assessment models, for example, PHREEQC, EQ3/6, and CRUNCH, HYTEC.

Each of these models has been developed for a specific application and has intrinsic and specific limitations. Readers are therefore encouraged to check the relevance of the tool used with the objectives to achieve. General comparison between most of them can be found in the recent report from IAEA (IAEA, 2014).

3.9 Conclusion: how to reliably predict any future RN migration

Predicting the RNs migration in a complex environment, such as a NORM storage or a contaminated site, is a complex task that requires being able to identify and model the processes governing the following: (1) the RN release rates from the initial material (mine tailings, industrial scrap, treatment residues); (2) the aqueous complexation reactions to define the most relevant aqueous species; (3) the retention at the solid–liquid interface; and (4) the different possible RN transport processes, either in the aqueous phase, in a biphasic gas/water environment, or even for the volatile/gaseous RN in the atmosphere via aerosols or dust particles. The most difficult challenge is first of all to catch all of the relevant processes governing the long-term behaviour of the RNs while avoiding unnecessary details or second-order processes that could hinder any further understanding. There is hence a mandatory step of conceptualization and simplification before shifting to numerical modelling in order to develop a sensitive and representative simulation without altering the reliability and relevance of the results. Indeed, numerous dedicated numerical simulation tools exist and can even be downloaded free on the Web. However, using them without any preliminary expertise and assessment would, in many cases, lead to misunderstandings and wrong conclusions. It is therefore recommended to have a stepwise approach, considering first simple screening models such as a box model to understand the key processes/RN/species/parameters, and the overall dynamics of the system, before shifting in a second step towards a more detailed modelling approach focussing on the key features. Such an approach would prevent a dead-end approach and misunderstandings, and would allow focussing on the necessary experimental site characterization on the most significant parameters, a major input for successfully achieving any remediation or storage project.

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Appendix: main physical and chemical properties of the most significant natural and artificial radionuclides to be found in NORM and legacy sites

Table A.1 **Physical and chemical properties of some relevant natural radioelements**

RN	Physical properties	Main relevant chemical species	Possible immobilization reactions	Possible mobilization reactions
^{234}U	$t_{1/2}=2.5\times10^{5}$ years α-emitter	UO_2^{2+}-carbonate/hydroxo complexes, UO_2 (hydrated)	Sparingly soluble hydrated UO_2 forms under reducing conditions; bioreduction	Under oxidizing conditions UO_2^{+} forms stable complexes and is moderately mobile; under reducing conditions, relatively immobile but colloid formation may increase solubility and mobility?
^{238}U	$t_{1/2}=4.5\times10^{9}$ years α-emitter			
^{228}Th	$t_{1/2}=1.91$ years α-emitter	ThO_2, carbonate/hydroxo-carbonate complexes	Poorly soluble; strongly sorbing	Formation of anionic carbonate complexes; colloid formation?
^{232}Th	$t_{1/2}=1.4\times10^{10}$ years. α-emitter			
^{234}Th	$t_{1/2}=24.1$ days β-emitter			
^{231}Pa	$t_{1/2}=3.3\times10^{4}$ years. α-emitter	$PaO(OH)_3$; PaO_2	Poorly soluble; strongly sorbing	Formation of anionic carbonate complexes; colloid formation?

Continued

Table A.1 **Continued**

RN	Physical properties	Main relevant chemical species	Possible immobilization reactions	Possible mobilization reactions
^{226}Ra	$t_{1/2} = 1.6 \times 10^3$ years α-emitter	Ra^{2+}; Ba(Ra) SO_4	Sorption at clay minerals; solid solution formation with $BaSO_4$	Potentially mobile as Ra^{2+} cation
^{222}Rn	$t_{1/2} = 3.8$ days α-emitter	Gaseous Rn	Tight coverage of site	Mobile via gas phase
^{210}Pb	$t_{1/2} = 22.3$ years ß-, γ-emitter	Pb^{2+}; as oxide, sulphide	Sorption to mineral phases; coprecipitation with sulphates, sulphides	Formation of anionic carbonate complexes; colloid formation? Attachment to aerosols following RN decay
^{210}Po	$t_{1/2} = 138$ days α-emitter	Po(IV)/Po(II) mostly associated with particulates, colloids	Sorption to mineral phases; coprecipitation as Po(II)S	Colloid formation; Attachment to aerosols following RN decay

Table A.2 **Physical and chemical properties of some long-lived radionuclides in nuclear waste originating from energy production by nuclear fission**

RN	Physical properties	Main relevant chemical species	Possible immobilization reactions	Possible mobilization reactions
^{3}H	$t_{1/2} = 12.34$ years ß-emitter	HTO	–	Mobile in presence of water
^{79}Se	$t_{1/2} = 360{,}000$ years ß-emitter	S^{2-}, Se(0), SeO_3^{2-}, SeO_4^{2-}	Sparingly soluble Se(0), $Fe(Se,S)_x$ form under reducing conditions	Under oxidizing and high pH conditions, mobile SeO_3^{2-}, SeO_4^{2-} can form
^{36}Cl	$t_{1/2} = 300{,}000$ years ß-emitter	Cl^-	Retention by ion- or isotope exchange, e.g. with solid NaCl	In general as Cl^- very mobile
^{14}C	$t_{1/2} = 5.700$ years ß-emitter	CO_3^{2-}, CH_4, R-COOH	Retention by $CaCO_3$ formation	Very mobile if CH_4 is formed anaerobically

Table A.2 **Continued**

RN	**Physical properties**	**Main relevant chemical species**	**Possible immobilization reactions**	**Possible mobilization reactions**
^{41}Ca	$t_{½} = 103 \times 10^3$ years ε-emitter	Ca^{2+}	Retention by $CaCO_3$ formation or by isotopic exchange with Ca-containing minerals	Potentially mobile in Ca rich groundwaters
^{129}I	$t_{½} = 15.7 \times 10^6$ years ß-, γ-emitter	I^-, IO_3^-	Significant retention mechanism not yet verified	Very mobile
^{135}Cs	$t_{½} = 2 \times 10^6$ years ß-, γ-emitter	Cs^+	Relatively strong sorption onto clay minerals	(Very slightly) mobile
^{99}Tc	$t_{½} = 213{,}000$ years ß-emitter	TcO_4^-, $TcO(OH)_2$, TcS_2	Sparingly soluble $TcO(OH)_2$, TcS_2 form under reducing conditions	Under oxidizing conditions, mobile TcO_4^- forms; under reducing conditions, colloid formation may increase solubility and mobility?
^{237}Np	$t_{½} = 2.1 \times 10^6$ years α-emitter	NpO_2^+, NpO_2 (hydrated)	Sparingly soluble hydrated NpO_2 forms under reducing conditions	Under oxidizing conditions NpO_2^+ is relatively mobile; under reducing conditions, relatively immobile but colloid formation may increase solubility and mobility?

Continued

Table A.2 **Continued**

RN	Physical properties	Main relevant chemical species	Possible immobilization reactions	Possible mobilization reactions
^{238}U	$t_{½}=4.5\times10^9$ years α-emitter	UO_2^{2+}-carbonate/hydroxo complexes, UO_2 (hydrated)	Sparingly soluble hydrated UO_2 forms under reducing conditions	Under oxidizing conditions UO_2^+ forms stable complexes and is moderately mobile; under reducing conditions, relatively immobile but colloid formation may increase solubility and mobility?
^{239}Pu	$t_{½}=24.000$ years α-emitter	PuO_2^{2+}-carbonate/hydroxo complexes PuO_2^+, PuO_2 (hydrated) Pu^{3+}-carbonate/hydroxo complexes	Under reducing conditions poorly soluble hydrated PuO_2 and sorbing Pu^{3+} forms	Under oxidizing conditions PuO_2^+/PuO_2^{2+}- and their aquatic complexes are relatively mobile; relatively immobile under reducing conditions but colloid formation may increase solubility and mobility?

Poinssot and Geckeis (2012).

Stakeholder involvement in the remediation of contaminated nuclear and NORM sites

4

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4.1 Introduction

As highlighted within the previous chapters of this book, there are a wide range of sites and facilities that, within their lifetime, are likely to require some level of environmental remediation. Contamination may be present in the form of radionuclides, chemicals or heavy metals and may reside in the soil, surface water and groundwater or may become airborne. The actual drivers for undertaking remediation and the actual timing may be varied and could include the following:

- The required remediation may be part of a wider decommissioning strategy;
- There may be a perceived (or actual) risk to human health and/or the environment;
- A site operator may wish to de-licence a site or part of a site;
- There is a regulatory directive;
- A known problem may be increasing (an advancing groundwater plume for example);
- An opportunity to gain access to the problem that may not present itself at a later date;
- Work is needed in support of determining a desired site end state; and
- Public perception must be considered.

Most, if not all, of these drivers will be considered within a formalised decision-making process supporting a specific piece of work or project. Such a process will invariably study a range of options and ultimately decide on an approach commensurate with the desired objective and level of remediation to be undertaken. It is this decision-making process and the actual level of remediation (clean-up criteria or dose targets) to be carried out that is likely to be of greatest interest to the various stakeholders, especially where there is a concern that contamination has the potential to have an impact on human health and/or the environment. Because of the perception of radiological contamination, as compared with non-radiological contamination, many stakeholders might expect to see all contamination being removed, even when this might not be necessary to maintain adequate and acceptable protection of human health. A more passive approach (such as monitored natural attenuation, for example, where contaminants may not be physically removed from the site in question) will be of particular interest, as this is sometimes perceived to be a 'do nothing' option. Adequate explanation of such an adopted approach in a transparent manner is therefore crucial if support and trust of the decision maker are to be obtained.

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Stakeholder engagement is now recognised globally as being an integral part of any decision-making process. With respect to the remediation of nuclear and NORM sites, engagement with a wide range of stakeholders is imperative because of a number of interrelated reasons. First, there is often a perception that radiological contamination is more hazardous than conventional contamination, and, notwithstanding the fact that in some instances this may be true, it is equally important to note that it may not always be the case. Radiological contamination can be spread through various media and in extreme cases like that in relation to accidents (Chernobyl and Fukushima), contamination has the potential to affect a geographical area much greater than the site and its immediate surroundings.

Although the subject knowledge held by stakeholders will vary, there is, in general, a lack of understanding within the wider community about radiological matters, coupled with a genuine concern and a lack of trust of those operating such plants and facilities. Although the civilian nuclear industry in most if not all countries is strictly regulated, such regulation may not always be in place for the NORM-related industries.

The aim of Chapter 4 is therefore to highlight why engaging with stakeholders when you are planning and implementing the remediation of nuclear and NORM sites is crucial. The success or failure of a project can often be determined by the level of support acquired through such interactions.

4.2 Definition of stakeholders and the importance of engagement at nuclear and NORM sites

4.2.1 Definition of stakeholders

There are many similar definitions used nowadays to state what we mean by a stakeholder. For the purposes of this book, we have chosen to use the definition that states that ‘a stakeholder can be described as a group or individual with an **interest** in or a **role** to play in a project, or a decision-making process’.

The reason why this definition is favoured is that it captures a number of key sentiments about stakeholder engagement. First, a stakeholder may purely be an individual, or may be part of a wider group. Such individuals may have an interest in a decision that is being made, but more importantly, they may have a role to play in that particular decision. Last but not least, decisions are normally made within a formalised process, and this process should ideally be transparent and take cognisance of stakeholder views, concerns and aspirations.

4.2.2 Importance of engagement at nuclear and NORM sites

Radiological contamination, whether it emanates from a licenced nuclear site, an accident, a uranium mining/milling site, from weapons testing or from the oil and gas industry, is often perceived to be more hazardous than many other types of contamination. In some instances this may be true, but in many cases the actual levels of contamination are relatively low and may bear minimal or no risk to human health or the environment. This means that the nuclear industry and/or those industries that produce radioactive wastes or the processes and activities of which may lead to radiological contamination have to work a lot harder to justify the management and remediation decisions that they make. Importantly, they need to demonstrate, in a transparent manner to their stakeholders, that they are managing such issues appropriately.

The nuclear industry has historically been somewhat secretive in nature. In many instances, this was because nuclear sites were associated with the defence industry in their early years, whereas in other cases there was merely a genuine requirement to keep records classified and to maintain safety and security. Nowadays there is heightened security at power plants and other nuclear-related facilities. The defence and weapons testing sites are understandably kept secure and, even though they generally cover large swathes of land, in most instances public access is virtually impossible.

For industries that are not necessarily classed as nuclear (mining, oil, gas, desalination, etc.) but that may generate radioactive wastes and create soil/groundwater contamination, there is also often a sense of secrecy surrounding their operations. Most, if not all, of such sites will have general security preventing unauthorised access; but in a cultural sense, few organisations will willingly volunteer to talk about radioactive wastes or potential contamination, especially when there is no foreseeable solution to a potential problem or challenge.

So, taking all of these points into consideration, there is not surprisingly a view from the general public that these sites may have something to hide or that they are not communicating what materials may reside within the site boundary and the potential implications of those materials to human health and the environment. Even though there may be a robust regulatory regime in place the role of which will be to protect human health and the environment, there is still a feeling that decisions are often made based more on cost reduction than on reducing hazard and risk. In a modern society where sustainability is being encouraged, there is clearly a fine line to be drawn between costs and benefits. It is for reasons like this that the decision-making processes surrounding environmental remediation need to be transparent and revolve around a commitment to stakeholder engagement. It is only through this kind of approach that stakeholders will gain a greater understanding of the constraints that a site operator may have and for the operator to understand and consider the concerns and aspirations of the stakeholder community. (NB. The ‘problem holder’ will in most cases be a site operator but in other instances, the responsibility may lie elsewhere, Fukushima being a good example. For consistency within this chapter, the term ‘site operator’ is used.) The case study relating to the UK’s SAFEGROUNDS Learning Network, highlighted in Section 4.7.1, provides an example of where different communities, through improved communication, have started to understand and trust each other more.

In understanding the views of a given stakeholder community, a key question to first consider is why they might be interested in the decision-making process underpinning an environmental remediation programme. First, and perhaps most crucially, they may be potentially affected by the decision that is ultimately made. The effects of a decision may be positive or negative, so a number of interrelated and underpinning concerns will surface, including the following:

- Will the decision adequately reduce the risk to human health and the environment?
- Might a chosen approach make the situation worse if not correctly applied?
- Will a chosen option create short-term detriments while the work is being carried out (visual impacts, noise, dust, increased vehicle movements, etc.)?
- Could the available funds have been better spent elsewhere?
- Might there be benefits offered to the region such as employment, compensation and improved infrastructure?
- Will there be an impact either in the short or long term on employment?
- Might there be a new use for the site in question?

Stakeholders may therefore wish to provide a degree of input into the decision-making process rather than merely be informed about what is going to be undertaken. This additional involvement can be positive in that it allows them to have some potential influence over a chosen remediation approach and how it is to be carried out.

Engagement should, however, not be seen as purely ticking a box and hoping that stakeholders will go away. Actively engaging with the general public because they expect it is clearly important, but proactive engagement is equally crucial in regions where, because of culture and background, individuals might otherwise be placing themselves in danger. Examples of this may be found around uranium mining sites in less developed countries. Farmers may wish to graze their livestock on what appear to them as large swathes of un-owned land, or people may be attracted to demolished buildings to try to take metals and concrete for reuse, not knowing that such items may be contaminated. Seepages from the mine tailings may also migrate into aquifers or surface water features, and such waters could be used for recreation, agriculture or drinking purposes.

4.2.3 Stakeholder categories and their interests, concerns and aspirations

Although the term ‘stakeholder’ was defined in Section 4.2.1, it must be noted that there are many different types of stakeholders, each with potentially different interests. Before any stakeholder engagement programme is established, it is necessary to map out who might have an interest in a project or programme (IAEA, 2014). Missing out on a particular stakeholder or group can, in some instances, be extremely detrimental to the project. Table 4.1 highlights some examples of different stakeholder categories and their areas of potential interest. The table also shows that some stakeholders may be classified under more than one category.

In a slightly similar sense, as well as having specific areas of interest, stakeholders can also be considered in terms of their aims and aspirations and therefore their motivation to engage. Table 4.2 highlights some of these aims and aspirations.

One of the most crucial aspects of stakeholder engagement is the establishment of trust (Collier, 2011; SNIFFER, 2010). Not surprisingly, engagement is rarely successful if trust has not been established or if it has been lost. With its relatively secretive nature, it is likely to be a lot more difficult to gain trust within the nuclear industry than

Table 4.1 Stakeholder categories and their areas of potential interest

Stakeholder category	Stakeholder type	Areas of potential interest
Political	Government Local and regional councils	Overall costs, incentives and investments, impact on the local community, community sentiment
Economic	Funding organisations Local and regional councils Government Local community Workers' unions	Overall costs, incentives and investments, improved infrastructure, employment security, impact on the local community
Environmental	Environmental regulators Local community Nongovernmental organisations (NGOs) Local and regional councils	Transportation, visual impacts, impacts on groundwater and rivers, noise, dust, water use, human health, environ mental conservation
Social	Site workforce Local support services Local community Tourist industry Workers' unions Media outlets	Health and safety, work duration, employment security, impact on the local community, incentives and investments
Technical	Nuclear regulator R&D institutions Universities Consultants	Nuclear safety, education, research, innovation, technical consultancy support, radioprotection

in others. Relationships need to be built over time, and engagement should be seen as a continuous rather than a one-off process. Unfortunately we do not live in an ideal world, and things do sometimes go wrong. Openness is vital, and it is important to admit previous mistakes, to acknowledge uncertainty, and to provide all of the available information rather than selective snippets. Reliability is also an important trait in that you must undertake what you say you will. It can be very damaging to promise something that you later fail to deliver.

Building trust can be greatly enhanced if the following principles are considered and adhered to:

- Be open and honest, and be ready to admit mistakes from the past;
- Demonstrate your sincerity in genuinely wanting to form a greater understanding of your stakeholders' concerns;
- Carefully explain the limitations that you might have within your decision-making process at the outset, and never promise something you cannot deliver;
- Be very clear about the role that you wish the various stakeholders to take and the limit of their involvement. Unduly raising expectations about their ability to influence a decision can be very damaging;

Table 4.2 **Motivations to engage by different stakeholder groups**

Stakeholder group	Aims and aspirations
Funding entities	They will want to ensure that the funds that they provide are being spent appropriately and that the project does not involve overspending
Regulators	Their role is to ensure that the site operator is complying with the statutory nuclear, environmental and safety requirements
General public	They will wish to see a demonstration of health and environmental protection and gain of sustainable development in their region
Local communities	They will wish to see potential local benefits from any remediation work while also minimising any negative impacts that the work may create
Tourist industry	They will want to ensure that remediation work does not lead to a reduction in tourists to the region, and that there will be no detriment through visual and noise impacts
Local authorities	They will wish to see evidence of benefits rather than detriments to the local community
Elected officials	They will wish to ensure that the remediation work achieves its goals and improves the local environment so that their electorate will continue to support them
Neighbouring countries	They will wish to ensure that remediation activities do not affect them in a negative way
Universities	They will look for opportunities to deliver education programmes and to provide technical support through research and innovation
R&D organisations and consultants	They will wish to secure project work and provide innovative approaches
Workers' unions	They will wish to protect their workers in terms of both safety and job stability
Media outlets	They play an important role in the dissemination of information, thus leading to increased business

- Always provide as much information as possible, but explain what type of information may not be available and why;
- Demonstrate that you really are listening to them and considering their views and not merely ticking a box;
- Communication is not just about providing information, as you can always learn from others. Demonstrating that other people's views are being considered and even incorporated within the decision-making process can help build trust;
- Keep the communication and engagement channels open, and regularly update people on progress. Engagement needs to be continuous, and a sudden lack of proactive engagement can quickly cost you the trust that you might have gained;
- Try not to appear defensive, especially if stakeholders request something that you do not ideally wish to implement; and
- Provide positive messages. Environmental remediation is all about improving an existing situation but recognising that there undoubtedly will be a trade-off between the various components (risk, cost, wastes, visual impact) in delivering a final solution.

So why is engagement difficult? As previously mentioned, there is a lack of trust in those industries with nuclear or radiological connotations. For example, the production of energy through nuclear power plants is still, in some people's minds, linked to defence-related issues and the production of nuclear weapons. The nuclear industry also suffers from a perceived lack of solutions for the stockpiles of long-lived and highly active waste materials. Scientists use terminology that, in itself, can confuse people, and such scientists need to provide a better explanation about naturally occurring radioactive material and background radiation levels. As we cannot actually see radiation and radioactivity, it is more difficult for the non-scientific community to understand its potential impact. The scientific community is also, perhaps, still failing to adequately communicate risk that needs to be put into the correct context. The fact that at both Chernobyl and Fukushima it was necessary to set up exclusion zones unfortunately provides only the negative message that radiological contamination poses a serious risk to human health. The general public, therefore, find it hard to trust the technical community when community spokespersons say that the risk is low or is manageable rather than that there is actually no risk at all. Risk communication is therefore one of the aspects of stakeholder engagement that needs to be improved.

This lack of trust of the nuclear industry unfortunately often has a knock-on effect on the public's perception of the uranium mining and NORM-related industries too, primarily because of the radiological connotations. So even when a site operator is looking at applying a remediation solution to improve an area of contamination, there will always be a certain amount of suspicion and distrust.

The media should be viewed as one of the key stakeholder groups because they have the ability to affect and influence the general public (in both a positive and negative sense). The media, if they choose to do so, also have the ability to provide a bias to news stories or even to sensationalise certain situations. In a world in which news and visual pictures can be streamed live onto mobile devices, it is important for site operators to look at how to work closely with the media or to be able to counter any information that might be, in some instances, factually incorrect. The visual images of the hydrogen explosions at the Fukushima nuclear power plant following the March 2011 tsunami had a negative impact on the public's perception of the nuclear industry and the potential dangers of radiological contamination, perhaps more so than we have previously seen. Putting such images into context and providing a correct and accurate explanation is therefore crucial.

4.2.4 Benefits of engagement

The first rule in stakeholder engagement is that you should never assume that you know what people care about or what their aspirations might be. The stakeholder community will interpret such pre-conceived assumptions from a site operator as arrogance, and trust will be lost very early in the process. It is only through actually talking with stakeholders and asking them for their views that an understanding of their concerns and aspirations can be made.

So, looking at engagement from the perspective of the site operators, there are many reasons why they should wish to engage with stakeholders. These reasons will again vary from site to site and between the different kinds of challenges, but will generally include the following:

- Site operators must have a willingness to demonstrate that the level of work being proposed is commensurate with the problem in hand, with the objective of gaining community support;
- Site operators may need someone's approval for what they wish to implement. This approval could be regulatory or as part of a public inquiry;
- Operators may believe that they are not trusted but may wish to build trust;
- Operators may, for historical reasons, have previously been secretive, and now wish to change this policy;
- The decisions that site operators make will undoubtedly have an impact on others. Localised transportation issues, generation of wastes or loss of jobs are a few examples, and so these potential impacts need to be shared and discussed;
- It may be important to inform the local population about the consequences of accessing contaminated areas and ensuring that such access is avoided;
- Stakeholder engagement may be a regulatory or legal requirement in that particular country;
- People may have concerns about an area of contamination, or they may be afraid that the proposed work could make the situation worse. These fears will need to be allayed; and
- Site operators may wish to undertake risk communication.

So, organisations should ideally embrace the engagement process and see it as a positive rather than a negative exercise. In reality, environmental remediation is intended to improve an existing situation, whether this is related to contamination in soil, groundwater and air or through general impacts on human health. It should therefore be seen as good news. The crux of engagement is really about demonstrating that the most appropriate and sustainable solution is being adopted to make improvements to human health and the environment. The applied remediation would hopefully provide a reduction in hazard, reduce potential visual impacts and facilitate the reuse of land and property.

Having highlighted the reasons why a site operator should embrace the engagement process, it is also important to restate that engagement can be a difficult process, and, in some instances, it can go wrong. For example, some groups may purposely obstruct the process; it may lead to longer project timescales and costs; and it can sometimes lead to decisions that go against the decision maker. However, there will be many examples of where avoiding engagement has caused greater problems.

4.3 Evolution of stakeholder engagement

As highlighted in Section 4.2, the nuclear industry and those industries the activities of which have the potential to generate radioactive waste or contamination have historically been somewhat secretive in nature. The levels of engagement may also vary depending on political, cultural and geographic differences. For example, there has been a greater expectation for industry to engage with stakeholders in western countries for many years, whereas increasing pressure from NGOs and the general public is only a more recent expectation in other countries. When the Chernobyl nuclear accident in 1986 occurred, for example, there was no immediate announcement by the authorities at the time to either the general public or the international community that a problem had arisen. Accidents like that in Chernobyl and more recently Fukushima have heightened many people's perspectives about the nuclear industry in general and the potential effects of radiological contamination in particular.

Historically, engagement has often taken the form of what we term '**Decide–Announce–Defend**'. Essentially what this means is that a site operator will undertake an assessment of a contamination problem, decide the approach that they intend to take via an evaluation of the technical and regulatory criteria and then, after the application of the solution, provide feedback to stakeholders. If any questions arise, they will steadfastly defend the approach that they have taken. This approach is still applied in many countries, and decisions are often made purely by the site operators, sometimes even without consultation with the regulatory bodies.

Although outdated, this approach is taken for a number of reasons. It is partly because, in a cultural sense, engagement has not previously been expected, and in other instances there is an attitude that the scientists and decision makers know best and that people would not understand the issues even if they were discussed.

The next level is commonly referred to as **stakeholder communication**, whereby the site operator undertakes an assessment of the problem and then communicates this and the approach that they intend to take to resolve it. Although this clearly is better than the Decide–Announce–Defend approach, this is still a one-way process and does not allow for stakeholders' aims, concerns and aspirations to be factored into the decision-making process. Many organisations pursue this approach, believing that they are fully engaged with their stakeholders. However, some dialogue is always better than none, so this approach is at least a good start for those organisations that have previously not actively communicated and that now wish to commence such a process. Realistically this is the bare minimum that an operator should look to achieve.

Taking stakeholder communication further, we should aim to undertake **stakeholder engagement**. Although there may be some semantics around words like 'communication' and 'engagement', the latter essentially reflects a two-way rather than a one-way process. Here the site operator will provide an overview of the problem and the initial thoughts of resolving it and then share these with stakeholders to gain their views. Various mechanisms can be used to facilitate this process and are discussed in more detail in Section 4.4. It must be remembered here that it is the site operator – not the stakeholder – who owns the problem and is therefore accountable for the eventual solution chosen to resolve it. So, engagement provides a mechanism whereby the site operator can gain the views of stakeholders and factor these into the overall decision-making process; but the stakeholders themselves cannot be held responsible for the outcome of the chosen way forward.

Last but not least, we have **active participation** whereby stakeholders may actually assist in the decision-making process through their attendance at workshops. At these workshops, there would usually be an appraisal of a range of environmental remediation options to potentially resolve a contamination problem. The options would be assessed against a suite of attributes generally through a Multi Attribute Decision Analysis (MADA) process. Such processes include Best Practical Environmental

Table 4.3 Summary of the evolution of stakeholder engagement

Stakeholder engagement process	Summary details
Decide–Announce–Defend	One-way process, usually after the event, to explain what has been undertaken
Stakeholder communication	One-way process whereby the site operator explains the work that is going to be undertaken and why
Stakeholder engagement	Two-way process whereby the views of stakeholders are sought
Active participation	Stakeholders are invited to work alongside the site operator to appraise a range of options

Option (BPEO), Best Available Technique (BAT) or Best Practical Means (BPM), which are all essentially variants of MADA.

Table 4.3 provides a summary of the evolution of stakeholder engagement.

For the engagement process to be effective, it should ideally be proactive rather than reactive in nature. This is essentially because people will feel that the site operator is genuinely interested in stakeholder views and is not merely going through the motions.

4.4 Mechanisms of engagement

There are a range of mechanisms that can be used for engagement. These will again vary from project to project and in different regions and countries. There is ‘no one size fits all’ with stakeholder engagement, because what might work well at one location may not necessarily work in another. Engagement can, in many instances, be culture specific, and it is important to recognise and factor in how different communities live.

Table 4.4 provides a summary of the various mechanisms that can be used. As the table shows, it is important to apply the correct mechanisms against the type of engagement being adopted. There will also be examples of where some mechanisms will suit more than one type of engagement process (e.g. facilitated meetings can be useful when feedback is being sought, but also when stakeholders are actively being asked to contribute to the decision-making process). The adopted mechanism can also influence the number of people being targeted. Distributing leaflets through doors and press articles have the potential to reach a lot of people, whereas workshops and surgeries can, by definition, only reach lower numbers.

A good stakeholder engagement programme is one that aims to encompass a range of these approaches, thereby providing both passive and proactive mechanisms (SNIFFER, 2010), and thus hopefully accommodating all types of stakeholders. Providing detailed information on a company Web site in a transparent manner is a positive approach, but still relies on people first knowing that the Web site exists and then being able to access it and understand the messages provided. A good Web site will be designed in a manner that allows contact with a site operator to be made and further questions to be asked.

Table 4.4 Mechanism for engagement

Engagement process	Nature	Mechanisms
Decide–Announce–Defend	Passive in nature. Generally providing information once a decision has been made.	Internet Web sites Newsletters Video Leaflets Press articles Advertising
Communication	Passive in nature. Generally informing people about a current situation and the potential solutions being considered to alleviate it.	Internet Web sites Newsletters Displays Site visits Video Leaflets Press articles Telephone hot lines Road shows Visitor centres
Engagement	Proactive in nature. Informing and gaining feedback. A demonstration of being interested in people's views.	Consultation exercises Site visits Workshops Facilitated meetings Questionnaires Road shows Open days Liaison groups Visitor centres Surgeries
Active participation	Proactive in nature. Informing but also gaining people's views on a potential problem and how they might like to see it resolved.	Consultation exercises Workshops Facilitated meetings

There are a number of engagement approaches that have proved to be successful, and two of these are highlighted below.

The first example demonstrates proactive engagement, and can be seen within the work of Wismut GmbH (http://www.wismut.de/en/), who have undertaken extensive uranium mining remediation work in the German state of Saxony. Large areas of contaminated land have been returned to public use, including industrial areas, parkland and a golf course. The company has taken a transparent and successful approach to public engagement, including an annual 'day of the open door'. On this day, local residents are invited to the areas where the remediation has been undertaken, and can discuss with Wismut personnel the progress being made as well as the associated work related to the monitoring of radon gas and groundwater. At the Ronneburg site in 2012, this one-day event (which is aimed at all generations of the community) attracted 10,000 visitors, thus demonstrating the success of this engagement approach.

The second example is in the United States, where many of the United States Department of Energy (USDOE) sites (http://www.hanford.gov/page.cfm/hab) use site-specific advisory boards (SSAB) as a mechanism to involve stakeholders more directly in remediation decisions. This approach, especially where public input is acquired, is believed to result in more sustainable decisions being made. There are now eight local boards in existence, including the Oak Ridge SSAB, Savannah River Site Citizens Advisory Board, Portsmouth SSAB and the Hanford Advisory Board. At the local board level, membership represents different cultures, views and demographics from those who are likely to be directly affected by site clean-up activities. A wide range of stakeholders are represented, including those from academia, industry, local government, tribal nations and environmental groups. The local boards are responsible for the provision of advice and recommendations relating to site-specific environmental remediation, representing the community and keeping the public informed on key issues.

4.5 Constructing an engagement programme

Although there is no simple formula by which an engagement programme can be built, there are clearly some generic messages and learning that can be adopted. At the outset, there are a number of fundamental issues to consider, the first of which is to clearly understand the objective of the engagement and what we want to communicate.

In many cases, this will relate to describing the nature of the problem, the different options and solutions that could be adopted, and the potential impacts or benefits of these. These impacts may be negative or positive, so they need to be compared with the impact of doing nothing. For work related to environmental management and remediation, it is common to undertake environmental risk assessments to determine the impact of a particular decision or option on human health and the environment. The communication of risk is therefore another key subject to carefully explain.

Once the programme objective has been established and the communication subjects identified, a further set of issues to consider relate to the stakeholders themselves. These will again potentially influence the success or otherwise of the engagement programme. Stakeholders will require access to the available information and adequate time to review it, so the mechanisms used need to be appropriately chosen to fit the different stakeholder groups. The information needs to be in an understandable form, but here lies another potential problem. Most information produced is generally technical in nature and full of industry jargon. On the one hand, if the information provided is too technical it may not be understood, yet if it is made too simple the site operator may be accused of either treating stakeholders as being ignorant or of hiding the real situation within the undeclared details. It is therefore very easy to lose trust if the approach is incorrect, and a balance needs to be made. A sensible approach would be to provide a higher-level summary document that is supported by all of the technical information, should a particular stakeholder group wish to view this.

Some stakeholders (representatives of the NGO community for example) may be engaging in a number of industry engagement projects at the same time, so competing demands of these individuals need to be considered. This community of stakeholders is often crucial for the process and they may need to be funded to be able to travel to the various workshops and meetings. In meetings and workshops of a public nature, there is always a possibility that certain individuals who are more adept at public speaking may influence the audience than those who are not. However, the latter may have equally important views, and also may feel less confident to show their support to a site operator in a public forum in front of others. It is important therefore to somehow accommodate such stakeholders rather than incorporating only the views of those who are louder and potentially more persuasive.

In addition to considering the issues highlighted above, it can be worthwhile to incorporate these plus any additional items into a formal checklist (Collier, 2011). Such a checklist helps to ensure that you have captured all of the relevant stakeholders, will focus on their likely concerns and aspirations, and will adopt the most appropriate engagement methodology. This checklist could include the following:

- Compile a list of the different stakeholder categories and groups to ensure that you have considered and captured key factors such as aspirations, age, geographic area, ethnicity, culture and concerns;
- Produce a database of all potential stakeholder groups and named contacts;
- Consider whether you have worked with any of these people in the past and how you can further develop the relationship (or, in some cases, repair it);
- Research whether there are any other engagement programmes being undertaken that might duplicate your programme or divert resources from it;
- Determine how you might accommodate stakeholders who were missed off the original list;
- Work out how you will factor the stakeholder engagement process around the project timescales (which itself might subsequently need to be revised);
- Consider whether other organisations might have undertaken similar work from which you can learn;
- Consider whether you have the right engagement mechanisms for the different stakeholder groups;
- Determine how you will review the engagement process as it proceeds; and
- Ensure that you communicate within your own organisation about the engagement plan and its outcomes.

During the development of an engagement programme, there are a number of key stages to consider:

- Define the objective of the programme;
- Define who the stakeholders are;
- Plan the programme;
- Review the plan;
- Promote the programme;
- Provide information to the stakeholder community (through the nominated mechanisms);

- Consult with the stakeholders (through the nominated mechanisms);
- Undertake the programme (through the nominated mechanisms);
- Compile the information to be fed into the decision-making process;
- Acquire feedback on the programme from the participants; and
- Evaluate the programme.

Last but not least, choosing the right personnel to undertake the engagement is essential (SNIFFER, 2010). Ideally the engagement process should be led by experienced public affairs or communications experts. These individuals should aim to be developing long-term relationships and should be supported as and when required by their technical community or by senior personnel within the organisation. Support from the technical community allows specific details to be discussed, and the presence of a company CEO from time to time demonstrates the organisation's commitment at the highest level to the engagement process.

4.6 Future trends

It is clear in today's society that environmental issues and the protection of human health are of great interest to stakeholders, irrespective of the region or country concerned. This interest is complemented by a greater expectation for organisations to discuss the decisions that they are making in relation to the environment. Even in countries that have traditionally adopted a policy of Decide–Announce–Defend, there is evidence of greater transparency in decision-making processes, even if it relates merely to greater communication. This will only increase, because the nuclear industry especially requires the support of a range of stakeholders – especially the general public – if it is to gain continued acceptance.

Engagement will still need to be flexible, be commensurate with the problem in hand, and reflect different cultures. What might work in one region may not necessarily work in another, although many approaches are generic in nature.

Getting a greater number of people involved in the engagement process like that in the US with the site-specific stakeholder groups is proving to be effective and is therefore likely to be adopted in other countries. Some countries are already considering adopting this approach. In the United States, there are also examples of training individuals such as Navajo tribal members to become involved in the site characterisation and remediation work. This approach clearly takes engagement to a different level.

Because we base the majority of environmental remediation decisions upon an assessment of risk, dose or contamination levels, it is likely that engagement will focus more on providing a better explanation about background radiation and naturally occurring radioactive materials. We are also likely to see an increase in the effective communication of risk.

Social media are also being used more extensively for the communication of technical information and for registering disagreement over a problem or specific situation. This form of communication is very likely to increase, as it can, in many instances, provide an almost instantaneous mechanism for relaying news and information including pictures and video clips.

4.7 Case studies

4.7.1 SAFEGROUNDS learning network

The United Kingdom's SAFEGROUNDS Learning Network (http://www.safegrounds.com) provides an interesting case study of how nuclear site owners/operators and a wide variety of stakeholder groups, through working together, developed a greater understanding of each other's roles, responsibilities, constraints and concerns. The word 'SAFEGROUNDS' was derived from **SAF**ety and **E**nvironmental **G**uidance for the **R**emediation **O**f **U**K **N**uclear and **D**efence **S**ites. Although now combined with the sister networks of SAFESPUR and SD:SPUR, it was originally set up to identify and disseminate best practices in the health, safety and environmental aspects of managing contaminated land, especially that with radioactive contamination.

The network had a number of primary objectives:

- To produce, maintain and promote guidance;
- To provide a forum for debate and encourage stakeholder participation;
- To provide information on policy, regulatory and technical issues; and
- To develop further supporting documents.

As the network was relevant to contaminated land across all UK nuclear and defence sites, it was not project specific. It was a project managed by the Construction Industry Research and Information Association (CIRIA) and run by a Steering Group made up of a diverse set of stakeholders, including site owners/operators, regulators, local councils and members of the NGO community. Funding to run the network was provided from a range of its members but primarily from site operators and regulators. During its time, it had more than 200 members representing more than 100 organisations, and its function and objectives were underpinned by five key principles (which were produced through consensus during a series of workshops):

- Principle 1: Protection of people and the environment
- Principle 2: Stakeholder involvement
- Principle 3: Identifying the preferred land management option
- Principle 4: Immediate action
- Principle 5: Record-keeping

Before the production of these key principles, an inaugural SAFEGROUNDS workshop was held with the aim of determining which aspects of contaminated land management were deemed to require immediate attention and focus. It was facilitated by an experienced independent organisation (the Environment Council) and was attended by representatives from more than 50 companies, institutions and groups. These attendees included personnel from industry, regulatory bodies, local councils, academia and the NGO community. The workshop allowed stakeholders to identify their concerns and interests, which included technical guidance, advice on effective communication systems and the ability to feed into policy and regulatory decisions. The workshop itself had a number of simple ground rules that were agreed upon at the outset by all participants and that included the following:

- The facilitation team would be responsible for the process;
- All participants would be responsible for the content, especially the accuracy of the records;
- Decision making would be by consensus; and
- There would be no confidentiality in the discussions unless specifically stated.

The output of this initial workshop was developed into a 3-year programme by the Steering Group. The fundamental subject areas were seen to be health and safety aspects of site characterisation and the formulation of key principles for contaminated land management. The former led to the development of a SAFEGROUNDS best practice guidance document, and the latter were developed as stated previously through a series of workshops.

The ability to formulate and to agree upon key principles for managing contaminated land was viewed as the crux for the entire project. This was because the variance in viewpoints among the range of stakeholders were known to be considerable. At the outset, a set of questionnaires were sent to a range of stakeholders with the aim of gaining their views on a variety of contaminated land issues. The output from this was collated and fed into a series of workshops that were aimed at working up the key principles and, where possible, achieving agreement on the underlying definition for each of these. Key Principle 2 – Stakeholder Involvement, for example, was defined as ‘Site owners/operators should develop and use stakeholder involvement strategies in the management of contaminated land. In general, a broad range of stakeholders should be invited to participate in decision making’. Although a definition like this might appear to be straightforward, the process was far from being simple in that a series of workshops were ultimately required for consensus to be gained. An important point to note was that consensus was achieved only through both end members of the stakeholder spectrum (the site operators and the NGO community, and especially the latter) agreeing to relax their initial stance and viewpoint.

These workshops allowed the stakeholder community to better understand the constraints faced by a site operator and for industry to hear first-hand the concerns and aspirations of the NGO community. It was through such dialogue and increased understanding that these key principles were formulated and a range of subsequent best practice guidance documents were produced. Where consensus was not established, the documents produced always stated where the differences of opinion lay.

SAFEGROUNDS was designed to function as a long-term learning network with the needs of its members, including the following:

- To update and improve the SAFEGROUNDS guidance;
- To publicise case studies of managing radioactively contaminated land;
- To act as a link between local and national stakeholders;
- To act as a repository for know-how gained through the management of radioactively contaminated land;
- To enable feedback from NGOs on whether the management and remediation of contaminated land is matching expectation;

- To help build trust among stakeholder groups;
- To challenge existing assumptions through dialogue;
- To share best practices;
- To promote research and development; and
- To allow non-technical parties to understand the issue and to express their opinions.

The network should be seen as a success story, because it provides an example of a level of trust (not necessarily complete trust, but trust nonetheless) being established that allowed industry and stakeholders to work together. The guidance produced has been regularly updated and is used extensively in the United Kingdom and referenced internationally. Site operators in the United Kingdom generally expect their contractors to provide evidence that they will work according to the guidance and the underpinning key principles when undertaking contaminated land-related work. Fifteen years after the creation of SAFEGROUNDS, the guidance documents are still heavily referenced.

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International recommendations and guidance on regulation of contaminated nuclear and NORM sites, and aspects of national level application

5

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5.1 Introduction

The rapid development of commercial and military uses of radioactive material in the twentieth century, particularly from the 1950s to the 1980s, led to the development of many nuclear facilities worldwide. In many countries, these facilities were built and operated before the regulatory infrastructure was in place to ensure that they were effectively decommissioned and returned to beneficial use at the end of their operating life. The legacy from this underregulated build-up is that many countries now have partially remediated or abandoned nuclear facilities or areas where spills or accidents have occurred, that are contaminated with long-lived radioactive and toxic residues that give rise to environmental and health concerns. Many factors, including a lack of resources, lack of trained staff and lack of a national policy and/or regulatory framework for their management, have contributed to sustaining this nuclear or radiological legacy (hereafter just called a legacy), so that it still exists today.

A substantial overview of legacy issues was recorded by the International Atomic Energy Agency (IAEA) in IAEA (2002a). It was concluded that future international efforts are necessary on the issue of environmental restoration to resolve policy issues such as those relating to criteria for the restoration of areas affected by radioactive residues. In addition, it was said that, in the case of the restoration of residual contamination resulting from unplanned events such as nuclear and radiation accidents and from poorly controlled past practices, it was becoming evident that the international guidance on the subject provided by International Commission on Radiological Protection (ICRP) and IAEA is controversial. The controversy was said to have arisen because of the difficulty, in some cases, of distinguishing between practice situations and intervention situations,[1] and also because of evidence that decisions on restoration actions are strongly influenced by local factors such as public opinion and legal and political constraints.

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[1] Practices and intervention situations are now generally referred to as planned situations and existing situations (ICRP, 2007; IAEA, 2014a).

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There are many different types of legacy that can arise for many different reasons, typically characterised by the following:

- Unsatisfactory technical condition of the facilities;
- Poor characterisation of the current radiation situation;
- Lack of records on history of the site;
- Radioactive contamination of the environment (or suspected);
- Threat of further releases of radioactivity to the environment;
- Other physical and chemical hazards present at the site;
- History of absence of regulatory supervision over the site;
- Unclear ownership and unclear responsibility for management;
- Lack of funds and other resources to carry out the responsibilities mentioned above;
- Lack of a long-term strategy for management and future use of the site;
- Current weak or missing regulatory requirements and guidance necessary to address the existing abnormal conditions and related remediation; and
- Lack of facilities and other arrangements for management of radioactive waste produced in management of the site, including final radioactive waste disposal.

Not necessarily do all such legacies have all these characteristics, but some major examples are shown in Figures 5.1–5.5.

The common feature is that all sites and associated facilities are in an abnormal condition that is associated with loss of physical and/or regulatory control over radioactive material. Such loss of control has resulted in contamination (or suspected contamination) of the environment at levels of safety concern, and/or degradation of the control measures so that future unplanned releases are clearly possible if no further action is taken.

Figure 5.1 Abandoned uranium mine and mill tailings.

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Figure 5.2 Poorly maintained sites for storage of spent nuclear fuel and radioactive waste (pictured: Andreeva Bay, Kola Peninsula, northwest Russia).

FMBA.

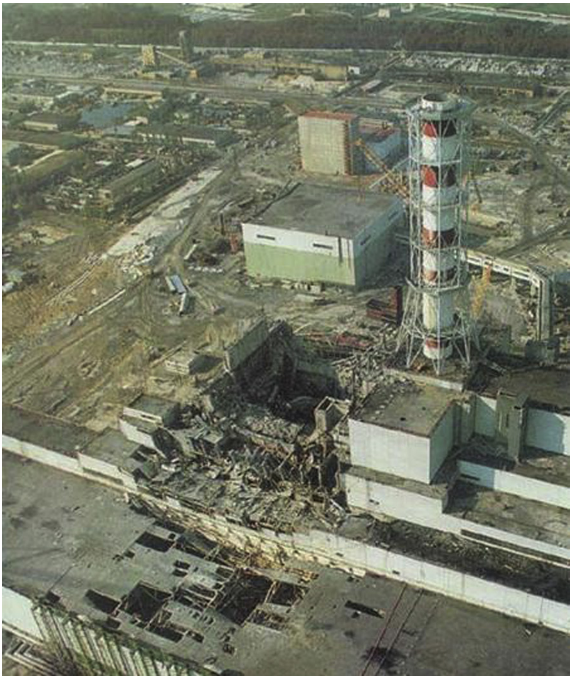

Figure 5.3 Accidents (pictured: Chernobyl).

‘Chernobyl Disaster’ by Soviet Authorities. Licensed under fair use of copyrighted material in the context of Chernobyl disaster via Wikipedia - http://en.wikipedia.org/wiki/File:Chernobyl_Disaster.jpg#mediaviewer/File:Chernobyl_Disaster.jpg.

Figure 5.4 Nuclear weapons testing (pictured: Nevada test site).
Sedan Crater - NF-12187. Photo courtesy of National Nuclear Security Administration/Nevada Field Office.http://www.nv.doe.gov/library/PhotoLibrary/nf121.jpg.

Figure 5.5 Processing and use of naturally occurring radioactive material (NORM) (pictured: phosphate processing plant, S Spain (García-Tenorio, 2010)).
Presentation to workshop of BIOPROTA, www.bioprota.org.

Noting the above as very real issues to be addressed, it is interesting that there is no globally agreed-upon definition of a nuclear legacy. The word does not appear in the IAEA Interim Basic Safety Standards (IAEA, 2014a) or in the IAEA Safety Glossary (2007a). This reflects the mix of issues and circumstances under which legacies, in the broad sense, arise. For the purposes of discussion here, abnormal conditions defining a legacy are taken to mean circumstances arising due to the previous absence of, or loss of, effective control of radioactive material, so that current standards for radiation and nuclear safety and security are not met, and they therefore attract the attention of regulatory authorities. Control measures may include physical barriers for containment of radioactive material, such as the engineered features of a radioactive waste store or disposal facility, but also institutional measures, such as control of land use and security measures.

Addressing these abnormal conditions presents a range of challenges to regulators. These have been highlighted in IAEA (2002a) and at the national and bi-lateral level, as illustrated by Ilyin et al. (2005) and Sneve (2012), but also by many others.[2] In response to this lead from Member states, the IAEA has instituted an International Working Forum for Regulatory Supervision of Legacy Sites (RSLS) with the overall objective to promote effective and efficient regulatory supervision of legacy sites, consistent with the IAEA Fundamental Principles (IAEA, 2006a) as well as various IAEA Safety Standards and good international practices.

5.2 Regulatory challenges

From a regulatory perspective, the key issue is that the levels of radioactive contamination and/or the degraded state of the control measures are cause for the relevant regulatory authorities to be concerned about nuclear and radiation safety and security. It is noted that a site that once met regulatory requirements so as to be cleared for unrestricted use may later return to the condition of being of regulatory concern, and hence a legacy, because of changes in regulatory requirements. This may arise because of changes in scientific understanding that contributed to the clearance decision; that is, the required level of safety and protection has stayed the same, but derived standards need revision because new scientific information has altered the assessed risk of harm from a given situation. It may also arise because the regulatory requirements have changed in response to societal requirements for improved levels of safety and protection provided through the application of standards, that is, society has decided that it wants higher safety standards, so derived safety standards need revision.

A site may also fall into new or renewed regulatory interest because new information, or recovery and recognition of old information, leads to suspicion that a site or facility is radioactively contaminated or contains ill-controlled radioactive material. Clearly, in the case of an accident, an emergency situation arises. Not so obvious is that, when a legacy situation comes to light as a result of new or revised information, then the situation also requires urgent consideration and is effectively an emergency.

Another key aspect is that legacy concerns are not one-dimensional. The range of regulatory factors that needs to be considered can include, but is not limited to, the following:

- Nuclear safety;
- Nuclear security and physical protection;
- Operational radiological protection for workers;
- Radiation protection of the public and the environment;
- Environmental and source monitoring;

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[2] See, for example, the proceedings of recent waste management conferences organised by the American Nuclear Society and others, notably the sessions on legacy management, at www.wmsym.org.

- Control of effluents discharge;
- Emergency preparedness and response during remediation works;
- Radioactive waste management (categorisation, conditioning, storage, disposal);
- Clearance of radioactive materials from regulatory control; and
- Criteria for site release and termination of remedial activities.

NRPA has noted, with others in bi-lateral cooperation (illustrated in NRPA, 2007), that in most countries, more than one authority is responsible for this collection of issues. Also, it needs to be recognised that what might provide optimal protection of the public may not do so for workers, or that short-term benefits may be detrimental to long-term safety, or that security considerations may conflict with safety; and so on. These are difficult enough issues to address and to coordinate coherently, even if all the regulatory responsibility is in one organisation. They are more difficult to coordinate when they are addressed by multiple organisations.

Another particular problem not bulleted above, since it is not specifically a radiation protection issue, is the need to consider all of the above as well as the chemical, physical and any other hazards at a legacy site. Optimisation of all these issues is an immense challenge; in addition, consideration also has to be given to social, political and economic issues.

5.3 International recommendations and guidance and examples of national regulatory requirements

The IAEA provides a very wide range of recommendations and guidance documents to support regulators in meeting the above challenges, based on the Fundamentals Principles in IAEA (2006a) and the Interim Basic Safety standards (IAEA, 2014a). These underlying documents address a variety of topics and circumstances, such as:

- Remediation of areas contaminated by past activities and accidents (IAEA, 2003a, 2007b)
- Exclusion, exemption and clearance (IAEA, 2004a, 2005)
- Monitoring and surveillance of residues from the mining and milling of uranium and thorium (IAEA, 2002b)
- Environmental contamination by NORM and technological options for mitigation (IAEA, 2003b)
- Remediation of sites with dispersed radioactive contamination (IAEA, 2004b)
- Remediation of sites with mixed contamination of radioactive and other hazardous substances (IAEA, 2006b)
- Monitoring and surveillance of radioactive waste disposal facilities (IAEA, 2014b).

The above examples are only illustrative, but overall it can be seen that no single document covers all of the potentially relevant issues from a legacy perspective. It is notable that some guidance relevant to legacy management is also relevant in planned situations, e.g. on clearance, whereas other guidance is more specific to abnormal situations. It raises the question of which guidance is relevant in a particular circumstance, especially for sites that are contaminated from past accidents or poor practices, but that also are in continued operation or are being considered for renewed operation.

Many examples of national requirements on how to address aspects of nuclear legacies are available, but again, usually address just one issue, such as radioactively contaminated land (e.g. SAFEGROUNDS, 2010), or managing potentially polluted sites (ASN et al., 2011). Mannaerts and Pépin (2014) outline a methodology for environmental remediation of legacy/NORM sites simultaneously looking at both the radiological and other environmental protection issues, but there are significant differences among these types of assessments.[3]

The science needed to support these kinds of assessments has been addressed in the IAEA program EMRAS II (see, for example, the work on Reference Approaches to Modeling for Management and Remediation at NORM and Legacy Sites (IAEA, submitted for publication)) and the follow-up MODARIA program. This work in turn builds on bi-lateral and national level research and activities (NRPA, 2008). Such progress, both internationally and nationally, should be mutually supportive and iterative, particularly as regards the continuing development of international recommendations and standards.

Other work takes an overall view of particular types of legacy, such as the Nuclear Energy Agency's (NEA) consideration of management of the environmental and health impacts of uranium mining (NEA, 2014). This includes a review of the historical development of mining regulation and licensing. In parallel, an extensive compilation of international and national references is being prepared by the IAEA's RSLS (IAEA, in preparation). However, comprehensive guidance on the regulation of legacies at the national and international level is currently lacking.

5.4 Progression from recognition to resolution

As mentioned above, legacies can arise and come to be recognised for different reasons. In the case of a present-day accident on a site known to hold radioactive material, it can be obvious that at least some initial investigation is needed. In the case of past practices and incidents that took place years ago, the existence of a legacy may already be known and under renewed or revised regulatory supervision; or it might only now be brought to regulatory attention. Examples of the former include major nuclear technology facilities such as those in Russia described in Ilyin et al. (2005) and at Mayak PA, referred to in Sneve (2012). The latter case has arisen, for example, in the United States as a result of the 2013 National Defense Authorization Act. This only now requires the US Department of Energy to prepare a report on the location, status, risks and hazards, and costs to reclaim or remediate abandoned mines that provided the initial uranium procured for defense purposes. A smaller-scale example, which nevertheless created significant safety and communication challenges, concerned the discovery of contamination of parts of an urban area in Hanover, Germany (König, Drögemüller, Riebe, & Walther, 2014). This urban development was built on the site of the abandoned Eugen de Haën chemical plant, where, in the nineteenth century, uranium, thorium and other materials were processed. It became apparent

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[3] See discussion in the workshop report linked to the reference for Mannaerts and Pépin (2014).

during the process of managing this site that relevant and consistent regulatory guidance was not available to address either the radiation or non-radiation hazards. This situation introduced delays in the timely and effective resolution of the problem, as well as unnecessarily prolonged concerns of individuals living in the area. It is also interesting that, when the existence of the contamination was first recognised, this effectively created an emergency, potentially requiring emergency countermeasures and the application of the full panoply of emergency preparedness and response.

Misunderstanding and miscommunication of technical terms and protection standards is a continuing problem. As noted by Gonzalez et al. (2013), 'while the term [contamination] is commonly used by experts to quantify the presence and distribution of radioactive material in a given environment, it became widely misinterpreted as a measure of radiation-related danger.' Similar considerations apply to the expression 'remediation,' i.e. 'The ultimate purpose of "remediation" is protecting human health and the environment against potential detrimental effects from radiation exposure, rather than eliminating contamination per se'. Further substantial issues are raised in Gonzalez et al. (2013), but in particular this paper highlights the problem of managing the transition from an emergency to an existing situation. Since international reference levels for these two situations are different (IAEA, 2014a), this is of substantial regulatory significance. Gonzalez et al. (2013) also raise the issue of the difficulty of technical communication regarding radiation protection standards and units, as well as non-radiological effects, including psychological impacts that might be mitigated by more effective communication. Both aspects influence decisions on the management from emergency to existing situation, as illustrated in discussion in UNSCEAR (2014).

Nuclear legacies are generally regarded as existing situations, for which reference levels have been developed internationally. However, once a legacy has been recognised and management action is taken under regulatory supervision, one might expect that such action would be planned, and that therefore a planned exposure situation would then arise, to which dose constraints would apply, as given in IAEA (2014a). The technical terminology does not fit with the ordinary meaning of the words.

This discussion only goes to highlight the importance as well as the difficulties of clarifying the transition from emergency, to existing situation and the relationship of either to a planned situation. This is recognised in IAEA (2014a) where it is said, 'The descriptions that are given … of the three types of exposure situation are not always sufficient to determine unequivocally which type of exposure situation applies for particular circumstances'.

5.5 Distinguishing different nuclear legacy situations

The following main groups of legacies are suggested here as of main concern:

1. Sites affected by major accidents and incidents
2. Inadequate storage and disposal sites and facilities
3. Abandoned or insufficiently remediated
   NORM and uranium mining and milling facilities
4. Obsolete or abandoned nuclear technology and development centres
5. Sites of peaceful nuclear detonations and weapons testing sites.

The distinguishing features from a radiation protection and regulatory perspective include the following:

- Radionuclides involved in all cases are relatively long-lived; otherwise there would be no legacy. The definition of 'long-lived' will depend on the circumstances. However, some legacies can be managed within a realistic, socially manageable time frame (say, 100 years) and without a separate need for off-site disposal, whereas others may require longer-term management, thus placing a further burden on future generations, and also separate consideration of disposal off-site.
- Some legacies involve large areas and large volumes of material contaminated at levels that attract regulatory attention, whereas others are small.
- Large-volume legacies are not usually very radiologically hazardous to individuals, but have the potential to affect a large number of people; small-volume legacies may present a serious hazard, although, in that case, only a small number of people are likely to be affected.
- Some legacies involve radioactivity mostly at the surface, which is relatively easy to measure; however, some are the opposite, or involve radionuclides that are not easy to detect.
- Some legacies involve many different radionuclides with different radiative, chemical and physical properties; other legacies involve only one or a few radionuclides, which are then relatively easy to analyse.
- Some legacies also involve physical and chemical hazards, whereas others present solely a radiological hazard.
- Some legacies have a linked social or political legacy that complicates decision making; others do not.

These distinguishing features, and not the cause of the legacy, are suggested as the key features that affect not only the most effective management strategy but also the most appropriate regulatory strategy.

5.6 Factors to consider in addressing regulatory challenges at nuclear legacy sites

Clearer guidance is needed internationally on the distinction between emergency, existing and planned exposure situations. Such guidance needs to take account of many radiation protection issues; but also, in parallel and proportion, this guidance should allow for accommodation of all the other environmental and human health issues, as well as economic, social and other factors. In short, radiation protection is not the whole story.

The clarification of the different exposure situations is important, to allow the identification of the relevant reference levels and constraints that apply. It is not just a semantic tangle but has real implications for the practical interpretation of international guidance. At the same time, one might argue that regulatory guidance could simply be reduced to a requirement to consider all of the different issues and to optimise accordingly. The most appropriate approach may depend on national tendencies to have more, or less, prescriptive requirements.

Although control of radiative material on a site may be critical to management of radiation exposure, a regional or national waste management strategy will also be needed in many cases as a corollary to effective legacy management. Otherwise there will be no mechanism for managing the wastes arising in remediation.

Overall, there is little experience in application of reference levels at nuclear legacies sites, since this is a relatively new concept. However, there is substantial historical experience with management of such sites, including their regulatory supervision, which can be useful, both as shared experience at the bi-lateral level and as input to the development of improved international guidance. From a radiation protection perspective, the source or cause of the legacy is not very important; what matters are the distinguishing features that materially affect the options for control of future exposures, as illustratively proposed above.

Cooperation and coordination are needed between the different regulatory bodies, both within a country and across borders, both to support each other and to support development of enhanced international recommendations. NRPA's recent experience with sister authorities in the United States and the Russian Federation has been constructive and productive. The following key issues for collaboration on legacy site supervision have been identified as follows:

- Sharing of information on development and application of regulatory requirements.
- Decision making on transition from emergency exposure to existing exposure situation and further transition to later stages.
- Exercises to practice communication processes at each stage of management.
- Sharing of scientific information that supports decision making on introduction and ending of countermeasures, remediation techniques and waste management.
- Practical implementation of optimisation processes during remediation and a common base for joint recommendations for application of optimisation.

Arising from the last bullet point is the question of whether some minimal level of harm or risk (i.e. not just dose, thereby allowing better integration with other risks) can be defined, below which optimisation can be considered already complete.

Such developments will necessarily need to rely on good science. Scientific research in radiation protection needs to include and link the following: radioactivity in the environment; potential for exposure; conversion of that potential to doses to humans and other biota, and the health risks associated with those doses. The whole chain needs to be addressed, through coordinated and focused scientific research in specific areas, for example, radioecology as promoted through the International Union of Radioecology. Noting the different disciplines involved, coordination of the identification of research priorities and interpretation of the results is very much to be encouraged.

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Modelling of radionuclide distribution in contaminated nuclear and NORM sites

6

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6.1 Introduction

This chapter describes the concept of environmental modelling for nuclear and NORM sites. The rationale for the use of models is described in Section 6.2, and available models and the tiered or graded approach in environmental and human risk assessment are described in Section 6.3. Section 6.4 focuses on the use of models as part of a general assessment procedure, and highlights the possibilities and challenges related to the application of modelling tools to nuclear and NORM sites. A Norwegian case study is presented in Section 6.5 in which human and environmental risk assessment is performed using different modelling tools applied to a disused mining site contaminated with NORM. Future trends in modelling and risk assessment are outlined in Section 6.6.

6.2 Background

6.2.1 Why model?

For operational sites (i.e. planned exposures), monitoring and modelling are necessary to show compliance with national regulations or, in the case of lack of such national regulations, compliance with international guidelines of the IAEA or the ICRP. If compliance is not met, the operator must initiate mitigating actions to ensure safe conditions for workers, the public and the environment in the future. For legacy sites (i.e. existing exposures), monitoring and modelling should be used to determine whether the site constitutes a danger to people or the environment today or in the future, that is, whether remediation is necessary.

According to ICRP (2007) all exposure situations should be managed in a safe way. Contaminated nuclear and NORM sites could be categorized as planned exposures if they are still operational sites in which earlier activities have been managed under adequate regulations. In many cases, however, such sites would be actual legacy sites in which operation has stopped and the former activities were performed under a lack of good regulation, leading to situations of unsafe or unknown existing exposure.

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ICRP (2007) states that reference levels (~acceptable levels) for existing exposure scenarios for the public would be in the range 1–20 mSv/y, preferably below 10 mSv/y. For planned exposures, the dose limit for occupationally exposed workers is 20 mSv/y while the dose limit for the public is 1 mSv/y. The dose limit should cover all exposure sources and all exposure pathways during a year. Please note that exposures from long-term remediation operations or from protracted employment in contaminated areas should be treated as part of planned occupational exposures, even if the source is 'existing' (ICRP, 2007).

ICRP has so far not defined any dose limit for animals and plants. They use a concept of 'derived consideration reference levels' (DCRLs), that is, a band of dose rates within which there is some chance of deleterious effects to individual organisms (ICRP, 2008a). The proposed DCRLs of ~4–40 µGy/h can be used as a point of reference to optimize the level of effort expended on environmental protection. Other groups, however, have defined what they call screening levels, that is, levels below which no adverse effects to animals and plants are presumed. In the ERICA Tool (Brown et al., 2008), this screening level is set to 10 µGy/h. The UNSCEAR 2008 Report (UNSCEAR, 2010) states that: 'Overall, the Committee concluded that chronic dose rates less than 100 µGy/h to the most exposed individuals would be unlikely to have any significant effects on most terrestrial communities and that maximum dose rates of 400 µGy/h to any individual in aquatic populations of organisms would be unlikely to have any detrimental effect at the population level'.

The dose limits for humans and the screening dose rates for animals and plants to be used for a given assessment will thus depend on a country's national regulations.

Based on monitoring data from a given site, it is possible to calculate existing exposures to workers, the public and the environment. Monitoring data are, however, not enough because it is too time-consuming and costly to measure everything–all environmental compartments, all animals, plants and humans. Also, the conversion from activity concentrations to radiation doses or dose rates must be performed, as most regulations are dose/dose-rate based. (An exception here is, for example, the United States, where some regulations are based on activity concentrations rather than doses.)

Calculations of exposures can be done by choosing relevant exposure scenarios and applying mathematical equations describing the transfer in the environment, the transfer through the food chain, and the energy deposited in humans and biota from ionizing radiation. This can, of course, be done manually for each case, but today a large number of modelling tools and codes are available that are specifically developed for assessing radiation risk to humans and the environment.

Some modelling tools and codes would also allow for the calculation of future exposures, which cannot be calculated in a simple way directly from monitoring data. Future exposures should be taken into account when considering the necessity of remediation of sites. Once remediation is deemed necessary, modelling can also be used to assess which countermeasures are the most efficient to reduce the exposure to below a given regulation value. The modelling will then be part of an optimization procedure.

Instead of waste disposal, it may be attractive to use slightly contaminated material (in particular for NORM residues) for other purposes such as land fill, road fill, road base, building materials and concrete extenders. Again, modelling is necessary to show whether such recycling or reuse of material is safe for workers, people and the environment.

6.2.2 Source term and the complexity of the system considered

As discussed in the previous chapters, natural and anthropogenic radionuclides come from a variety of sources. The actual source term will influence the possible transfer and uptake in the environment. For any modelling of exposure, it is thus important to consider the characteristics of the source term such as physico-chemical form, redox potential, particle sizes and environmental factors surrounding the source.

NORM is present in different ecosystems in varying quantities. NORM waste is often found in large quantities with slightly to moderately elevated activity concentrations. Many are serial primordials, that is, they form part of a decay series from the isotopes ^{238}U, ^{232}Th and ^{235}U. These radionuclides have very long half-lives, whereas some of their daughters have short half-lives. In an undisturbed system, a secular equilibrium would occur with time in which the activity concentrations of all nuclides in a chain would be equal. In nature, however, this is rarely the case, for example, due to emanation of radon gas through porous media. The different elements in the decay chain have different physical and chemical characteristics that can result in significant disequilibrium in the decay series. For instance, chemical leaching of radionuclides from solid material will occur at differing rates due to different solubility of the elements, which is dependent on parameters such as pH, redox potential, temperature, salinity, and organic and inorganic complexing (NRPA, 2004). The leaching may also be facilitated by the direct alpha-recoil into water or increased leaching of dislocated atoms due to the alpha-emitting decay process. In natural environments such as terrestrial, freshwater or marine areas, the mobilization, dispersion and sedimentation of radionuclides will depend on both chemical and physical properties (NRPA, 2004). The uptake and transfer through the food chain will also be element specific. NORM is naturally occurring as well as a contaminant, which makes calculations of the incremental dose more challenging than for artificial radionuclides.

Operational nuclear sites are in general well regulated, and they were planned to operate according to strictly defined safety levels. This chapter will thus focus on the nuclear legacy sites, that is, sites from former activities not operated under adequate control, which has resulted in areas, constructions or wastes contaminated with anthropogenic radionuclides above exemption or clearance levels. Contrary to NORM sites, the activity concentrations at nuclear legacy sites will often be rather high. They are often a mix of medium- and long-lived radionuclides, either contained as waste or dispersed in the environment and in constructions. Modelling is useful for determining the dispersion, migration and uptake of anthropogenic radionuclides in animals and plants which will be different for different radionuclides, and also depend on soil properties, environmental factors and species present. The present and future exposures of workers, the public and the environment can be modelled and compared to dose limits, reference levels or screening levels in national or international regulations. This will form part of the basis for determining whether remediation of the site is necessary.

In some cases the contamination levels at nuclear legacy sites are so high that it complicates the remediation work, for example, the Andreeva Bay in Russia, where certain areas were so contaminated that workers could hardly enter the premises (Sneve et al., 2008). If the source term is known, modelling can show how the exposure will evolve over time and when it will be possible to start remediation work in a safe manner.

6.3 Modelling concepts and available models for environmental and risk assessments

When a risk assessment is to be performed for a site with unknown exposure levels, it is wise to use a *graded approach*. This term used by the ICRP is equal to the term *tiered approach* used, for example, in the ERICA Tool. A graded approach is based on the principle that efforts to control exposures should be proportional to radiation risk (ICRP, 2007; Liland et al., 2012). For NORM and nuclear legacy sites, an assessment should be done to ensure that the optimal level of control is achieved. Monitoring and modelling are good tools to justify continuation or discontinuation of control measures, and whether remediation is necessary. The concepts of justification and optimization would apply, and the principle of ALARA (as low as reasonably achievable, social and economic factors taken into account) is always valid when the source of exposure can be controlled. The optimization of protection is a forward-looking iterative process aimed at preventing exposures before they occur (ICRP, 2006). For situations like NORM and nuclear legacy sites, modelling is imperative to calculate possible future exposures that might need to be prevented. Also, modelling gives the advantage of easily comparing all exposure pathways and enabling the selection of the most important ones to limit.

A range of models exist, from simple screening tools with few input parameters to very sophisticated modelling codes with many input parameters. A graded approach starts with a conservative screening, then moving up in sophistication in modelling, depending on the contamination challenge. This concept is described in Section 6.3.1, and available models are detailed in Section 6.3.2.

6.3.1 The tiered or graded approach

6.3.1.1 Conservative screening (Tier 1)

For the sake of simplicity, it would be wise to start with a conservative screening tool to see whether the sites could potentially pose a radiation hazard to people or the environment. Few input parameters are required, and parameter values should be chosen that are conservative, that is, that give the highest calculated doses or dose rates. You can also use default parameter values if you do not have site-specific ones. The conservatism of the tool ensures that the results generated represent a ‘worst case’ scenario.

Some available existing screening tools are listed in Table 6.1 in alphabetical order. Several are freely available, and others would have to be purchased. Some models are only screening tools, whereas the rest could be operated in either screening mode or in a detailed, more sophisticated mode as necessary. For the ERICA Tool, Tier 1 would be appropriate for the first screening, as an example.

Table 6.1 Available screening models for contaminated environments

Model name	Scope	Radioactive medium	Type	Mechanism	Availability	Website link
DandD	Screening	Building and surface soil	Steady state	Analytical	Free	http://www.orau.gov/DDSC/dose/compcode.htm
BPRG+BDCC	Screening	Setting up of cleanup goals for contaminated buildings	Steady state	Analytical	Free Internet-based calculator	http://epa-bprg.ornl.gov/ http://epa-bdcc.ornl.gov/
PRG+DCC	Screening	Setting up of cleanup goals	Steady state	Analytical	Free Internet based calculator	http://epa-prgs.ornl.gov/radionuclides/ http://epa-dccs.ornl.gov/
SPRG+SDCC	Screening	Setting up of cleanup goals for contaminated surfaces	Steady state	Analytical	Free Internet based calculator	http://epa-sprg.ornl.gov/ http://epa-sdcc.ornl.gov/
RCLEA	Screening	Dose assessment from land use, buildings	Steady state	Gaussian plume and box models in steady state	Free	http://www.rclea.info/download.html
AMBER	Screening to detailed	All environmental media	Time-dependent	Analytical	Commercially	http://www.enviros.com/index.cfm?fuseaction=23
CROM	Screening to detailed	Gaseous and liquid discharges	Steady state	Gaussian plume and box models in steady state	Free	ftp://ftp.ciemat.es/pub/CROM
ECOLEGO	Screening to detailed	Surface, near surface	Time dependent	Analytical	Commercially except ECOLEGO player free	http://ecolego.facilia.se/ecolego/show/Downloads
ERICA	Screening to detailed	Dose rates to nonhuman biota	Steady state	Semiempirical	Free	https://wiki.ceh.ac.uk/display/rpemain/ERICA+Tool
MODEL-MAKER	Screening to detailed	All environmental media	Time dependent	Analytical	Commercially	www.modelkinetix.com/modelmaker
RESRAD-BUILD	Screening to detailed	Building, surface, near surface	Time dependent	Analytical	Freely available upon request	http://web.ead.anl.gov/resrad/home2/
RESRAD-OFFSITE	Screening to detailed	Surface, near surface	Time dependent	Analytical	Freely available upon request	http://web.ead.anl.gov/resrad/home2/

Adapted from IAEA (in press).

If the results from this screening do not exceed the regulation values, there is probably no need to perform more advanced modelling. The decision maker, however, might decide to do a more specific analysis anyway, based on, for example, the ALARA principle.

6.3.1.2 More realistic modelling (Tier 2)

If the screening results in Tier 1 exceed the regulation values, a more sophisticated model should be used with more realistic parameter values. The models listed in Table 6.1 as ‘screening to detailed’ could be used for such purposes. For the ERICA Tool for instance, the Tier 2 would be appropriate for the next level of sophistication. There are also other models available for detailed assessment (Table 6.2).

6.3.1.3 Full, detailed assessment (Tier 3)

If the results still do not comply with regulatory requirements, a detailed, site-specific full assessment should be done using a sophisticated model that takes into account all exposure pathways. Models marked ‘screening to detailed’ or ‘detailed’ could be used for this purpose. Tier 3 of models such as the ERICA Tool should be used.

6.3.2 Description of models

In the final report of the Working Group 2 (*Reference Approaches to Modeling for Management and Remediation at ‘NORM and Legacy Sites’*) of the IAEA EMRAS II programme, a detailed description was given for many of the models in Tables 6.1 and 6.2 as well as for some in-house models used by the participants in the group. This report will be available at http://www-ns.iaea.org/projects/emras/emras2/default.asp.

It is not feasible to describe all available models in this chapter. Below is a description of some selected models that could be useful for a number of contamination scenarios in which environmental remediation might be warranted. The descriptions are a condensed version of the model descriptions given in the final report of the Working Group 2 of the IAEA EMRAS II programme.

6.3.2.1 DandD

The DandD (Decontamination and Decommissioning) screening tool was developed by Sandia National Laboratories (USA), based on NUREG/CR-5512 Volumes 1 to 4 (NUREG, 1992, 1999a, 1999b, 2001). The code allows probabilistic dose assessments, and has the capability to conduct sensitivity analysis to identify parameters that have the greatest impact on the dose distribution. The code considers initial contamination:

- in buildings for a building occupancy scenario; and
- in soil for a residential scenario.

The *building occupancy scenario* relates volume and surface contamination levels in existing buildings to estimates of the total effective dose equivalent from external exposure, inhalation exposure, and secondary ingestion.

Table 6.2 Available detailed models for contaminated environments

Model name	Scope	Radioactive medium	Type	Mechanisms	Availability	Website link
CHAIN	Detailed	Solute transport in surface and near surface soils	Time dependent	Analytical	Freely available upon request	http://gcmd.nasa.gov/records/USDA_ARS_CHAIN.html
CHAIN 2D	Detailed	Solute transport in surface and near surface soils	Time dependent	Analytical	Freely available upon request	http://www.ars.usda.gov/Services/docs.htm?docid=8914
PC-CREAM 08	Detailed	Gaseous and liquid discharge	Steady state	Gaussian plume module, other modules	Commercially	https://www.phe-protectionservices.org.uk/pccream
SATURN	Detailed	Building, surface and near surface	Time dependent	Analytical	Commercially	http://www.saturn.facilia.se/saturn/show/Downloads
MICROSHIELD	Detailed	Photon/gamma shielding and dose assessment	Time dependent	Analytical	Commercially	http://www.radiationsoftware.com/mshield.html
MILDOS AREA	Detailed	Uranium mining dose assessments from buildings, surface and near surface	Time dependent	Gaussian plume and analytical	Freely available upon request	http://web.ead.anl.gov/mildos/history.html
MULTIMED DP	Detailed	Multimedia waste disposal unit	Time dependent	Analytical	Freely available upon request	http://www.epa.gov/ceampubl/mmedia/multidp/index.html

Adapted from IAEA, IAEA (in press).

The *residential scenario* calculates the annual total effective dose equivalent from drinking water from wells and from multiple pathways associated with contaminated soil using a simple three-box water-use model that accounts for radionuclide decay, progeny ingrowth and environmental transport. The three boxes (or layers) are the surface soil, unsaturated soil and the aquifer. The generic treatment of potentially complex groundwater systems provides a conservative analysis that may only suggest when additional site data and more sophisticated modelling are warranted. The pathways considered for the residential scenario are as follows: external exposure, dust inhalation, ingestion of drinking water, food grown from irrigation water, land-based food, soil and fish. The types of land-based food considered are leafy vegetables, other vegetables, fruit, grain, beef, poultry, milk and eggs. Three types of animal feeds are considered: forage, stored grain and stored hay. The simulation does not consider the radon exhalation pathway and buried contaminated material.

The input parameter distributions for each scenario and exposure pathway were developed consistent with conducting conservative screening, thereby increasing the likelihood of overestimating rather than underestimating potential doses. The DandD code allows a simple, straight-forward approach to modify scenario selection, exposure pathways, source profile and many of the modelling parameters to accommodate site-specific conditions. DandD can be downloaded from http://www.orau.gov/DDSC/dose/compcode.htm free of charge.

6.3.2.2 CROM

CROM is a generic environmental model code developed by the Spanish research organization CIEMAT in collaboration with the Polytechnic University of Madrid, based mainly on IAEA Safety Report Series 19 (2001). It was designed to calculate radionuclide concentrations in different compartments of the environment and their impact on the food chain, as well as the effective doses to humans. CROM uses generic models for diffusion and dilution. The software implements a default database with data for 152 radionuclides.

In addition to default parameter values, local parameters can be inserted for more realistic calculations. To estimate the radionuclide concentrations in the environmental media, the source term, the mode and characteristics of the discharge and the receptor points, up to five, should be specified.

The *atmospheric dispersion* model is a Gaussian plume model designed to assess annual averaged radionuclide concentrations in air for distances <20 km. It can be used for the calculation of the rate of deposition at various points in the region of interest from long-term releases. The basic meteorological variables required for each individual air concentration calculation are the wind direction and the geometric mean of the wind speed at the physical height of the release point.

The *surface water* models accounts for dispersion in rivers, small and large lakes, estuaries, and along the coast of seas and oceans. These models are based on analytical solutions to advection–diffusion equations describing radionuclide transport in surface water with steady state uniform flow conditions. All of the models contain a great quantity of default values that can be used in the absence of local specific information.

The *terrestrial food chain* models accept inputs of radionuclides from both the atmosphere and the hydrosphere, and take account of the build-up of radionuclides on surface soil over a 30-year period. The food categories considered are milk, meat and vegetables. The uptake and retention of radionuclides by aquatic biota (freshwater fish, marine fish and shellfish) uses selected element specific bioaccumulation factors. The model assumes an equilibrium state between the concentrations of the radionuclide in biota and in water.

The estimated radionuclide concentrations in air, soil, sediment, food and water are combined with the annual rates of intake, the occupancy factors and the appropriate dose conversion factors to obtain the maximum effective dose in 1 year for the combined external and internal exposure using dose conversion factors from Safety Series No. 115 (IAEA, 1996) and the Federal Guidance Report No. 12 (Eckerman & Ryman, 1993). The total effective doses are calculated for the six age categories recommended by the IAEA (1996) and the ICRP (2008b).

CROM 7 (CIEMAT, 2007) is freely available by contacting the IAEA or downloading it from ftp://ftp.ciemat.es/pub/CROM/CROM_7/. CROM is currently being updated based on a revised version of the IAEA SRS19.

6.3.2.3 RESRAD

The RESRAD Family of codes was developed by the Argonne National Laboratory for the US Department of Energy (DOE) to provide a firm, scientific basis for determining the radiation dose, radiation risk and authorized limits (i.e. radiological release or cleanup criteria) at numerous DOE sites. Figure 6.1 shows the different models which can be freely downloaded from their Website. The original RESRAD code was developed to calculate site-specific RESidual RADioactive material guidelines as

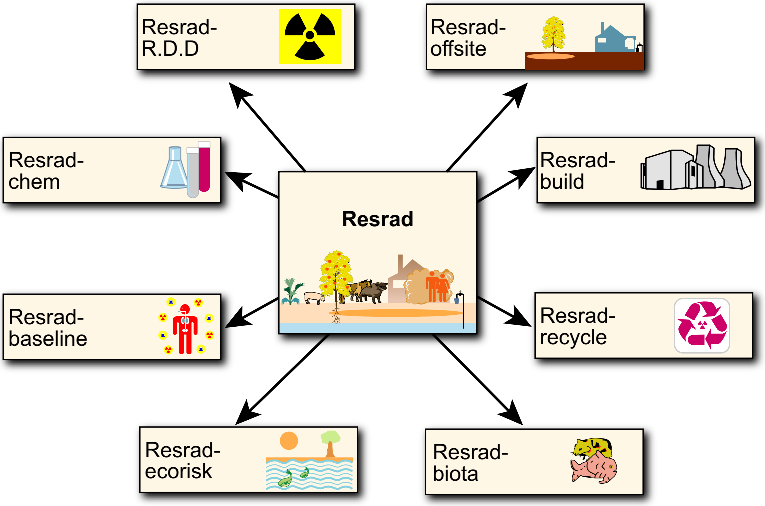

Figure 6.1 The RESRAD family of codes.
www.evs.anl.gov/resrad.

well as radiation doses and excess lifetime cancer risk to a chronically exposed onsite receptor. To distinguish from other, later RESRAD models, the original RESRAD code is now called RESRAD (onsite) code. For contaminated nuclear or NORM sites, RESRAD (onsite) or RESRAD-OFFSITE are particularly useful.

The eight major exposure pathways considered in the RESRAD (onsite) code are as follows:

- Direct exposure to external radiation from the contaminated soil material;
- Internal exposure from inhalation of airborne radionuclides;
- Internal exposure from inhalation of radon progeny; and
- Internal exposure from ingestion of:
  - Plant foods grown in the contaminated soil and irrigated with contaminated water;
  - Meat and milk from livestock fed with contaminated fodder and water;
  - Drinking water from a contaminated well or pond;
  - Fish from a contaminated pond; and
  - Contaminated soil.

RESRAD was developed as a multifunctional tool and has many current and potential applications, including the following:

- Derivation of soil cleanup criteria for contaminated site remediation activities in compliance with regulatory requirements;
- Compute potential annual doses and lifetime cancer risks to workers or members of the public;
- Estimate future concentrations of radionuclides in various media;
- Support an ALARA or cost–benefit analysis for use in the decision-making process concerning decontamination and decommissioning; and
- Prioritize budget and effort in collecting data on soil properties and hydrogeological properties that affect the environmental distribution of radioactive waste and consequently the decision on waste management.

The RESRAD (onsite) model can be used to handle situations such as buried waste and landfills (Yu, Loureiro et al., 1993; Yu, Zielen et al., 2001). It has limited source region geometry, and is not designed to predict offsite impacts. The model handles a wide range of nuclides, and allows users to change the cut-off half-life for setting short-lived daughters in equilibrium with their parent radionuclide.

The RESRAD-OFFSITE code extended the RESRAD (onsite) to also estimate the radiological consequences to a receptor located outside the area of primary contamination. RESRAD-OFFSITE calculates radiological dose, excess lifetime cancer risk, radionuclide concentrations in the environment and derived soil cleanup concentrations (Yu, Gnanapragasam, Cheng, & Biwer, 2006; Yu et al., 2007). It considers initial contamination in soil with or without a clean cover layer on top of it and with up to five partially saturated layers below it. The code can model the radiation exposure of an individual who spends time directly above the primary contamination (onsite) and away from the primary contamination (offsite). The individual could consume food produced onsite or derived from offsite agricultural fields that are contaminated by material from the primary contamination. Drinking water can be drawn from a well or a surface water body located onsite or offsite. A surface water body can also be the source of aquatic food for consumption.

The following eight exposure pathways are considered in RESRAD-OFFSITE:

- direct exposure from contamination in soil;
- inhalation of particulates and radon;
- ingestion of plant foods;
- ingestion of meat;
- ingestion of milk;
- ingestion of aquatic foods;
- ingestion of water; and
- incidental ingestion of soil.

By selecting relevant pathways, RESRAD-OFFSITE can be used to simulate various exposure scenarios such as:

- rural resident farmer;
- urban resident;
- industrial worker; and
- recreational scenarios.

These features are represented graphically in Figure 6.2.

The types of releases considered from the primary contamination include wind erosion (atmospheric release), leaching and surface runoff. Accumulation of radionuclides at offsite locations are calculated from deposition and irrigation events.

The RESRAD Family of Codes is well documented and gives detailed information on the transport models used. For instance, the RESRAD-OFFSITE groundwater transport model considers the convection and dispersion in the liquid phase, decay of the parent radionuclide, ingrowth of progeny radionuclide(s) and their respective retardation due to sorption/desorption in the solid phase. Numerical analysis methods are used to solve the differential equations that characterize the behaviour of radionuclides.

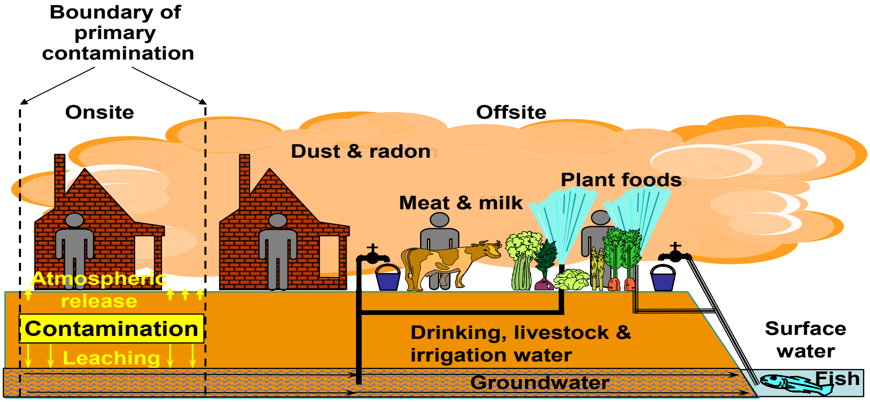

Figure 6.2 Graphic representation of the RESRAD-OFFSITE conceptual model.
Yu et al., 2007.

The RESRAD-OFFSITE package uses the ICRP 38 database of radionuclides (ICRP, 1983). There is a map interface that allows the primary contamination and the offsite areas to be specified and displayed on a map of the region of interest. Different exposure scenarios can be specified by activating or suppressing pathways and by modifying usage and occupancy parameters. The code calculates media concentration, dose and risk progressively over time and generates output reports after each run providing a listing of all input parameters, the maximum dose and the minimum soil guidelines.

RESRAD-OFFSITE can also perform sensitivity and probabilistic analysis to study the influence of input parameters and to generate graphic results for the analysis. It can accept input of temporal data of the following:

- radionuclide concentrations in the primary contaminated zone and the mixing layer;
- radionuclide fluxes to the groundwater, to the surface runoff and to the atmosphere;
- dimensions of the cover, mixing layer and primary contamination; and
- eroded soil mass.

Users can choose default dose and risk factors or set up their own dose/risk library.

RESRAD-OFFSITE can be downloaded free of charge from the RESRAD Website (http://www.evs.anl.gov/resrad) after completing the online registration. The RESRAD Website contains useful information including the latest version of RESRAD family of codes, training events, frequently asked questions and many supporting documents for download.

6.3.2.4 ERICA assessment tool

The ERICA Tool (Brown et al., 2008) is specifically developed for performing environmental impact assessments. The software assesses the radiological risk to terrestrial, freshwater and marine biota, but not to humans. It was developed by key radioecologists in Europe under the European Commission's 6th framework programme for research and development as part of the ERICA project (https://wiki.ceh.ac.uk/display/rpemain/ERICA).

The Tool has simple transport models embedded to enable conservative estimates of media activity concentrations from discharge data if environmental measurements are not available; the transport models are taken from IAEA (2001): generic models for use in assessing the impact of discharges of radioactive substances to the environment. IAEA Safety Report Series No. 19. The tool calculates dose rates to animals and plants from both internal and external exposures. It is based on the concept of 'reference organisms', for which a selection of animals and plants has been chosen based on:

- Radioecological sensitivity;
- Radiobiological sensitivity; and
- Ecological relevance

and that are supposed to be representative for sensitive and/or important species of the ecosystems. The reference organisms are currently biased towards European species.

The software can be used from simple screening to full, detailed assessments with site-specific, probabilistic data. It uses a tiered (or graded) approach:

Tier 1 assessments are media concentration based and use precalculated environmental media concentration limits to estimate risk quotients.

Tier 2 calculates dose rates but allows the user to examine and edit most of the parameters used in the calculation, including concentration ratios, distribution coefficients, percentage dry weight soil or sediment, dose conversion coefficients, radiation weighting factors and occupancy factors. The user can also input biota whole-body activity concentrations in Tier 2 if available rather than rely upon concentration ratios.

Tier 3 offers the same flexibility as Tier 2 but allows the option to run the assessment probabilistically if the underlying parameter probability distribution functions are defined.

The calculated dose rates from the ERICA Tool can be put into context by comparing them to known dose–effect relationships and background dose rates. The interlinked FREDERICA Radiation Effects Database (http://www.frederica-online.org/mainpage.asp) contains more than 30,000 data entries on dose–effect relationships from the scientific literature. The calculated dose rates can also be compared to screening dose rates or regulation values (if any). The ERICA project has defined a screening value of 10 µGy/h for total dose rates (internal + external) to animals and plants, below which negative impacts are not foreseen. Other organizations and nations have defined other screening dose rates, as mentioned earlier.

The ERICA Tool is freely available from: http://www.erica-tool.com/, and development is ongoing.

6.3.2.5 MICROSHIELD

MICROSHIELD is a photon/gamma ray shielding and dose assessment program that is used for designing shields, estimating source strength from radiation measurements, minimizing exposure to people and teaching shielding principles. The model can be used for calculating external exposures only. It could be useful for contaminated sites in which external exposure is the only exposure pathway or in combination with other models for internal exposure pathways.

The model is interactive and uses input error checking. Integrated tools provide graphing of results, material and source file creation, source inference with decay, projection of exposure rate versus time as a result of decay, access to material and nuclide data, and decay heat calculations (http://www.radiationsoftware.com/mshield.html).

Embedded in the software is the ICRP Publication 107 (2008b), which supersedes the former ICRP Publication 38 (1983), and both libraries along with the original Grove Library are provided with the software. ICRP Publication 107 provides an updated nuclear library containing 1252 radionuclides of 97 elements. Source decay can be calculated with daughter products generated. Several geometry–source configurations are included such as point, sphere, cylinder, rectangular area, cone and infinite plane.

The model, available for purchase from Grove Software Inc., has been used by the oil and gas industry and other industries that have sought to evaluate direct exposure from contaminated equipment and materials.

6.3.2.6 Ecolego

Ecolego (http://ecolego.facilia.se/ecolego/show/Ecolego) is a software tool for creating dynamic models and conducting risk assessments of complex dynamic systems evolving over time with any number of species. Ecolego can be applied in a variety of areas, but is mainly used for risk assessment in radioecology, safety assessment for radioactive waste management and environmental physics. To facilitate the use of Ecolego in the field of radiation risk assessment, specialized databases and other add-ons have been developed.

The models in Ecolego are represented with the help of interaction matrices instead of the traditional flow diagrams, which greatly facilitates construction and documentation of large and complex models. The typical Ecolego model is a compartmental model that requires a solver of differential equations. There are a wide array of numerical solvers to choose from. Some are optimized for stiff and numerically difficult models, others for trivial models. With an extensive list of probability density functions, together with Monte Carlo and Latin hypercube sampling and parameter correlation settings, Ecolego holds all of the required tools to perform advanced probabilistic analysis.

Ecolego can also create reports that contain everything from interaction matrices, to parameter values, equations, decay chains, plots and tables. A real-time validation engine reports problems to the user, such as not-yet-defined objects, objects lacking values or having invalid equations.

Ecolego is a commercial package, but it includes a Player that is freely available (http://ecolego.facilia.se/ecolego/show/Ecolego%20player). The software features the same functionality as Ecolego, with the exception that the integral structure of the model cannot be changed. However, with a module library created in Ecolego, the user can assemble models by combining components from the library. With the Ecolego Player, you can:

- Select species and other indices;
- Review model structure and equations;
- Assign parameter values and probability density functions;
- Assign time-dependent inputs;
- Select simulation outputs;
- Specify simulation settings;
- Run best estimate or Monte Carlo simulations;
- Create charts and tables from simulation output; and
- Generate reports.

6.4 Applications to contaminated nuclear and NORM sites

6.4.1 Modelling as part of a general assessment procedure

In the IAEA EMRAS II programme, the final report from the WG2 (‘*NORM and Legacy Sites*’) (IAEA, in press) presented a General Assessment Methodology describing all the steps in a risk assessment process. Figure 6.3 shows the flow diagram for such a methodology. The grey boxes show where the use of models is needed in the process. Some of the steps from IAEA (in press), are outlined below.

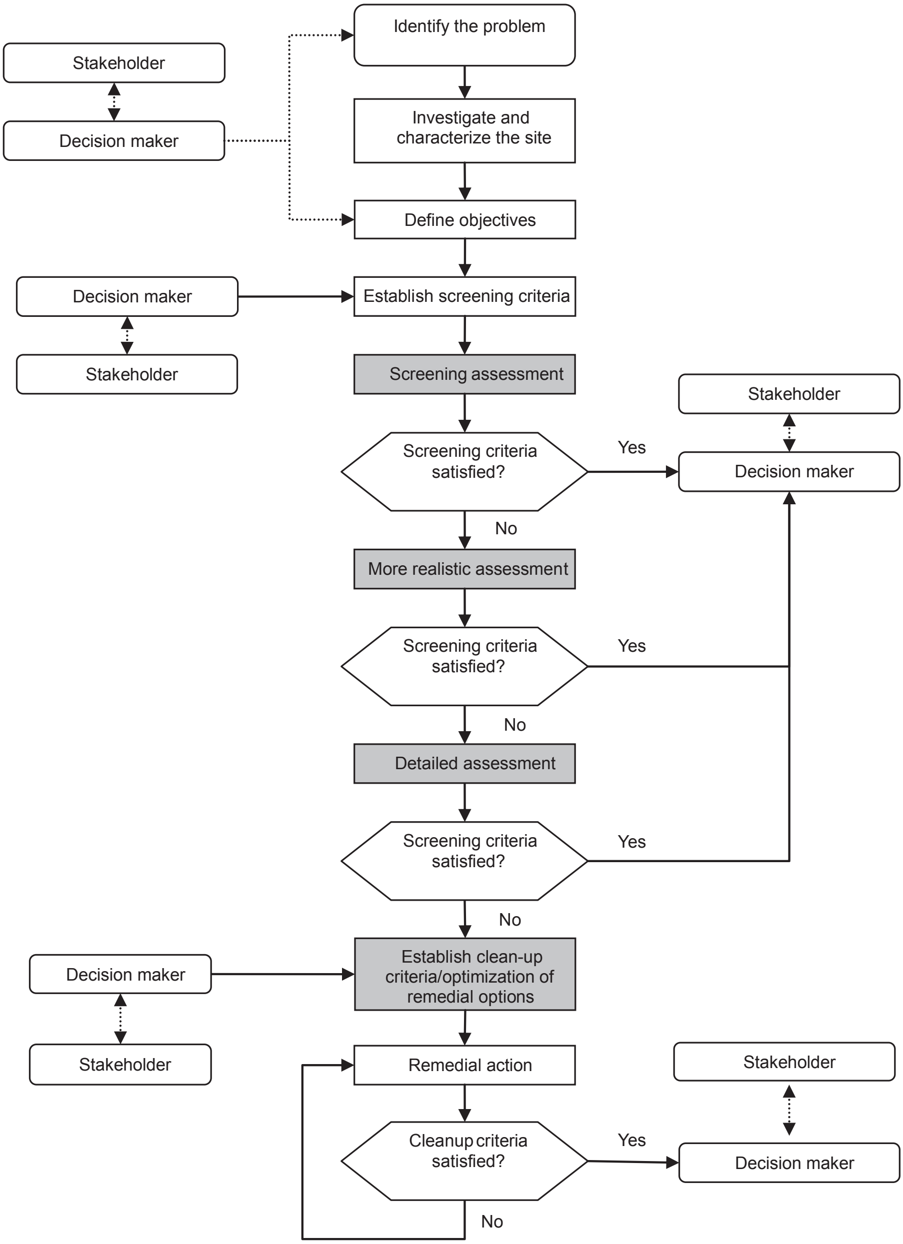

Figure 6.3 General Assessment Methodology for a contaminated site (IAEA, in press). The grey boxes show where models are necessary.

1. Carry out a screening assessment against agreed screening criteria.
    - **a.** Define the objectives (of the screening assessment).
    - **b.** Estimate the impact using conservative assumptions and exposure scenarios; the model used for this estimation may be quite simple (IAEA, 2001) or detailed.
2. If the screening criteria are not satisfied, carry out a more realistic assessment.
    - **a.** Use more realistic assumptions and exposure scenarios.
    - **b.** Collect more data to improve the estimation of transfer parameters and the estimation of the source term.
    - **c.** Use more complex models if appropriate.
3. If the screening criteria are still not satisfied, carry out a detailed assessment.
    - **a.** Use assumptions and exposure scenarios that are as realistic as possible.
    - **b.** Identify sensitive parameters using sensitivity analysis methods.
    - **c.** Collect the data on sensitive parameters and data needed to improve the estimation of transfer parameters and the source term.
    - **d.** Use more complex models if appropriate.
4. If the screening criteria are exceeded, even after a detailed assessment, the decision maker should order implementation of remedial actions based on the following steps:
    - **a.** Define the objectives of the remedial action and establish cleanup criteria.
    - **b.** Collect additional data if necessary.
    - **c.** Establish appropriate exposure scenarios, both for the workers involved in the remedial action and for the future use of the site and surrounding area.
    - **d.** Carry out an assessment of the different remedial options available using *modelling* tools, and select the option that gives the optimal result, taking into account not only reduction in dose to the public and nonhuman biota but also the doses/risks to workers, the public, and nonhuman biota while the work is being carried out.
    - **e.** Carry out the remedial action that is required to meet the cleanup criteria.
    - **f.** Collect data from the remediated areas, to verify that the cleanup criteria have been satisfied.
    - **g.** Continue this process (iteratively) until the cleanup criteria are satisfied.

6.4.2 Possibilities

The above process using adequate modelling tools has the advantage of being a scientific basis for decision making. It can show compliance with national or international regulations, or it can assist in choosing the optimal remedial actions. For the detailed modelling codes, the assessment will highlight the most important exposure pathways for given scenarios, and it can show the evolution on a given site over time. A prerequisite is that the site is well characterized so that the right input data can be used for site-specific assessments.

6.4.3 Challenges

Although this might seem like a trivial task, once the site is characterized and the necessary modelling codes are at hand, there are still challenges faced by the modeller once he or she moves past the screening stage. The most important part is to make sure that you use adequate parameter values for your site.

First of all, you need to describe well your source term. For some sites, this may be a simple task, for instance if you have one pile of homogeneous NORM contaminated waste with adequate sampling performed. In other cases, there might be several pits, waste dumps, contaminated surfaces or buildings that need to be characterized and built into your model.

Furthermore, for most sites it will be necessary to have realistic meteorological and hydrological data for the area that could be used in a site-specific assessment. In particular, the underground hydrology might be difficult to determine. Also realistic environmental data such as pH, soil type, land use and agricultural practices would be necessary. When calculating doses to humans, occupancy factors and dietary habits must be known. For calculating doses to biota, one needs to know which species are present and assign them to a reference organism (or a reference animal and plant, according to ICRP).

6.4.4 Implications for remediation

In many cases it will be necessary to calculate both existing and future exposures. In particular, for the latter, one must define plausible exposure scenarios for future activities. This could also be linked to the desired use of a site after termination of operations or after remediation. The cleanup criteria and the future exposure scenarios chosen will be different if the site is to be used for industrial purposes versus recreational purposes versus agricultural land or as a housing area. Often both a land use scenario and an intrusion scenario would need to be modelled to ensure the future safe use of a contaminated site. An intrusion scenario could be, for instance, that in 100 years' time, a family settles on what seems to be a nice green hill and builds a house there and starts farming. The former knowledge that this is a covered waste pile with NORM containing material is forgotten, and there is no regulatory control of the area anymore. Such a scenario would be a worst-case one, with both external and internal exposures of the humans settling there.

The possible exposures for decades or a few hundred years into the future is necessary to take into account when you plan for remediation and waste disposal for low-level waste. The permanence of the chosen mitigating actions would need to be taken into account in the modelling as well. For instance, if a NORM landfill is covered with a plastic lining and then covered with clean soil and regrown, it must be taken into account that the integrity of the plastic liner might be degraded after 30 years (Kerry Rowe, Quigley, & Brachman, 2004). A degraded plastic liner would lead to emanation of radon and increased exposures over time.

Modelling for remediation should encompass both the 'do nothing' option and various remedial actions that could be undertaken. The modelling should calculate the efficiency (in terms of averted doses or risk) of each action and the costs associated with the implementation in order to rank the various options according to cost-efficiency. Other aspects of the remedial actions should also be taken into account during the decision making, such as environmental impact, legal constraints, feasibility, waste disposal, socio-ethical considerations and stakeholder opinion (Howard et al., 2004). The modelling results are very useful as part of an optimization process (based on ALARA).

6.5 Case studies

The final report from WG2 (*'NORM and Legacy Sites'*) in the IAEA EMRAS II programme available at http://www-ns.iaea.org/projects/emras/emras2/default.asp contains detailed descriptions of six real NORM and nuclear legacy sites where a risk assessment has been done using various modelling codes. One of these is the Soeve mining site in Norway which is described below. For other examples, the reader is encouraged to consult the above-mentioned report.

6.5.1 The Soeve mining site in Norway

The Soeve site is a disused mining site in Telemark, Norway, where niobium was extracted between 1953 and 1965. It lies in an area with unusual geology exhibiting enhanced levels of naturally occurring radionuclides from the ^{238}U and ^{232}Th decay series. Some remediation works were performed after the closure of the mine in the late 1960s, but over time slag waste has become visible at the surface in certain locations. In Figure 6.4, an overview of the site in 1961 (during mining operations) and in 2010 is given (Dowdall, Brown, Hosseini, & Mora, 2010). The buildings at location A were demolished, and today it is a gentle slope towards the lake shore in the north covered with sand, rubble and crushed stone from the site (Location 1 in the left picture). The buildings at location B remains more or less the same, but the slag materials at Location 2 were covered with sand after the mining activity was stopped. Due to erosion, slag material has reappeared at the surface in spots. Location 3 is the tailings reservoir of the site, which currently appears as an overgrown floodplain with a stream running towards the lake.

6.5.2 Screening assessment for human exposure

In 2010, numerous measurements of ambient dose rate were performed onsite showing an average value of 0.44 μSv/h with a maximum value of 8.9 μSv/h (Dowdall et al., 2010; FOR-2010-11-01–1394). This indicates that the exposures might be in violation

Figure 6.4 The Soeve mining area in 2010 (left) and 1961 (right).
Reprinted with permission from Dowdall et al. (2010).

of the Norwegian regulations for radioactive waste and discharges (FOR-2010-11-01-1394). The three numbered locations in Figure 6.4 are of greatest concern (Brown, Liland, O'Brien, & Mora, 2011):

1. Wash house soils–The top layer consists of sandy materials of explosion-pulverized stone (from wall rocks) and crushed concrete. This resulted from the preliminary covering and improvement operations conducted when the mine was decommissioned.
2. Slag heap–Dumped slag was covered with carbonate sands after the cessation in mining activity. The sand is fine grained (with low variability in texture) and, as a result, exhibits little erosive resistance. There are large erosion scars at the top of the incline, caused by running water. The surface layer comprises decomposing vegetation material (from trees) and some rubbish.
3. Sludge disposal site–This resembles a floodplain and has a stream running through it. The material is mainly fine grained (<1 mm), with some slag lumps on the surface.

The activity concentration above which material is classified as radioactive waste in Norway, is 1 Bq/g for ^{238}U, ^{226,228}Ra, ^{228,232}Th and ^{210}Pb. It thus seems appropriate to use these values as screening activity concentrations for the purposes of the screening assessment. In addition, a 1-mSv/y value for human exposures was selected as a dose rate screening value.

A number of measurement results exist for the Soeve site. These results were divided by the screening values of 1 Bq/g to calculate the risk quotients as shown in Table 6.3. Since the risk quotients exceed 1 in almost all cases, it is clear that the screening criteria are not met and a more realistic assessment (Tier 2) should be performed. If we consider an external dose-rate value of 1 mSv/y, a person would need to spend about 118 h on the most contaminated spots to receive this exposure (Dowdall et al., 2010). This can be calculated using the MICROSHIELD software. The doses from inhaled radon would be in addition to this. The Soeve area is open to the public and sometimes used for recreational purposes, so external exposure of individuals is a realistic scenario.

Table 6.3 **Measured activity concentrations (IFE, 2006; NGI, 2009) and calculated risk quotients (Brown et al., 2011) at the Soeve site**

	Activity concentration (Bq/g)						
Sample location	**^{238}U**	**^{226}Ra**	**^{210}Pb**	**^{232}Th**	**^{228}Ra**	**^{228}Th**	**RQ**
Wash house soils a	10.9	12.5	13.6	15.4	18.8	19.5	91
Wash house soils b	5.2	3.3	2.7	7.7	8.7	8.3	36
Wash house soils c	1	0.88	0.89	1	0.99	1.1	6
Slag heap a	ND	5.4	ND	ND	5.2	ND	>10
Slag heap b	ND	5	ND	ND	5.2	ND	>10
Slag heap c	ND	0.04	ND	ND	0.04	ND	0.08

ND = not determined; RQ = risk quotient.
Reprinted with permission from Brown et al. (2011).

6.5.3 Detailed assessment using RESRAD-OFFSITE

RESRAD-OFFSITE was used for a more detailed assessment (Brown et al., 2011). The exposure pathways were limited to external exposure from the primary contamination onsite, radon inhalation and ingestion of fish and crustaceans from the nearby lake. The physical extent of the source and the position of the receptors were defined in the code. A combination of default and site-specific parameters were chosen for the modelling, as seen in Table 6.4.

To keep the assessment results conservative, the maximum activity concentrations reported for the site in NGI (2009) were used as input data. Despite the lack of measurement results, ^{210}Po was included in the model run with activity concentrations set equal to those of ^{210}Pb. The occupancy factors are conservative values for a representative worker on the site.

The model was run for 1000 years, and the result is shown in Figure 6.5. The ingestion pathway is almost zero, whereas the direct radiation from soil is around 10 mSv/y. This is predominantly due to the ^{232}Th decay chain (Dowdall et al., 2010). The main exposure comes from inhalation of ^{222}Rn with annual doses of approximately 110 mSv/y falling to around 60 mSv/y after 1000 years. The modelled external dose rates correspond well with the measured external dose rates from fieldwork at the

Table 6.4 **Parameters used in RESRAD-OFFSITE modelling of the Soeve site**

Parameter	Value	Source
Occupancy factor outdoor	36 days	Conservative values chosen for Soeve area
Occupancy factor indoor	110 days	Conservative values chosen for Soeve area
Annual precipitation rate	0.815 m/y	Specific for Soeve area[a]
Runoff coefficient	0.2	Default value RESRAD-OFFSITE
Annual irrigation rate	0	Specific for Soeve area; no irrigation occurs
Total porosity of donor compartment	0.4	Default value RESRAD-OFFSITE
Dry grain density of donor compartment	1700 kg/m^3	Specific for Soeve area[a]
Hydraulic conductivity	347 m/y	Specific for Soeve area[a]
Hydraulic gradient	0.04	Specific for Soeve area[a]
Thickness of clean top-soil	0.1 m	Specific for Soeve area
Thickness of waste	1 m	Specific for Soeve area
Leach rate for ^{226}Ra	6.51E-04 y^{-1}	Specific for Soeve area
Leach rate for ^{238}U	1.06E-02 y^{-1}	Specific for Soeve area
Leach rate for ^{232}Th	1.07E-04 y^{-1}	Specific for Soeve area
All other parameters		Default values RESRAD-OFFSITE

[a] NGI (2009).

Soeve site. The radon values, however, are significantly higher than effective doses calculated from *in situ* radon measurements. This could be due to the lack of certain site-specific parameters and/or to the fact that conservative values were chosen for the activity concentrations in the waste (Dowdall et al., 2010). Nevertheless, the combination of monitoring data and modelling results clearly shows us that the site is in need of remediation to ensure safe conditions for workers and the public at the site.

6.5.4 Tier 2 screening assessment for biota using the ERICA tool

The ERICA Tool was used to calculate total absorbed dose rates for selected reference organisms. A Tier 2 assessment was performed for terrestrial ecosystems based on mean activity concentrations in soil of the wash house area (Location 1). The results were compared to the ERICA screening dose rate of 10 µGy/h (Figure 6.6). All of the terrestrial reference organisms receive exposures substantially higher than the screening level, some more than 10 times higher. All of the organisms except grasses/herbs and lichen/bryophytes are still less than 100 µGy/h, which is considered by UNSCEAR as unlikely to cause deleterious effects on most terrestrial communities. Also, these organisms are among the most radio-resistant terrestrial species. The calculated values are expected to be conservative, that is, overestimating rather than underestimating the exposures. Also, the ERICA Tool does not allow for a consideration of disequilibrium between parent and daughter radionuclides within particular decay chains, which might be the case at the Soeve site. It is still a good indication, however, that the site may be of concern also for environmental exposures.

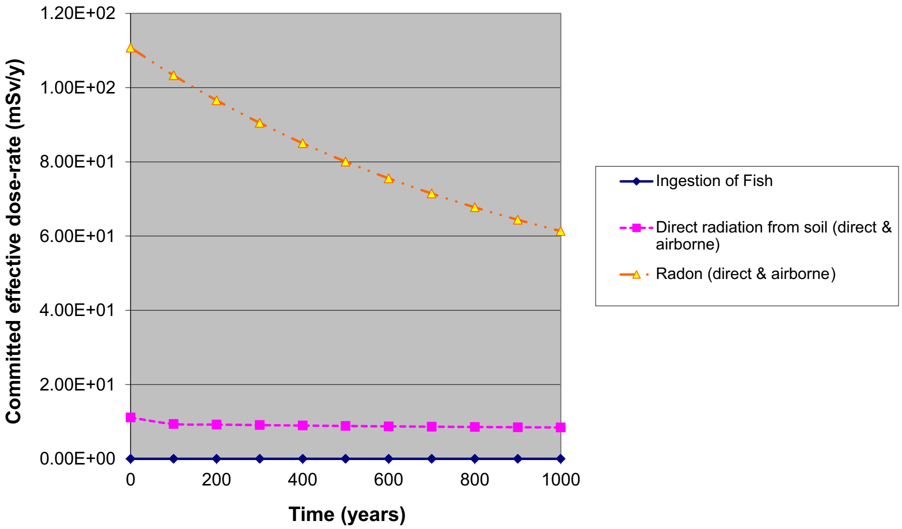

Figure 6.5 Committed annual effective dose rates at the Soeve site modelled with RESRAD-OFFSITE for 1000 years.
Reprinted with permission from Brown et al. (2011).

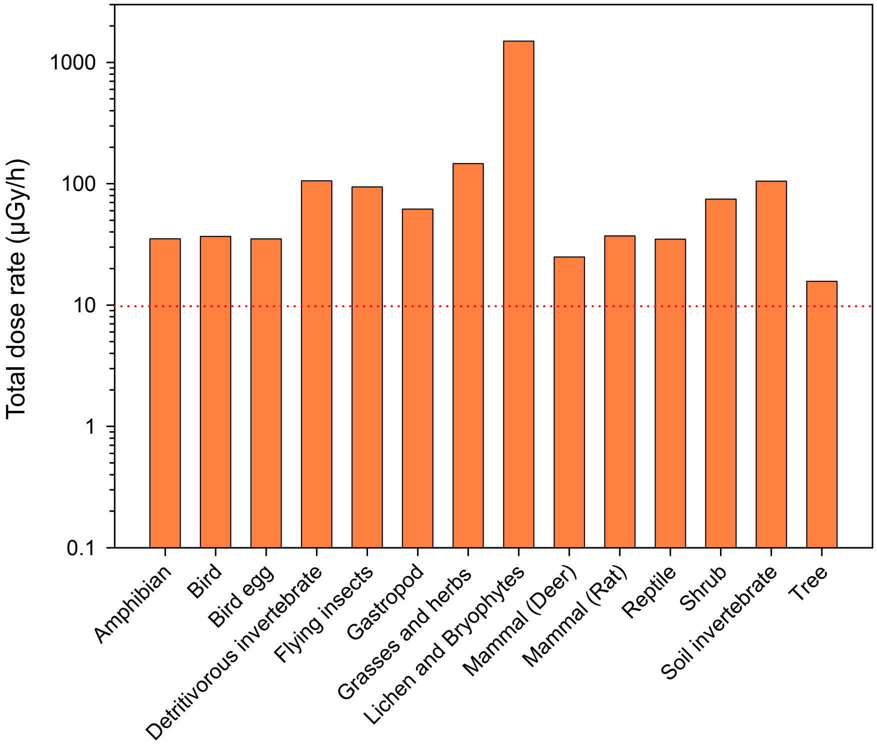

Figure 6.6 Total absorbed dose rates to ERICA default reference organisms. Dotted line represents ERICA screening level.

Reprinted with permission from Dowdall et al. (2010).

6.5.5 Modelling of remediation options

It was clear from the risk assessments for humans and the environment that remediation is necessary to ensure the safe use of the site in the future. Options could include:

- Removal of radioactive waste and redisposal at a given location onsite with a cover of clean soil to reduce the external exposure; or
- Removal of radioactive waste and disposal at an approved repository away from the site.

The first option was modelled using the MICROSHIELD software and considering several thicknesses of the clean soil cover. The results are shown in Figure 6.7 for thicknesses between 1 and 100 cm of clean soil.

The results show that 50 cm of clean soil cover would reduce the dose rate to humans above the site to around 0.1 µSv/h, that is, only 1% of the original exposure without shielding. Even if a person was standing there 24 h a day, 7 days a week all year around, the total dose would still be <1 mSv/y. However, the calculation cannot predict the situation in the future when, for example, erosion could reduce the shielding, or if an intrusion scenario was to take place.

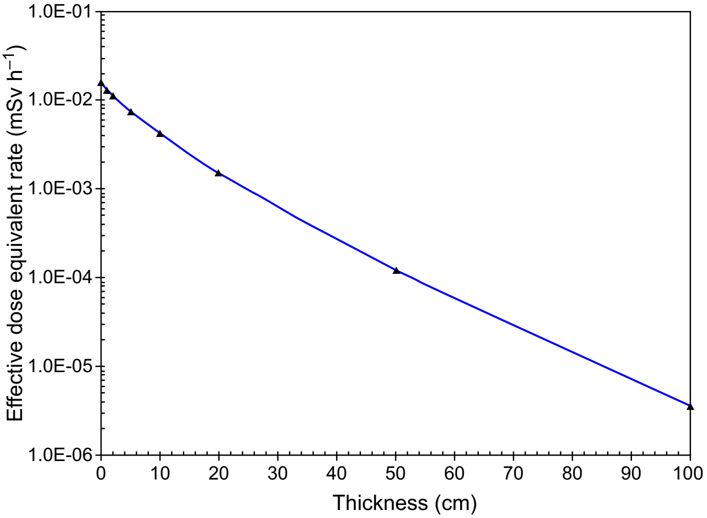

Figure 6.7 Reductions in dose-rate by applying a varying thickness of clean soil cover.
Reprinted with permission from Brown et al. (2011).

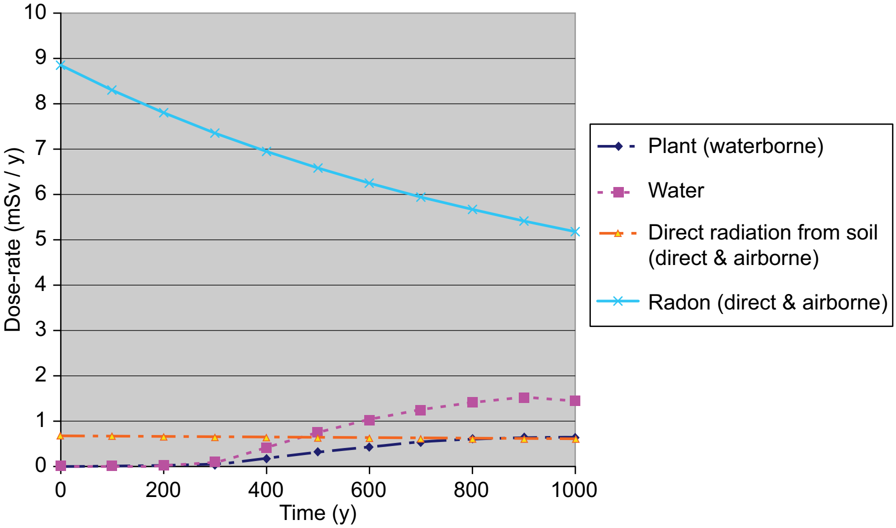

Figure 6.8 Modelled dose-rates over 1000 years for an agricultural scenario with all exposure pathways.
Reprinted with permission from Brown et al. (2011).

RESRAD-OFFISTE was used to model the second option, in which it was assumed that the site would be cleaned up to a level of 1 Bq/g for all radionuclides. A clean layer of soil of 10 cm was assumed. The scenario chosen was the use of the land for agricultural purposes with an extraction well for drinking water near the site. The assessment was run with all exposure pathways 'open' for a period of 1000 years. The modelling results are given in Figure 6.8.

The modelling predicts that, even after several hundred years, the external doses would be less than 1 mSv/y, and the same for ingestion of crops grown onsite. The dose from drinking water, however, is predicted to increase to more than 1 mSv/y after 600 years. The total doses from these three exposure pathways would stay below 1 mSv/y for the first 400 years and then slowly increase with time. The main dose, however, is predicted to come from radon starting off at around 9 mSv/y and slowly decreasing to about 5 mSv/y after 1000 years. The results show that it might not be sufficient to clean the area to a screening benchmark of 1 Bq/g for all radionuclides. Before deciding on remediation, several remedial actions should be evaluated in detail, using as many site-specific parameter values as possible and taking into account the socioeconomic aspects as well.

6.6 Future trends

The focus on NORM sites have become more apparent in the recent years, and it is likely that more assessments will be necessary for this which includes the use of human and environmental impact modelling codes. For nuclear legacy sites, several are under consideration for future remediation around the world, where modelling will play a key issue. For instance, in 2010 the IAEA created the International Forum on the Regulatory Supervision of Legacy Sites (http://www-ns.iaea.org/projects/rsls/). This project will compile lessons learned from past experience with legacy site remediation, and provide recommendations as to what constitutes good practice for regulatory supervision of legacy sites in the future.

Even if super-computers and sophisticated codes provide numerous possibilities for very detailed calculations, it is a trend that models should be ‘fit for purpose’, and not necessarily have as many parameters as possible. Sensitivity analysis to determine the most influential parameters is a good way to reduce the number of input parameters necessary in modelling codes. In particular, the parameter values that can be changed by the user should be reduced to what is strictly necessary. At the same time, the modelling code and supporting documentation should be transparent such that it is not a black box where the user has no understanding of how the calculations are performed. The demand for more user-friendly tools is apparent, and, for instance, in the post-accident community, the modellers have cooperated with the users of various models for dispersion and countermeasure implementation to adapt the tools to their needs (http://resy5.fzk.de/NERIS-TP/index.php?action=neris-tp&title=rtd).

Another trend is to see how the human and biota risk assessment can be combined in a common radiation protection framework. Within the European Commission radioecology project STAR (www.star-radioecology.org), work is ongoing to integrate humans and biota in the same framework and to combine the CROM code (for humans) with the ERICA Tool (for biota) into a new holistic risk assessment tool.

6.7 Sources of further information and advice

6.7.1 IAEA programmes

The former IAEA modelling programmes EMRAS I and II (Environmental Modelling for Radiation Safety) had working groups on environmental modelling for NORM and/or nuclear legacy sites. Reports from EMRAS I work can be found here: http://www-ns.iaea.org/projects/emras/default.asp?s=8.

and for EMRAS II here: http://www-ns.iaea.org/projects/emras/emras2/default.asp.

The EMRAS programmes were followed by the MODARIA programme (Modelling and Data for Radiological Impact Assessments), which is still running. Information is available here: http://www-ns.iaea.org/projects/modaria/default.asp?s=8&l=118.

The following 10 working groups are listed there for MODARIA:

Remediation of contaminated areas

- Working Group 1–Remediation strategies and decision aiding techniques
- Working Group 2–Exposures in contaminated urban environments and effect of remedial measures
- Working Group 3–Application of models for assessing radiological impacts arising from NORM and radioactively contaminated legacy sites to support the management of remediation

Uncertainties and variability

- Working Group 4–Analysis of radioecological data in IAEA Technical Reports Series publications to identify key radionuclides and associated parameter values for human and wildlife exposure assessment
- Working Group 5–Uncertainty and variability analysis for assessments of radiological impacts arising from routine discharges of radionuclides
- Working Group 6–Common framework for addressing environmental change in long-term safety assessments of radioactive waste disposal facilities
- Working Group 7–Harmonization and intercomparison of models for accidental tritium releases

Exposures and effects on biota

- Working Group 8–Biota modelling: Further development of transfer and exposure models and application to scenarios
- Working Group 9–Models for assessing radiation effects on populations of wildlife species

Marine modelling

- Working Group 10–Modelling of marine dispersion and transfer of radionuclides accidentally released from land-based facilities.

Scientists who would like to participate in the working groups can contact the IAEA to become members. It is open to all interested researchers.

6.7.2 *Scientific publications*

A special issue of the Journal of Environmental Radioactivity was published in 2014 in which a compilation of 12 manuscripts from a special session, ‘Environmental Radioactivity: Legacy Sites, Chernobyl and Fukushima’, held during the 12th ICOBTE Congress in Athens, Georgia, USA (16–20 June 2013), are presented. This special issue (Hinton et al., 2014) contains several papers on the modelling, speciation and environmental transport of radionuclides originating from nuclear accidents and from NORM and nuclear legacy sites.

6.7.3 *Other projects*

Many projects deal with modelling at NORM and nuclear sites. More information can be found at the Websites of the following, for example:

- BIOPROTA International Forum (www.bioprota.org), which focuses on the key issues in biosphere aspects of assessment of radioactive waste management.
- STAR project (www.star-radioecology.org) which focuses on radioecological research including modelling for human and environmental risk assessment.
- COMET radioecology project (www.comet-radioecology.org) which includes research to improve radioecological modelling.

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Risk assessment and cost–benefit analysis for the restoration of contaminated nuclear and NORM sites

7

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7.1 Introduction

Although nuclear and NORM sites comprise a small proportion of the total number of contaminated sites, the actual or potential existence of radioactive contamination ensures that they have a high profile, due to the general public perception that radioactive contamination is invariably more hazardous than chemical contamination. This is particularly the case for nuclear sites, due to the contentious nature of the industry, and because the public also generally perceives anthropogenic radioactive contamination to be more harmful than 'natural' radioactivity. This perception tends to be reinforced by the invariable separation of regulatory regimes for radioactive and nonradioactive contamination, and the application of different dose criteria as the basis for calculating clearance and exemption values for radionuclides of natural and artificial origin, (e.g. IAEA, 2004).

Previous chapters have described the types of contamination arising from different nuclear and NORM activities, together with the international regulatory frameworks and role of stakeholders in site restoration. This chapter discusses the application of risk assessment and cost–benefit analysis in devising remedial strategies. The main focus is on the remediation of radioactive contaminants, although the importance of other factors, including nonradioactive and physical hazards, is also described.

7.2 Site end states

The physical condition of a site after remediation is sometimes termed the 'end state'. A site may have more than one end state, with a number of areas remediated to standards appropriate for differing potential reuses. The achievement of end states may also be staged, with initial remediation on part of a site to achieve an interim end state whilst cleanup of the entire site to the final end state is delayed.

In some instances, a range of potential end states may be possible, depending on options for future land use, the associated land values and the costs of remediating soil and groundwater to the standard necessary to allow each use. Cost–benefit analysis

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may be undertaken to help discriminate between options, and may require the use of discounting methods where the timing of expenditure differs. For larger or more complex sites, socioeconomic and political factors can also be important, and can include considerations such as continuity of employment and affordability—both in the short term (can we pay?) and to society as a whole (should we pay?).

In other cases, the end state may be defined by regulations, such as when an industrial permit requires a site to be restored to the preexisting condition when the authorised activity is complete. Alternatively, a standard of remediation may be specified, as in the UK, where the criterion for delicensing a nuclear site is linked to the legal definition of 'no danger'. The regulator interprets this as meaning a risk of death of less than 10^{-6} per year from the land in any foreseeable future use (HSE, 2005). This is considerably more onerous than most other regulatory regimes, which require only land to be rendered safe for its next intended use.

The process of defining the site end state can therefore be both complex and iterative, and may require the evaluation of a wide range of factors in order to arrive at the optimal remedial solution.

7.3 Standards of remediation

It is probable that the majority of radioactively contaminated sites that have been cleaned up to date have been remediated in order to facilitate redevelopment, rather than as a result of regulatory pressure. The standards for redevelopment-driven remediation are frequently dictated by public perception rather than actual risk, leading to a strong emphasis on source removal as the remedial strategy. The remedial targets adopted, at least historically, have often tended to be the numerical thresholds for the classification of radioactive waste, such that all material contaminated above this level is removed from the site. The use of risk-based cleanup targets is comparatively rare in such a context, since only the complete removal of all 'radioactive waste' has generally been considered adequate to dispel public blight and to allow the maximum (or indeed, any) land value to be realised. The majority of sites to which this has been applied have therefore tended to be small and affected by contaminants that are relatively localised and/or immobile in soil, such as residues from radium production and luminising activities, and the disposal of related wastes.

Sites with more extensive and/or mobile contamination, such as those where groundwater has been affected, have been cleaned up relatively rarely. Furthermore, whilst the restoration of such sites is inevitably cost driven, cost–benefit analysis is generally carried out only at the most basic level, dictated by the business need of the developer to realise a profit. Where the restoration of such sites would be uneconomic, development is not progressed (indeed, transactions are often structured such that the developer does not proceed with the land purchase unless satisfied that redevelopment will yield a profit).

In contrast, dose- or risk-based remedial targets have tended to be applied principally at those radioactively contaminated sites where there is a regulatory driver for remediation, such as for delicensing or the restoration of larger areas with significant contamination. In a small number of cases, the costs of restoring such sites have fallen to private sector organisations with significant financial resources. In other instances, restoration costs have typically been funded from the public purse by regional or national Governments, international Government collaborations, or international funding bodies such as the European Bank for Reconstruction and Development or the World Bank.

7.4 Risk assessments

Risk assessments are invariably performed for regulatory reasons, to demonstrate that exposures to radioactive contaminants will not exceed the thresholds specified in national or international regulations and guidance. They may also be undertaken to demonstrate publicly and politically that land is safe (or will be made so after remediation) in order to increase the land value, unlock development potential and safeguard the reputation of the owner and/or developer.

In all cases, regulatory regimes require the assessment of risks to humans. In the case of exposures that are certain to occur, assessments consider the effective dose likely to be received, and are based on internationally established dose–impact relationships derived from extensive long-term epidemiological studies. For exposures that are not certain to occur, such as long-term exposure scenarios, assessments are based on risk rather than dose.

In recent years, the International Commission on Radiological Protection (ICRP) has expanded the scope of its system of radiological protection to include consideration of the risks to nonhuman receptors. However, compared to humans, much less research has been carried out into the effects of radiation on nonhuman species. The assessment of risks to biota therefore tends to be based on absorbed dose, often using theoretical ‘reference organisms’ due to the lack of species-specific data (Beresford et al., 2007).

7.4.1 Regulatory limits

Dose limits for human exposure are generally derived from International Atomic Energy Agency (IAEA) Basic Safety Standards (IAEA, 2014) unless lower limits are set in national legislation. The main dose limits that are generally applied are shown in Table 7.1.

Where exposure is not certain to occur, risk targets are usually applied instead of dose limits. This is generally the case for potential exposures that may occur to members of the public in the long term, after the period of institutional control has ended and the site is no longer actively managed. A risk target of 10^{-6} is generally applied, i.e., a risk of death of 1 in 1 million per year. In the UK, this is defined as the limit of broadly acceptable risk to members of the public (HSE, 2001).

There is currently no international consensus on limiting criteria for determining the significance of impacts on nonhuman biota. A range of numerical benchmarks have been developed by various organisations and research groups, including the

Table 7.1 Dose limits for planned exposure situations

Exposed person	Effective dose limit
Workers over the age of 18 years	20 mSv per year averaged over 5 consecutive years (100 mSv in 5 years), and 50 mSv in any single year
Apprentices and students aged 16–18 years	6 mSv in a year
Public exposure	1 mSv in a year In special circumstances, a higher value of effective dose in a single year could apply, provided that the average effective dose over 5 consecutive years does not exceed 1 mSv per year

Different limits apply to exposure to the lens of the eye or to the extremities (hands and feet) or the skin.
Additional restrictions apply to occupational exposure for a female worker who has notified pregnancy or is breast-feeding.
IAEA (2014) Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards. No. GSR Part 3, Vienna: International Atomic Energy Agency.

IAEA and European Commission. National approaches have also been developed, for example, by the UK Environment Agency (Allott, Copplestone, Merrill, & Oliver, 2009; Coppleststone et al., 2001) and US Department of Energy (RESRAD, 2004). All usually express limits or guidance levels in terms of absorbed dose rate, and allow the assessment of the likely significance of potential health effects for a defined range of organisms.

In addition to limits applicable to the exposure of humans and nonhuman receptors, national policy and regulations may impose additional constraints on public exposure from individual discharges or sites. For example, in the UK, when licensing new radioactive substances activities, regulators impose public dose constraints of 0.5 mSv per year to future discharges from a site, and a maximum of 0.3 mSv per year from any single source (HPA, 2009).

7.4.2 Assessment process

Potential receptors (humans or nonhuman species) may be exposed to radiation either directly (external radiation) or by uptake into the body (internal radiation). Exposure will occur only if a source of radioactivity is present, and a pathway exists by which the receptor will be exposed. The assessment process therefore involves the evaluation of all three components of the system–source, pathway and receptor–in order to estimate the dose likely to be received. For future situations in which exposure is not certain to occur, the likelihood of exposure in excess of the regulatory dose limit is taken into account, and the result is expressed as a risk.

A detailed overview of the survey and assessment of contaminated nuclear and NORM sites is given in Chapter 9. The key requirement is that the level of characterisation undertaken must be adequate to allow subsequent assessment and interpretation of the data. This means that the scope of investigation and sampling must be adequate to deliver the required level of confidence in the results. In some cases, the use of statistical methods for the design and delivery of characterisation programmes (MARSSIM, 2000) may be appropriate to demonstrate the quality and robustness of the assessment to regulators and the public. In addition to the location and numbers of samples taken, the analytical methods used must have limits of detection sufficiently low to enable the assessment results to be compared with regulatory limits. For certain radionuclides, the chemical form in which they are present may also be important, since this may affect their mobility via certain pathways, such as solubility and attenuation in groundwater, as well as their uptake into the body. For the assessment of airborne pathways, the physical form of radionuclides (e.g. particle size) may also be important, since this can affect both transport and uptake.

For any site, there is likely to be range of potential receptors, including site workers, members of the public and nonhuman species. The pathways by which each may be exposed will depend on their habits, and, in many cases, receptors may be exposed via several pathways, which must be summed to calculate the total dose received. For example, workers may be exposed via direct irradiation, inhalation, skin absorption and inadvertent ingestion, but their exposure duration will be limited by working hours. Different members of the public may receive widely differing exposure, for example, a local farmer who spends his entire time living and working adjacent to a radioactively contaminated site is likely to receive a markedly different radiation dose to someone living remotely from site who is exposed via the consumption of contaminated foodstuffs.

Because it is not practicable to assess doses to each individual member of the population, assessments are based on the exposure of 'representative persons', defined as 'an individual receiving a dose that is representative of the more highly exposed individuals in the population' (ICRP, 2007). This is equivalent to the term 'average member of the critical group' used in earlier guidance. Representative persons may be identified by carrying out localised surveys, or by a more generalised approach using national or regional data leading to the specification of 'generic' representative persons. The important factor is that the characteristics of the representative person are applicable to the time period of the dose constraints and dose limits and the time period for which the dose assessment will apply. Habits vary markedly with age, and the most affected age group is normally selected; this will depend on the radionuclides present and the environment around the source. The potential for future changes in habits must also be considered, for example, as a result of changes in land use or agricultural practices.

The exposure of nonhuman receptors will vary similarly, and there will be markedly different potential impacts to organisms in different ecosystems, such as to terrestrial and aquatic life. Some classes of receptor may also have statutory protection from contamination, depending on national and international regulations, for example, protected habitats or species. In Europe, water resources (groundwater, surface waters, etc.) have statutory protection as receptors in their own right, in addition to having the potential to act as migration pathways.

The risk assessment process is normally staged, with initial stages using simple, cautious methods to screen out lower-risk scenarios so that only those that remain are subject to more detailed assessment. A wide range of assessment methods are available, but detailed consideration is beyond the scope of this chapter. The assessment approach recommended by UK regulators (EA, 2012) is typical, and commences with an initial source assessment using a simple and cautious approach that applies generic screening criteria to estimate whether the dose to the representative person is likely to exceed 0.02 mSv per year. If this screening threshold is exceeded, a detailed assessment is carried out with the following stages:

- Detailed source and site assessment to determine the dose to the representative person for comparison with the source and site constraints and the dose limit.
- Short-term release assessment to determine the acceptability of short term release limits, where appropriate.
- Collective dose assessment to provide an assessment of the population doses for different discharge/disposal options.
- Variability and uncertainty assessment to establish how much caution has been applied at each stage of the assessment.

7.5 Derivation of remedial targets

The principal object of remediation is to break or inhibit the linkage among source, pathway and receptor, so that the dose or risk to representative persons or nonhuman receptors no longer exceeds regulatory limits. This could involve a single or combination of actions, such as the placement of a covering layer to isolate the contamination from the surface and provide shielding, or the relocation of a receptor further away (e.g. by means of physical barriers such as fencing and security). However, only removal of the contamination source is certain to be effective in controlling the doses and risks permanently. When this is required, an activity-based remedial target (Bq/g) must be used during remediation to ensure that all material that would give rise to an unacceptable hazard is removed. Appropriately calibrated monitoring instruments are then used during remedial works to identify areas above the remedial target for source removal and/or to validate areas that have been remediated before backfilling.

7.5.1 Use of waste classifications as remedial targets

As described in Section 7.3, activity thresholds for the clearance and exemption of radioactive wastes have frequently been adopted as activity-based targets for the remediation of contaminated soils at nuclear and NORM sites. This reflects the predominance of ‘dig and dump’ remedial techniques, and in many cases is likely to have resulted in more extensive (and expensive) remediation than strictly required to reduce doses and risks below regulatory thresholds. Whilst this may have been necessary to secure public confidence in the standard of remediation, in some cases changes in clearance and exemption limits could potentially result in the activity of soils left beneath a remediated site being reclassified as waste. Conversely, it is also possible that land after remediation could still give rise to doses and risks which exceed regulatory limits, necessitating re-remediation.

7.5.2 Dose- and risk-based remedial targets

The alternative is to develop remedial targets based on the results of a site-specific risk assessment that considers representative exposure scenarios based on current and intended future uses of the land. The risk assessment results are used to back-calculate the maximum concentration of activity that can be allowed to remain in the soil and that would result in a level of exposure equal to the dose or risk target. The calculated activity concentration is then usually reduced to allow an additional margin for safety, and the resulting concentration is used as the remedial target. Similar techniques may be applied to derive dose- or risk-based remedial targets for groundwater contamination.

7.6 Cost–benefit analysis

Cost–benefit analysis is a general tool used to inform decisions on the best way to allocate resources. In the context of radiation protection, it is used as a means of ensuring that activities leading to planned radiation exposure are justified and optimised (ICRP, 2007). Activities involving exposure to radiation are considered to be justified only if they 'are expected to yield sufficient benefits to outweigh the detriments associated with taking them, including detriments in the form of radiation risks' (IAEA, 2014). Optimisation is defined as the 'process for ensuring that the likelihood and magnitude of exposures and the number of individuals exposed are as low as reasonably achievable' (ALARA) 'with economic, societal and environmental factors taken into account' (IAEA, 2014)

Justification of potential remedial actions involves a wide range of factors other than radiation protection. The only role played by radiation protection in cost–benefit analysis involves considerations of the cost of radiation protection and the cost of the health detriment resulting from the exposure of individuals and the population to radiation. Cost–benefit analysis helps to ensure that the total benefit outweighs the total detriment, which includes all cost and negative aspects such as capital and operating costs, radiation protection costs, as well as the cost of health detriments. The total benefit includes the increase in land value after remediation, increased employment, and other socioeconomic benefits such as raising the standard of living.

However, although cost–benefit analysis may show a net benefit, there may be instances in which radiation exposure risks for some individuals may be unacceptably high. There is therefore an overriding requirement that regulatory dose limits must not be exceeded: otherwise, the proposed action is unjustifiable.

It is also required that the total detriment to society be kept ALARA. This is assessed by means of the collective dose, which is the sum of all of the effective doses received by individuals in an exposed population. Based on the assumption of direct proportionality between stochastic biological effects and dose equivalent, the collective detriment to health is usually taken to be directly proportional to the collective dose. This may be converted to the mean loss of life expectancy using risk factors published by the ICRP (2007). However, the measure of collective dose masks information on levels of individual dose and their distribution over time and space,

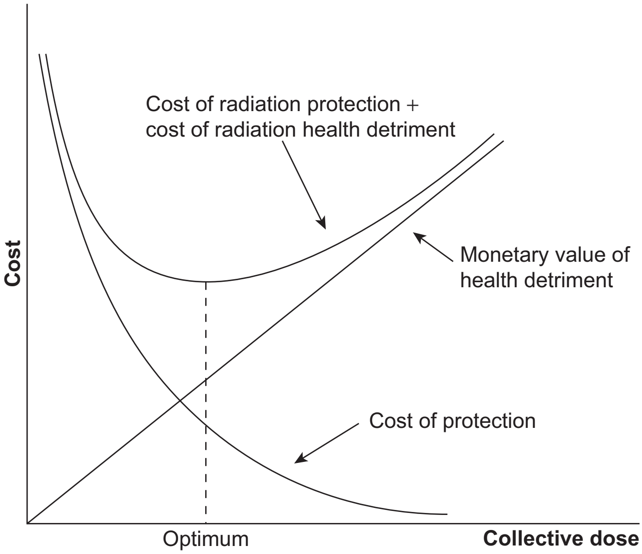

Figure 7.1 Optimisation of radiation protection.

and may also overestimate impacts if it sums a large number of small doses received over a long timeframe. Consideration of these limitations is beyond the scope of this chapter, but they should be borne in mind whenever the measure of collective dose is used. Readers are referred to Smith et al. (2007) for a detailed consideration of this subject.

To optimise radiation protection, the incremental costs involved in reducing the collective dose are compared with the incremental health benefits that would result. The ALARA value is that level of collective dose below which the cost of any additional radiation protection measures would exceed the value of health benefit gained. This is shown schematically in Figure 7.1.

The assessment may be facilitated by assigning a monetary value (α) to the cost of unit collective dose equivalent. However, where significant reductions in dose may be readily achieved at low cost, formal analysis may not be necessary. Conversely, it is sometimes evident without formal analysis that a possible improvement would be extremely costly, yet would result in only a trivial reduction in dose. In such instances, an order of magnitude estimate of α may be sufficient.

Although the legal requirements for justification and optimisation relate specifically to radioactive risks, the concepts extend more widely to include considerations of the risks resulting from nonradioactive contaminants, physical hazards associated with the land (e.g. slope instability) and hazards associated with the remedial work itself, which may include off-site risks such as transport accidents. Consideration of the potential economic, societal, and environmental factors associated with remediation is also important, but comparison of such diverse aspects makes the evaluation of remedial options problematic. Although certain aspects such as engineering costs can generally be estimated fairly accurately, the assignment of monetary values to certain detriments, such as loss of habitat or species diversity, may be more subjective.

7.7 Application of cost–benefit analysis to complex sites

In complex environmental situations, such as where a mixture of radiological and nonradiological contaminants is combined with physical hazards, the selection of cost-effective remedial measures requires an integrated assessment method that considers all improvements achievable in the different areas on a common basis, and relates them to the required financial expenditure. Rational decisions can then be made regarding those areas in which remedial action is necessary to address specific issues, and those in which expenditure on remediation is not justified. Such an approach will identify situations in which remedial activity to address one risk, such as from radioactivity, may inadvertently increase other risks, such as slope instability. It will also allow evaluation of the combined effects of remedial actions that address several risk issues, such as where the installation of low permeability capping reduces both direct radiation risks and the leaching of radioactive and non-radioactive contaminants into groundwater.

7.7.1 Evaluation of impacts

To facilitate comparison among the risks posed by radioactive contaminants, carcinogenic chemicals and toxic chemicals, human health risks are generally expressed in terms of the loss of life expectancy. This concept is directly applicable to lethal health effects such as cancer resulting from exposure to radioactivity or carcinogenic chemicals. For nonlethal health effects from toxic chemicals, the deterioration in quality of life is evaluated and combined with the lethal risks into the common assessment parameter ‘mean effective loss of life expectancy’ (MEL). This is then converted into an equivalent monetary value for the purpose of cost–benefit assessment.

Radiological risks to humans are estimated for each relevant source–pathway–receptor linkage as described in Section 7.4.2, using contaminant migration and dispersion models where necessary. The collective dose is then used to quantify radiological damage, and is converted to the MEL using ICRP risk factors (ICRP, 2007) unless national guidance requires alternative risk factors to be used. Separate assessments are also required to confirm that exposures during the remedial work will not exceed the legal dose limits.

Human risks from nonradioactive substances are assessed in a similar way. The additional cancer risk from exposure to carcinogenic chemicals is estimated using published risk factors, and risks from toxic chemicals are assessed by comparison with published toxicological parameters (No Observed Adverse Effect Level or Lowest Observed Adverse Effect Level). Authoritative sources of risk factors and toxicological parameters such as the United States Environmental Protection Agency (US EPA) are generally used unless national regulations require otherwise. In each case, the results are expressed as the MEL.

In many cases, one of the highest risks associated with remediation results from the potential for traffic accidents involving vehicles involved in remediation activities, such as the transportation of wastes or excavation materials. Other physical risks may include induced slope failures resulting from excavation or the stockpiling and placement of materials. Such risks may be assessed using a variety of methods, including reference to published accident statistics where appropriate, to derive the MEL for comparison with other assessment results.

As discussed in Section 7.4.1, there is no international consensus on methods to assess the significance of radiological impacts to nonhuman biota, although national approaches have been developed. In common with methods for the assessment of nonradiological impacts to groundwater and surface water, these generally involve the use of appropriate migration and dispersion models to estimate the concentration of contaminants that would reach the receptor. In each case, the predicted concentrations are compared against relevant quality parameters in legislation or guidance to assess the extent of relative impairment or improvement. If no relevant quality parameters are in place locally, the assessment is generally made against reference values published in other countries or internationally.

Exceedance of a statutory environmental quality parameter, such as a drinking water standard or Environmental Quality Standard, would rule out a remedial option from further consideration, as would significant contamination of a water body or ecosystem with statutory protection. However, remediation generally involves an improvement in quality, so the assessment of impacts tends to be based on the increase in amenity value rather than detriment.

7.7.2 Monetisation of risks and damages

Risks and damages from all causes are monetised so that they are comparable with each other and can be evaluated together with the costs of carrying out remediation. The monetary equivalent assigned (α) may be regarded as a measure of societal willingness to pay for preventing that damage, and will be highly dependent on the society concerned and socioeconomic factors. Since societal values are not static, it follows that the value of α will also change over time.

The most common methods of evaluating α are by precedent (i.e. payments actually made to prevent or mitigate damage of type concerned), surveys or engagement with stakeholders to ascertain their views, life valuation methodologies, or arbitrary assignment. In the case of radiation detriment, Ahmed and Daw (1980) cited a literature survey showing a wide range for the value of α ranging from USD 1000 to USD 100,000 per man Sv. More recent guidance in the UK by the Nuclear Decommissioning Authority (NDA) gives values of radiation detriment of GBP 50,000 per man Sv for individual doses <5 mSv per year and GBP 100,000 per man Sv for individual doses >10 mSv per year, scaled for doses between these values (NDA, 2010).

Once all potential impacts have been monetised, the total costs of remedial options can be compared. It is important that the options considered be realistic, and that they include all costs likely to be incurred. In the case of the short-term or 'do nothing' option, this should include costs for continued active management and monitoring of the site.

The use of discounting techniques may be appropriate to bring short- and long-term expenditures to a common reference basis. In common with all discounting techniques, results may be highly dependent on the discount rate applied, and sensitivity analysis may be required to increase confidence in identification of the optimum remedial solution. Consideration of uncertainties may also be necessary, particularly for expenditures that may occur far in the future, such as contingencies to cover the long-term effectiveness of remedial actions. These uncertainties may be evaluated by probabilistic methods to assess the range of possible outcomes.

7.7.3 Role in selection of remedial option

Although cost–benefit assessment is a potentially valuable tool, its function is only to provide a starting point for the decision process itself. The actual decision making has to consider a wide range of additional factors, such as the availability of funds, public acceptance and political will. It follows that the eventual decision may not necessarily follow the quantitative cost–benefit results. However, even where this is the case, the results of the cost–benefit assessment still provide a rational and transparent foundation for the decision-making process, enabling evaluation of the disadvantage associated with selecting a quantitatively suboptimal cleanup option for social or political reasons.

7.8 Case studies

7.8.1 Remediation of land in East Germany affected by uranium mining

Uranium mining and milling activities were carried out in East Germany for 40 years and produced more than 216,000 tonnes of uranium. Since German reunification in 1990, some EUR 5.8 billion of public money has been spent by the federally owned company Wismut GmbH on remediating the legacy of NORM-contaminated land, which covers a total area of 37 km^2 and includes an open pit (84 million m^3), five large underground mines (1.53 million m^3), 311 million m^3 of waste rock spoil and 160 million m^3 of radioactive tailings located in densely populated areas. Typical specific activities of the materials involved are 0.5–1 Bq/g for waste rock, 10 Bq/g for tailings and up to 500 Bq/g for water treatment residues.

Prior to the commencement of remediation, an area of approximately 100 km^2 was subject to a large-scale gamma survey to identify areas of significant contamination. This narrowed the focus for remedial investigations and work to five mining sites and two mill sites. Conceptual remedial designs and closure plans were developed for each site, often concurrently with the preparation of detailed designs and remedial work plans. The development of a standardised approach to remedial decision making only became possible at a later stage (Hagen & Jakubick, 2011).

An overview of the optimisation process is given by Pelz, Jakubick, and Kahnt (2003). This involves the use of an iterative, deterministic, or probabilistic ‘top down’ approach to model the remediation project as an integrated system. All relevant processes are initially captured, but as the model is developed, the balance of effort is concentrated on assessing those variables and processes that have the greatest influence on the results. In this way, resources available for modelling are deployed most efficiently, and meaningful conclusions can be drawn at an early stage, even though some parts of the system may not have been assessed in detail. This approach allows the identification of gaps in the knowledge base, permitting characterisation and studies to be directed to provide the data necessary for subsequent optimisation decisions to be made. This includes the gathering of data to assist in the assessment of socioeconomic impacts in addition to data for the assessment of health risks and direct costs.

The approach used by Wismut to assess remedial options is described by Goldammer and Nüsser (1999), and includes the quantification of risks to humans and ecosystems as a result of both radiological and chemical contaminants. Human health risks are expressed as loss of life expectancy. For nonlethal health effects from toxic substances, the deterioration in quality of life is evaluated and combined with the lethal risks as the MEL. This parameter is converted into an equivalent monetary value as the basis for cost–benefit assessment. Damage to aquatic ecosystems and drinking water resources is similarly expressed in monetary terms, based on the societal willingness and ability to pay for the prevention or mitigation of damage. On this basis, cleanup options are assessed in terms of their benefits in relation to the financial expenditure required. Uncertainties in the underlying data and assumptions are taken into account using probabilistic assessment techniques, leading to a rational and transparent basis for subsequent remedial decision making.

7.8.2 Remediation of former nuclear weapons test site in Australia

Between 1955 and 1963, the UK conducted a programme of nuclear weapons development tests at Maralinga in the remote outback of South Australia. This resulted in the widespread dispersal of radioactive contamination, the most significant of which related to safety tests involving the burning and explosive dispersal of plutonium, uranium and other radionuclides. At the Taranaki site, approximately 22 kg of Pu-239 and the same quantity of U-235 were deposited in plumes carried large distances by the prevailing winds.

Initial rehabilitation work was carried out by the UK Ministry of Defence in 1967 and included the collection of debris and contaminated structures and equipment for burial in a series of 22 pits, each approximately 2–3 m deep and covered by a 30-cm thickness of lightly reinforced concrete. The burial areas were fenced, and warning signs were erected. The most contaminated outlying areas were ploughed to mix the surface contamination into the underlying soil with the intention of reducing the risks. However, subsequent studies revealed contamination levels greater than previously acknowledged, and indicated that rehabilitation measures were not as effective as intended. In particular, the standard of capping over trenches was in some cases poor, resulting in the exposure of contaminated artefacts at the surface. Previous assumptions regarding the habits of persons exposed were also found to be flawed. Re-occupation by the indigenous population pursuing an Aboriginal lifestyle had not been foreseen, nor had the attraction of tourists and artefact collectors to the area been considered.

A Technical Assessment Group was set up by the Australian Government, and in 1993 the Maralinga Rehabilitation Technical Advisory Committee (MARTAC) was given responsibility for the establishment of cleanup criteria and remediation of the site, with the constraint that the land was to be returned to the traditional owners who would use it to support an outstation lifestyle. As a consequence, remedial assessment was based on the assumption that a European lifestyle would prevail, and alternative future land uses were not considered. Societal risk was not considered an issue because of the small numbers of inhabitants involved (some hundreds at most) (MARTAC, 2003). There was also an implicit understanding that, whatever cleanup option was adopted, the plan would be for risk reduction to the budgetary limit. In other words, at the time of the assessment in 1990, the concept of ALARA and use of best practicable technology that are mandatory for the regulation of current activities were deemed not directly applicable to the rehabilitation of contamination from earlier practices such as Maralinga (MARTAC, 2003). It should be noted that this would no longer be the case, since the ICRP and IAEA have subsequently extended the concept of cost–benefit optimisation of radiation protection from the regulation of planned exposure situations to interventions designed to reduce future exposures from existing sources.

The risk assessment/hazard consequence assessment adopted was based on conventional methods, comprising the definition of source terms, consideration of bioavailability and exposure routes, dose assessment, and uncertainty analysis. The boundary between acceptability and unacceptability of risk was determined to be an annual committed dose of 5 mSv, assuming full-time occupancy by Aborigines living an outstation lifestyle (TAG, 1990). This was deemed to correspond to an annual risk of fatal cancer following the inhalation or ingestion of contaminated soil of not more than 1 in 10,000 by the fiftieth year of life.

When determining the soil removal criteria, MARTAC took into account three dose pathways, namely, inhalation of resuspended dust, ingestion of soil or contaminated food, and wound contamination. Criteria were therefore established based on the maximum concentration of plutonium allowed to remain in surface soil, and a limit on the number and activity of contaminated particles and fragments near the surface.

A series of engineering work packages were placed with consultants in order to elicit proposals for cleanup options and costs for more complex areas, such as the former disposal pits. In other cases, such as for the erection of fencing, soil removal and trench disposal, costs were estimated by conventional means. In all, nine main options were identified, with 26 suboptions, with costs ranging from AUD 13 million to AUD 653 million (1988 estimates). These were presented to the Commonwealth Parliament, together with a paper identifying the preferred rehabilitation option. A consultation was also conducted with stakeholders including the local community and state government. A financial settlement was eventually reached, including a contribution to funding from the UK Government of GBP 20 million and payment of AUD 13.5 million in compensation to the local community (MARTAC, 2003).

The final remedial scheme consisted of defining the cleanup boundaries at each of the plutonium-contaminated areas, followed by the bulk removal of soil and burial within purpose-built trenches under at least 5 m of clean rock and soil. At Taranaki, 11 of the previous burial pits were treated by *in situ* vitrification, and the remainder were exhumed and their contents reburied in a custom-built trench. Remedial works were completed on time in 1999, for a total budget of AUD 108 million.

7.9 Future trends

In the UK, the nuclear industry has undergone radical restructuring since 2005, when the government established the NDA in order to focus on the decommissioning of legacy civil nuclear sites and to deliver best value for the taxpayer. There is now a formal industry requirement for the selection of decommissioning options and investment decisions to be based on sound business cases, underpinned by comprehensive assessments of costs and benefits throughout the entire project life cycle. The centralisation of policy and funding also allows broader investment decisions to be made, permitting the identification and enaction of opportunities to realise economies of scale across the NDA estate, whilst at the same time focussing expenditure in areas that would deliver the greatest hazard reduction and long-term cost–benefit. The NDA's remit also extends to considerations related the maintenance of capability and socioeconomic impacts, such as continuity and development of the skills base and workforce required to deliver decommissioning work.

There is therefore a high level of awareness of the importance of risk assessment and cost–benefit analysis within the UK nuclear industry. This also extends to other parts of Government, where a recent trend in increasing public scrutiny of expenditure has combined with a drive for major cost savings since the economic downturn in 2007. Similar pressures are present in other economies, and it is suggested that the UK approach is likely to be regarded as best practice for providing a robust and transparent basis for remedial decision making.

7.10 Sources of further information and advice

ICRP guidance on cost–benefit analysis in the optimisation of radiation protection can be found in ICRP (1983).

Detailed guidance on the requirements for robust characterisation of radioactively contaminated sites can be accessed from the MARSSIM pages of the US EPA Website http://www.epa.gov/radiation/marssim/

The US EPA IRIS database contains up to date, authoritative data on the health effects of a wide range of chemicals. http://cfpub.epa.gov/ncea/iris/index.cfm?fuseaction=iris.showSubstanceList

The Centre for Ecology & Hydrology (CEH) Wiki provides an authoritative oversight of issues and methods developed for the assessment of radiological risks to nonhuman species. https://wiki.ceh.ac.uk/display/rpemain/Radiological+protection+of+the+environment+-+sharing+knowledge

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Electrokinetic remediation and other physico-chemical remediation techniques for *in situ* treatment of soil from contaminated nuclear and NORM sites

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8.1 Introduction: *in situ* physico-chemical remediation technologies from contaminated nuclear and NORM sites

During the twentieth century, the rapid industrial development created an immense environmental problem due to improper waste management and disposal. It resulted in thousands of locations polluted around the world, and the problem, instead of being mitigated, is still growing, especially in emerging countries. Society has become aware of the harmful effects of the pollutants in the environment, natural life, and public health and has demanded a solution from politicians, technologists, and the scientific community.

The contamination of soil and groundwater has been an important issue in the political agendas in a number of European and North American countries since 1994. As a result, scientists, engineers, and regulators have devoted much effort to the development of innovative technologies to reduce the impact of the industrial activities on the environment and to decontaminate the polluted areas. Soils have an important capacity for the retention of contaminants that avoids the spread of the contaminants, but at the same time, contaminants modify the properties of the soil and cannot be used for agriculture or urban uses. Once the retention capacity of the soil is exceeded, the contaminants are released to the groundwater, generating a major problem. Soil and groundwater contamination with radionuclides is usually associated with the concentration and use of nuclear fuel. Due to the dangers of radioactivity, the decontamination of soils and groundwater with radionuclides is a priority.

Since 1994, much effort has been devoted to the research and development of innovative technologies for the remediation of soil and groundwater (USEPA, 2006). The first approach to soil treatment sites was "dig and dump" followed by "dig and incinerate" and "dig and wash." For the remediation of groundwater the "pump and treat" treatment method was the most common. However, the interest shifted from *ex situ* remediation to *in situ* remediation technologies and several techniques were

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developed and tested at laboratory and field scale. Vapor extraction, soil flushing, permeable reactive barriers, bioremediation, and electrokinetic remediation are just a few of the recent technologies tested for soil and groundwater polluted with both heavy metals and organic pollutants. As there was neither much knowledge about nor any experience with decontamination of soil, researchers, technicians, and politicians were rather optimistic in the beginning. Despite the good results obtained at bench-scale tests, the performance of the remediating technologies at field scale had poor removal results, long treatment times, and high costs. It reveals the difficulties of the implementation of the techniques to the field and the importance of the nature of the pollutants, the geochemistry of soils, and geotechnical properties of the soils (grain size, permeability, etc.) in the success of the remediation technology.

Considering the physico-chemical characteristics of radionuclides, only a few technologies can be applied for their successful removal *in situ* from soil and groundwater (Elless & Lee, 2002). Those technologies comprise electrokinetic remediation, *in situ* soil flushing, vitrification, solidification, and stabilization and some combined or coupled technologies that may include two or more technologies with the objective of generating a synergistic effect; thus the coupled technology results in better remediation than the individual techniques alone. The aim of this chapter is to review the information available for the removal of radionuclides as contaminants in soils and groundwater with *in situ* physico-chemical technologies.

8.2 *In situ* soil flushing

In situ soil flushing is a technology for the cleaning of contaminants from soil by pumping water into the subsoil (Roote, 1997). The flow of water into the subsoil forces the transport of the contaminants to wells where the mixture of water and contaminants is pumped out and treated. In the treatment process, the contaminants can be separated from water, so it can be reused in soil flushing (Figure 8.1). The effectiveness of the process relies on several factors: soil permeability, stratification of soil, and contaminant solubility.

The removal of the contaminants in soil flushing directly depends on the solubility of the contaminants. In aged contaminated sites, the fraction of the contaminants with high solubility in water tends to be very low, because those contaminants with high solubility are expected to have been dispersed in groundwater. One exception can be found in arid environments, where the lack of water in the environment permits the retention in the subsoil of contaminants with high solubility in water. When the concentration of water increases in soil, by natural or artificial means, those contaminants are mobilized, spreading the contamination to the neighboring areas. In general, the limitation of the technology is related to the solubility of contaminants in water. If that solubility is not enough for a feasible removal of contaminants in soil flushing, the processing fluid can be changed to a combination of cosolvents or other enhancing chemicals that can improve the solubility of the contaminants. Thus, acid solutions can be used to improve the solubility of heavy metals, because most heavy metals form soluble cations in acidic media. An acid solution can be used for

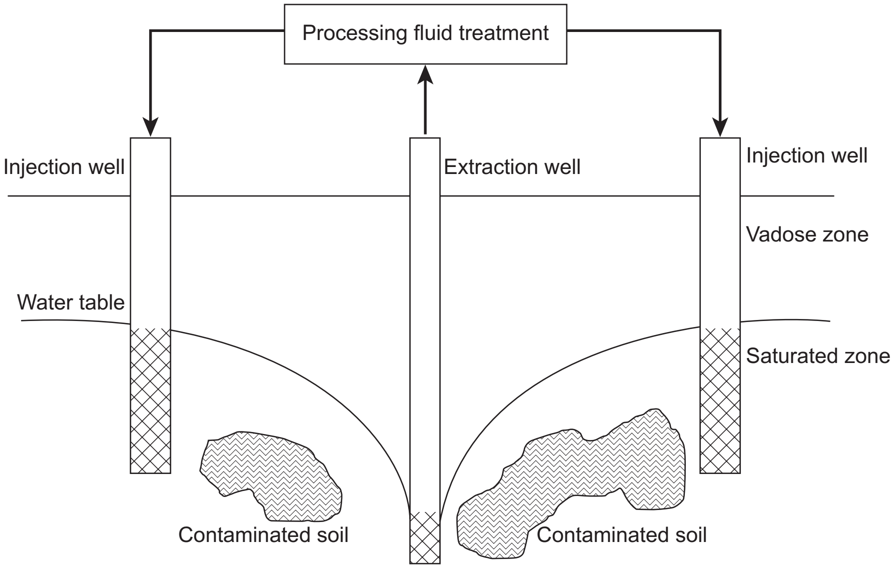


Figure 8.1 *In situ* soil flushing.

the *in situ* flushing of soils contaminated with heavy metals. However, other metals like chromium (IV) are also stable in solution in alkaline pH, so an alkali solution can be used as processing fluid. The addition of chelating agents may be useful for the extraction of many heavy metals because the chelating agent favors the extraction of the metal from soil and keeps the metal in solution, forming stable complexes or chelates in a wide range of pH. Organic acids, e.g., EDTA, citric acid, oxalic acid, are widely used for complexing and removal of heavy metals from soils. Cosolvents can be used to improve the solubility of hydrophobic compounds in water. Cosolvents are usually alcohols, ethanol or methanol, or other organic solvents miscible with water. Hydrophobic organics are much more soluble in the mixture of water and the organic solvent, than in water alone. Thus, the soil flushing can be effectively used for the removal of organics such as hydrocarbons, organochlorides, and other hydrophobic compounds. Similarly, detergents and other surfactants can be used in enhancing the removal of organics from soil by *in situ* flushing, since they enhance the solubility of hydrophobic compounds forming micelles, an organized structure of surfactant molecules with the hydrophilic part in contact with water and the hydrophobic end oriented to the inner part of the micelle, creating the proper environment for the solubilization of hydrophobic organics.

The selection of any chemical in the processing fluid for *in situ* soil flushing must be done considering the efficiency in the contaminant removal and the possible negative effects on the environment. In general, only harmless chemicals or biodegradable compounds should be used. After the soil flushing with a processing fluid containing chemicals, the interstitial fluid in the soil will show the same composition as the processing fluid. In order to remove the residual chemicals in soils, the flushing will process with only water to remove them. It is supposed that the removal of those additives will be effective with water because they are water soluble. However, a significant amount of the additives may remain in the soil adsorbed to the soil particles, or in low permeability layers. That is why it is very important to avoid any enhancing chemicals that may pose a threat for the environment and living organisms in the soil. Furthermore, regulations limit the addition of harmful substances to soil. This environmental risk and the second flushing with water can be avoided if only harmless chemicals are used. Biodegradable organic compounds are preferred; moreover, the residual concentrations of those organics after *in situ* flushing will enhance the microbial activity into the subsoil, favoring the biodegradation of biodegradable organic contaminants.

The second factor that clearly affects the efficiency of *in situ* soil flushing is the permeability of soil. In general, more permeable soils can effectively be treated by soil flushing, and the efficiency of the process dramatically decreases in low permeability soils. A hydraulic gradient is not effective in forcing the flux of water in low permeability soils, so the processing fluid tends to flow through those layers of soils with higher permeability, resulting in uneven remediation of the soil. High removal of contaminants will be found in permeable layers whereas negligible removal of contaminants will be observed in low permeability layers. The hydraulic gradient may also create fractures in the subsoil forming by-pass canals. The processing fluid will flow through those canals with no contact with the soil, resulting in very low contaminant removal.

The processing fluid is recovered in a well, pumping out a mixture of groundwater and the processing fluid with the contaminants. The distribution of the injection well and the extraction well must be designed to ensure the recovery of all the processing fluid with the mobilized contaminants. The pump-out in the extraction well must ensure a significant depression of the water table to ensure that the groundwater and the processing fluid are completely recovered in the extraction well, avoiding any dispersion of the contaminants, which is the major risk in *in situ* remedial technologies.

Several studies of remediation by soil flushing of contaminated sites with uranium and other radionuclides are reported in the literature. The chemical behavior of uranium from a mill tailing site and the contamination of groundwater were studied by Abdelouas, Lutze, and Nuttall (1998). The geochemical nature of the subsoil affects the absorption/desorption and the possible complexation of uranium, and therefore its transportation in the subsoil and the contamination of groundwater from the mill tailing. The authors concluded that the extracting solution to mobilize uranium must be selected considering the geochemistry of the subsoil. Serne, Cantrell, Kutnyakov, and Lindenmeier (2002) demonstrated that radionuclides form strong complexes with the organic complexing agents (EDTA, etc.) and the metal–ligand complexes exhibit reduced adsorption to soils, thus favoring their mobility and extractability from soils. Kantar and Honeyman (2006) tested the efficiency of citric acid as an extracting solution for soil contaminated with uranium in column tests (flushing). The results of soil washing and flushing experiments indicate that citric acid is highly effective in removing uranium, and that the extraction efficiency increases with increasing citric acid concentration, especially under slightly acidic to alkaline conditions in systems containing sand coated with secondary minerals (e.g., Fe). The enhanced U(VI) desorption in the presence of citrate may be explained through several processes, including the complexation of U(VI) with citrate and the extraction of secondary coatings (e.g., Fe), which result in the liberation of Fe–citrate complexes into solution. Wu et al. (2006) studied the biotransformation of U(VI) to the sparingly soluble U(IV) *in situ*. Although the objective of this study is the biotransformation of uranium, the authors used the contaminated groundwater in a flushing system to remove from the subsoil the soluble components that inhibit the biotransformation of uranium (aluminum, calcium, and nitrate) and increased the pH of groundwater to 5.5–6.0 in order to achieve the appropriate conditions for the natural bioreduction of uranium.

8.3 Vitrification

Vitrification is a remediation technology based on the transformation of contaminated soil into a glass-like material (USEPA, 2006). A set of electrodes is installed vertically in the soil, and an electric current through the electrodes produces enough heat to melt the soil. Soil starts melting on the surface of the ground, and then, with increasing temperature, it melts the soil deeper and deeper. The melting of soil also produces a reduction in its volume; as a result the electrodes move down into the soil, extending the depth of treatment (Figure 8.2). When all the mass of contaminated soil is treated (melted), the electric current is shut down and the temperature decreases; the soil solidifies forming a glass-like material containing the contaminants inside. This material is inert, so it does not interact with the environment and does not leach metals or other inorganic contaminants, which are trapped inside the glass structure. Even the breakdown of the glass-like material does not result in the release of the inorganic contaminants. The fused soil forming the glass-like material occupies less volume than the original soil, so the fused material remains below the ground surface. The hole can be filled with clean soil. Alternatively, the glass-like material can be removed from the subsoil and transported to a dumping area for inert materials. In the case of radionuclides, it is preferred that glass-like material is moved to a proper storage facility

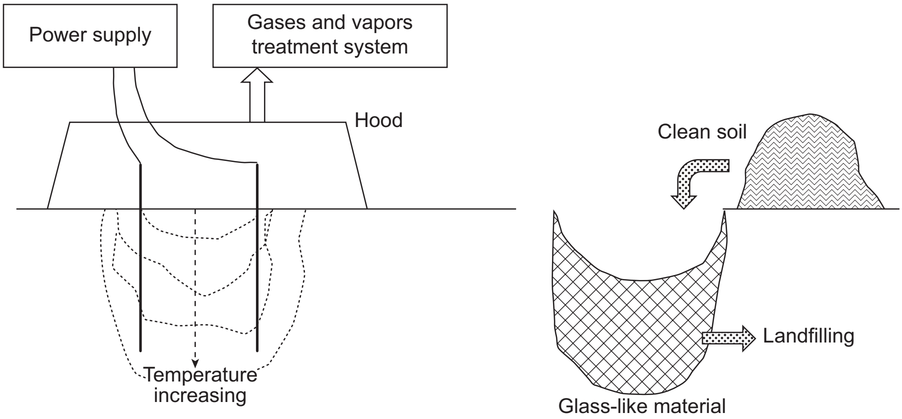


Figure 8.2 Vitrification of contaminated soil.

if the radioactivity is higher than the natural levels in the contaminated area. The contaminated site can be restored with clean soil and compost from organic wastes.

Vitrification technology can also be applied in contaminated soils with organics and mixtures of organic and inorganic contaminants. During the vitrification of soil, the electric current must be intense enough to reach more than 1000 °C to be able to melt the inorganic constituents of soil. At that temperature, any organic contaminant will be burnt into carbon dioxide and water. However, many organics can be volatilized before reaching that temperature. To avoid the release of organic contaminants to the atmosphere, the electrode system must be covered by a hood to collect all the vapors and gases released from soil. Those gases contain contaminants that must be treated. The gases are first cooled down, condensing water and the organics with higher boiling points. Volatile organics that do not condensate can be adsorbed in an activated carbon filter.

Overall, vitrification is a remediation technology that can be applied to polluted sites with both organic and inorganic contaminants. The main advantages are the application *in situ*, the short treatment time and the good stabilization of inorganic contaminants, and the removal of organics. Unfortunately, the melting of soil requires high power consumption. So, this technique should be applied in highly polluted soils.

Spalding (2001) proposed the fixation of radionuclides, ^{85}Sr, ^{57}Co, ^{134}Cs, and U, in soil and minerals by heating up to 1000 °C. The heating process clearly reduced the mobility of the radionuclides. The fixation to the solid matrix was evaluated by sequential extraction and the results were consistent with rapid high temperature ionic diffusion from the initially contaminated surfaces into the mineral matrices. The diffusion out of mineral particles at ambient temperature would be so low that radionuclides are considered sequestered for further potential environmental mobilization. Tzeng, Kuo, Huang, Lin, and Yu (1998) proposed plasma incineration for the treatment of radioactive waste, forming glass-like material that can finally be sent to a landfill. Ojovan and Lee (2003) reviewed the self-sustaining vitrification processes, that is, the energy released during exothermic chemical reactions in a mixture of waste and powder metal fuel to form a glass-like material without requiring an external power supply. Several wastes can be successfully immobilized in durable glass-like waste forms, including radionuclides. This vitrification technology does not require complex equipment or energy sources, so it is useful for the treatment of relatively small amounts of problematic wastes. The glass-like material is considered to be very stable and the risk of mobilization of radionuclides is low; several studies carried out long-term testing of radionuclide leaching from vitrified nuclear waste. The results will help in determining the risk of future radionuclide mobilization (Barinov, Ojovan, & Ojovan, 1996). The use of geological barriers will help in the future to reduce the risk of radionuclide mobilization and dispersion (Mallants, Marivoet, & Sillen, 2001).

8.4 Solidification and stabilization

Remediation of contaminated soils by solidification and stabilization refers to a group of techniques that tend to immobilize contaminants in the original location instead of degrading, destroying, or removing them. Thus, contaminants are confined and immobilized, reducing the leaching to a minimum, sometimes even zero, below the safe level for living organisms in the area. Although the contaminants remain in the same place, they do not show their negative effects in the environment because they are kept in the solid phase, with no or minimum dissolution in rain, surface water, or groundwater. In other words, the contaminants are not bioavailable (USEPA, 2006).

Solidification consists in trapping of contaminants in a solid block of material. This material is less permeable to water than the original contaminated soil. Thus, the solid block acts as a solid barrier for the contaminants. Stabilization implies a chemical transformation of the contaminants that pass from a soluble or bioavailable species to a nonsoluble and nonbioavailable species. For example, chromium (VI) forms two chemical species, chromate and dichromate, which are in equilibrium and the predominant species depends on the pH. Both species are soluble and easily bioavailable in water to plants, animals, and people. The stabilization of chromium (VI) implies the reduction to chromium (III) and its precipitation, increasing the pH and/or adding the appropriate anion to form a nonsoluble salt, e.g., carbonate. Solidification implies the use of binding materials to mix with the soil or waste to be treated. The binding materials stick together the particles of soil, reducing their mobility and the mobility of the contaminants themselves. Common binding materials are cement, pozzolan binders, asphalt, and clay. Stabilization also requires the addition of external chemical agents, but in this case, they will produce a chemical reaction to reduce the mobility and bioavailability of the contaminants. A common stabilization agent is calcium carbonate, which forms insoluble salts with most of the metals.

The application of solidification and stabilization at field scales implies the mixing of the contaminated soil with the chemical reagents and/or binder. If the contaminated zone is shallow, the soil can be excavated and mixed *in situ* with the additives. After the mixing operation, the soil can be leveled out and covered with a layer of clean soil to avoid direct contact with the atmosphere and the atmospheric agents. Alternatively, the treated soil can be transported to a landfill. In deeper contaminated soils, when the mixing cannot be done on the surface, multiple holes are drilled in the soil to mix the additives for stabilization and solidification. Then, the soil is usually covered with a layer of clean soil to protect the treated materials from the atmosphere.

Solidification and stabilization are commonly used combined for a better immobilization of the contaminants, assuring no leachability for a long time. This technology is appropriate for the treatment of soils with metals and radionuclides, although it was also reported in the immobilization of organochlorides and pesticides. The advantages of these technologies rely on the low cost, it is relatively simple to apply, and the treatment time is short compared to other technologies; however, the treatment time is affected by the depth of the soil to be treated and the characteristics of soil.

Falciglia, Cannata, Pacec, Romano, and Vagliasindi (2013) suggest that cement-based stabilization/solidification could be an optimal choice for treating radionuclide polluted soils due to the possibility of shielding the γ-radiation emitted by contaminant. Falciglia, Cannata, Romano, and Vagliasindi (2014) tested different binder mixtures of Portland cement and barite aggregates at different soil-binder ratios for the remediation of sandy soil contaminated with thorium oxide. Barite aggregates mixed with cement give a significant containment of the γ-radiation and an excellent reduction of contaminant leaching, but it slightly reduces the performance in terms of mechanical resistance. De Freitas and Al-Tabbaa (2013) proposed the use of low pH cements as an environmentally more suitable solution for the immobilization of radionuclides. However, as reported in the literature, the iron phosphate glass seems to be a very appropriate material for the immobilization of spent nuclear fuel (Mesko & Day, 1999). The chemical durability of the iron phosphate waste forms is as good as, and in many cases up to 15 times better than, the approved reference material (ARM-1) borosilicate glass. Recently, alternative materials for immobilizing radionuclide have been tested. Molten salt waste with radionuclides is difficult to treat with the conventional solidification/stabilization. Park, Kim, Cho, Eun, and Lee (2008) proposed the stabilization of the radionuclides by the addition of an inorganic composite, SAP (SiO_2–Al_2O_3–P_2O_5), that can be applied at the temperature of the molten salt, forming a stable material with leaching rates as low as 10^{-3} g/m^2 day for Cs as Sr.

8.5 Electrokinetic remediation

Electrokinetic remediation is a technology extensively investigated since 1994 that has shown some success in the remediation of soils, sediments, and sludges contaminated with both inorganic and organic contaminants (Reddy & Cameselle, 2009, p. 760). Electrokinetic remediation is also known in the literature as electroreclamation, electrokinetics, and electroremediation. The principle of electrokinetic remediation relies on the application of a low-intensity direct current through the soil between a couple of electrodes (cathode and anode). The electric field mobilizes charged species, causing ions and water to move toward the electrodes trough the soil. These phenomena have been well established since their discovery by Reuss in 1809 (Mattson & Lindgren, 1994). In the past, electrokinetics has been applied in a variety of engineering processes; mostly, these applications made use of the electroosmotic transport of the liquid phase. First applications included dewatering and consolidation of soils (Casagrande, 1983) and dewatering of sewage sludge, increasing the recovery rates of oil fields (Ricart, Cameselle, Lucas, & Lema, 1999). Segall, O'Bannon, and Matthias (1980) reported that electrokinetics may be applied to hazardous waste remediation from dewatering sludges rich in heavy metals, but it was at the end of the 1980s when a great interest arose for the environmental application of electrokinetics for the treatment of contaminated soils.

This technique can be performed *in situ* (Figure 8.3) and results in effective treatment of low hydraulic permeability soils, which are difficult to treat with other techniques. The advantages include low power consumption, close control over the direction of water and dissolved contaminants, and the confinement of pollutants in the electrode wells that makes the subsequent treatment of the removed pollutants easier (Page & Page, 2002).

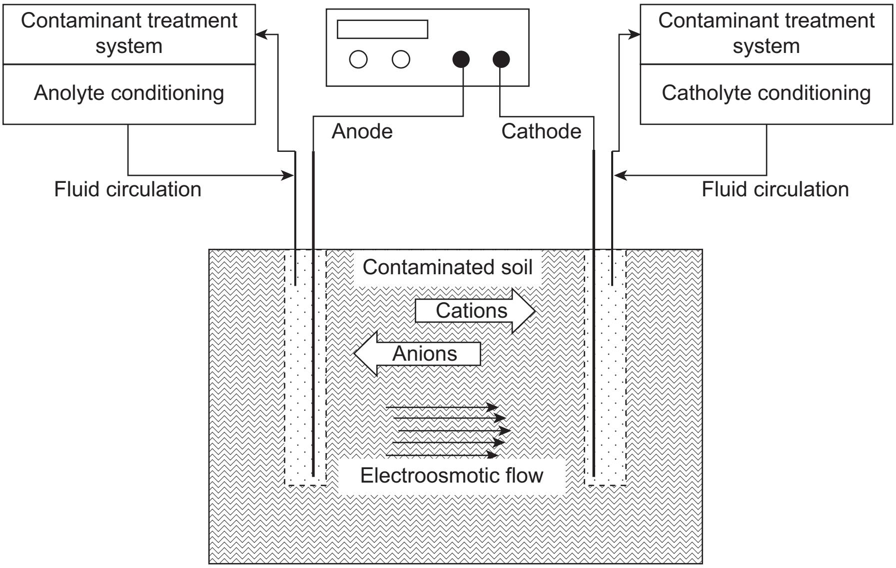


Figure 8.3 Application of the electrokinetic remediation in a contaminated site.

8.5.1 Principles of electrokinetic remediation

The application of an electric field to a porous material, such as soils, sediments, and sludges, provokes the transportation of contaminants and water through the porous matrix toward the electrodes: anode and cathode. Four transport mechanisms can be identified which are defined as follows (Probstein, 1994).

Electromigration: It is the movement of ions due to the electric field toward the electrode of opposite charge (Figure 8.4). The electromigration is responsible for the transportation of free ions such as H^+, OH^-, cations (heavy metals, ammonium, etc.) and anions (chloride, cyanide, fluoride, nitrate, etc.) and also ionizable organic compounds. The migration rate mainly depends not only on the volume of the ion and its charge but also on the interactions with the surface of the solid particles of soil that can greatly retard the movement.

Electromigration is the responsible mechanism for the transportation of heavy metals (Pb^{2+}, Cu^{2+}, Cd^{2+}, etc.), inorganic anions (F^-, As, CN^-, NO_3^-, etc.), and some ionic or ionizable organic molecules (acetate, oxalate, etc.) during the electrokinetic treatment of a contaminated soil. The actual contribution of electromigration to the transportation of a specific ion depends on the soil conductivity, soil porosity, pH, voltage gradient, the ion concentration, and the presence of other ions that may compete in the transport of electric charge.

The electromigration rate (v_{em}) of a specific ion is proportional to its electric charge and the voltage gradient (Eqn (8.1)).

$$v_{em} = u_i z_i n \tau F E \tag{8.1}$$

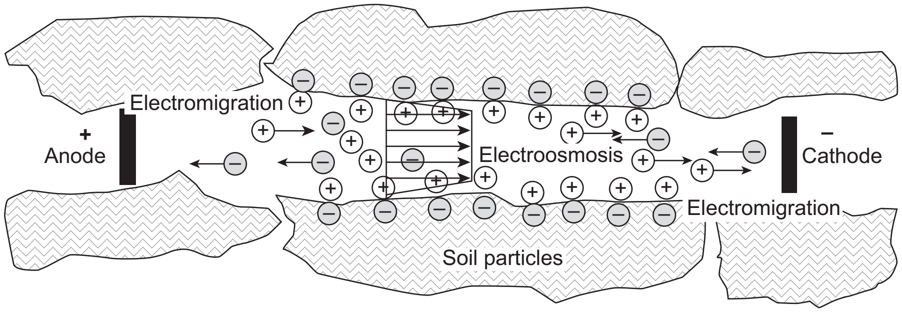


Figure 8.4 Transport mechanisms in electrokinetic remediation.

where

u_i is the ionic mobility ($m^2/V\,s$)
z_i is the ion electric charge
n is the porosity
t is the tortuosity
F is Faraday's constant (96,487 °C/mol e^-)
E is the strength of electric field (V/m).

Ionic mobility is defined as the rate of an ionic species under the effect of an electric field intensity, which is 1, and can be estimated with the equation of Nernst–Einstein–Townsend (Eqn (8.2)).

$$u_i = \frac{D_i\,|z_i|\,F}{R\,T} \tag{8.2}$$

where

D_i is the coefficient of molecular diffusion
R is the ideal gas constant (8.314 J/K mol)
T is the absolute temperature (K).

However, the ionic rate is affected by the characteristics of the medium. In aqueous solution, Eqn (8.2) can be used to predict the movement of the ion, but in a porous medium such as a soil, the ionic mobility of an ion is affected by the porosity and the tortuosity of the medium. So, an effective ionic mobility is defined for the migration in a porous medium that considers the ion charge, its molecular diffusion coefficient, and the porosity and tortuosity of the medium (Eqn (8.3)).

$$u_i^* = n\,\tau\,u_i \tag{8.3}$$

Table 8.1 contains the ionic mobility for selected ionic species. As observed in Table 8.1, the H^+ ion shows the highest mobility, which is almost double that of the mobility of the hydroxyl ion. Other ions show lower values for the ionic mobility. Thus, the H^+ ion responsible for the acidification of the medium will be transported

Table 8.1 **Ionic mobility and effective ionic mobility for a porous medium with a porosity of 0.60 and a tortuosity of 0.35**

	u_i (×10^8) (m^2/V s)	u_i^* (×10^8) (m^2/V s)		u_i (×10^8) (m^2/V s)	u_i^* (×10^8) (m^2/V s)
H^+	34.90–36.25	7.47	OH^-	19.76–20.64	4.24
Li^+	3.87–4.59	0.89	F^-	3.85–5.54	0.99
Na^+	5.01–5.19	1.07	Cl^-	6.42–7.91	1.50
K^+	7.20–7.62	1.56	Br^-	6.85–8.09	1.57
Rb^+	7.43–7.92	1.61	I^-	6.27–7.68	1.46
Cs^+	7.36–7.68	1.58	CO_3^{2-}	7.46	1.57
NH_4^+	7.37	1.55	NO_3^-	7.14–7.40	1.53
Ag^+	6.19	1.30	PO_4^{3-}	7.15	1.50
Ba^{2+}	6.37	1.34	SO_4^{2-}	4.13–8.29	1.30
Ca^{2+}	5.95–6.17	1.27	ClO_4^-	6.80	1.43
Cd^{2+}	5.40–7.36	1.34			
Mn^{2+}	5.31	1.12			
Ni^{2+}	5.41	1.14			
Cu^{2+}	5.40	1.13			
Zn^{2+}	5.35–5.47	1.14			
Pb^{2+}	5.60–7.00	1.32			
Fe^{2+}	5.35	1.12			
Fe^{3+}	6.80	1.43			
Cr^{3+}	6.94	1.46			
Al^{3+}	6.30	1.32			
La^{3+}	6.95	1.46			

Acar (1993).

very fast in electrokinetics and it will play an important role during the remediation of soils.

Electroosmosis: It is the net flux of water induced by the electric field in the porous structure of soil. In general, soil particles are charged. Since the matter is globally neutral, a series of counterions neutralize that charge. The counterions are concentrated in the diffuse layer of the electrical double layer (Figure 8.5). Under the effect of an electric field, the excess of ions in the diffuse layer close to the surface of the soil particle migrates in a plane parallel to the soil surface in the direction of the opposite electrode. Those ions are in aqueous solution, hence, solvated. In their movement, the ions drag the solvated water molecules. This movement is transmitted to the neighboring molecules due to dipole–dipole interactions, forming a flat rate profile of water flowing through the pore (Figure 8.6). In general, soil particles are electronegative, so the counterions will be positive; hence, the direction of the electroosmotic will flow toward the cathode. Electroosmosis is the dominant transport mechanism for inorganic and organic contaminants in solution or emulsified in the interstitial fluid.

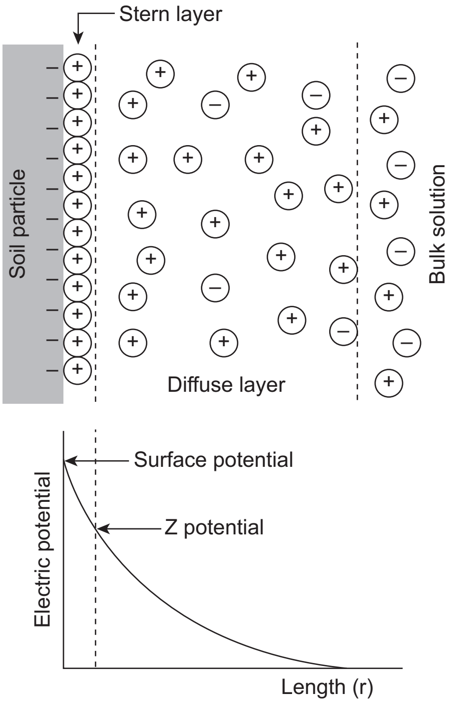


Figure 8.5 Electrical double layer.

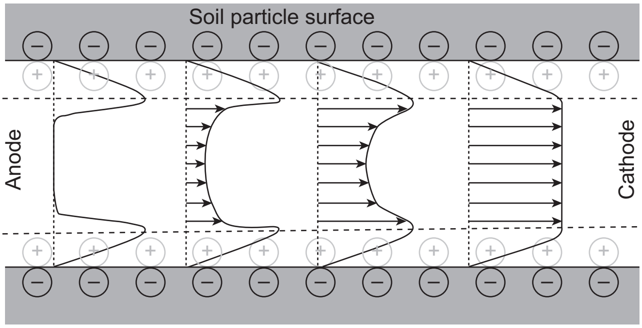


Figure 8.6 Development of the electroosmotic flow in a soil pore.

The electroosmotic flow is affected by the superficial characteristics of the soil particles, especially the surface charge, but the pH value, the ion nature and concentration, and the total ionic strength of the interstitial fluid are also very important. The pH plays a decisive role in the development of the electroosmotic flux as the pH can largely modify the charge in the surface of the soil particles. In electronegative soil particles, an acidic pH may result in the neutralization of the charge of the soil particles and even in the change to soil particles positively charged; as a result, the electroosmotic flow will reverse to the anode. The electroosmotic flow is an important factor in environmental applications of electrokinetics, since the flux of water that flows through the treated soil transports out of the soils any compound (ionic or not ionic) in solution in the interstitial fluid.

The electroosmotic flow rate (q_{eo}) can be expressed according to the Helmholtz–Smoluchowski theory as Eqn (8.4).

$$q_{eo} = nA\frac{D\zeta}{\eta}E_z = k_{eo}AE_z \tag{8.4}$$

where

n is the porosity
A is the area of the perpendicular surface to the direction of the flow
D is the dielectric constant of the fluid
ζ is the zeta potential (Figure 8.5)
η is the viscosity of the fluid
E_z is the voltage gradient in the direction of the flow (z in this case)
k_{eo} is the coefficient of electroosmotic permeability.

The comparison of the electroosmotic flow with the hydraulic flow will help to understand the importance of the electroosmotic flow for the removal of contaminants in low permeability soils. The hydraulic flow only reaches practical values in permeable soils, for instance, in sandy soils, with hydraulic conductivity higher than 10^{-3} cm/s However, the hydraulic flow in clayey soils is negligible due to their low hydraulic conductivity (between 10^{-6} and 10^{-9} cm/s). In fine sand, the electroosmotic permeability coefficient is $k_{eo} = 4.1 \times 10^{-5}$ V/s and hydraulic conductivity is $k_h = 10^{-4}$ cm/s. Those values are relatively proximate and comparable, so the electroosmotic flow will not result in a significant improvement in the flow of water through the soil. However, in the permeability soils, for instance, in kaolinite clay, electroosmotic permeability is $k_{eo} = 5.7 \times 10^{-5}$ V/s and hydraulic conductivity is $k_h = 10^{-7}$ cm/s. In low permeability soils, the electroosmotic flow is much more efficient than a hydraulic gradient; in fact, the hydraulic gradient to reach the same flow as electroosmosis will be impracticable.

Electrophoresis: It is the movement of colloidal particles in the electric field. In the case of low permeability soils where the average pore size is too small, electrophoresis and the movement of colloidal particles are not considered to be significant.

Diffusion: It is the migration of substances due to a concentration gradient. Since the purpose of electrokinetics is the transport and the removal of some components out of the soil, the induced concentration gradients play against the electrokinetic removal. A common practice in electrokinetics is the addition of chemical agents to the electrode wells to enhance the extractability and transportation of contaminants out of the soil. The concentration gradient between the soil and the electrode solutions will help in part in the introduction of the facilitating agents into the soil.

The diffusion flow is defined by Fick's equation:

$$J = D_{\mathrm{i}}\frac{\mathrm{d}C}{\mathrm{d}z} \tag{8.5}$$

where

J is the mass flow (kg/m^2 s)
D_i is the molecular diffusion coefficient (m/s)
C is the concentration (kg/m^3)
z is the length (m).

In general, the values of ionic mobility from Table 8.1 show that the ionic mobility of an ionic species is much higher than the diffusion coefficient, so the diffusion is usually negligible during the electrokinetic treatment.

Inorganic contaminants such as heavy metals, other metallic species, and inorganic anions (nitrates, fluorides, cyanides, phosphates, etc.) are usually found in their ionic form. Electromigration will be the predominant mechanism for their removal from soil. Electroosmosis will contribute partially to their removal as long as the electromigration and electroosmosis direction is the same. In soluble organic contaminants, which do not form ionic species, electromigration will be useless and their transportation will be due only to electroosmosis. In general, the relative contribution of electromigration and electroosmosis to the transportation of contaminants will depend on soil type, moisture content, chemical nature of contaminants, and their concentration. The mass transport of ionic species is considered to be 10–300 times higher by electromigration than electroosmosis. In low permeability soils, electroosmosis is much more efficient than a hydraulic gradient; however, the electrochemical changes in the soil pores along the electrokinetic treatment tend to decrease the zeta potential and therefore the electroosmotic flow.

The electroremediation process is also governed in part by the electrode reactions that are inherent to the process. The main reaction in extent and influence is the electrolysis of water. The oxidation of water at the anode generates H$^+$ ions and releases molecular oxygen. The chemical reduction of water takes place on the cathode forming OH$^-$ ions and releasing molecular hydrogen to the atmosphere (Eqns (8.6) and (8.7)).

$$2H_2O - 4\,e^- \rightarrow O_2 + 4\,H^+ \qquad E_0 = -1.229 \text{ (anode)} \tag{8.6}$$

$$2H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \quad E_0 = -0.828 \text{ (cathode)} \tag{8.7}$$

The production of H$^+$ combined with the electromigration effect of the electric field provokes the formation of an acid front from the anode toward the cathode. The H$^+$ ions electrogenerated in the anode migrate, acidifying the soil and favoring metallic precipitate solution and pollutant desorption from the surface of the soil particles. Once these contaminants are in solution in the interstitial fluid, they can migrate under the effect of the electric field, electromigration, or can be transported by electroosmosis. Generally, the acid front, inherent to the electrokinetic treatment, enhances the dissolution of pollutants and improves the effectiveness of the process. At the same time, the hydroxyl ions electrogenerated in the cathode form an alkaline front that increases the pH of the soil. High pH values tend to retain the metallic ions as hydroxide precipitates, clogging the pores and decreasing the efficiency of the electrokinetic treatment. The alkaline front moves opposite to the acid front and they meet in the middle of the soil in a point closer to the cathode due to the high mobility of the H^+ ions compared to the OH^- (the ionic mobility in an electric field of the hydrogen ion is almost double that of the ionic mobility of the hydroxyl ion). When both fronts meet, hydrogen and hydroxyl ions are neutralized, forming water. At this moment, the soil is divided in to two zones, with acid and basic pH, with a sharp pH jump in between.

In order to improve the electrokinetic treatment and avoid the premature precipitation of metal ions due to the alkaline front, the OH^- electrogenerated at the cathode can be suppressed by controlled addition of an acid. In this case, the anion of the acid will be transported into the soil instead of the hydroxyl ions, so the acid must be carefully selected to avoid any undesirable interaction with the soil or the contaminants into the soil. For instance, the anion of the acid must not form an insoluble salt with the metal to be removed.

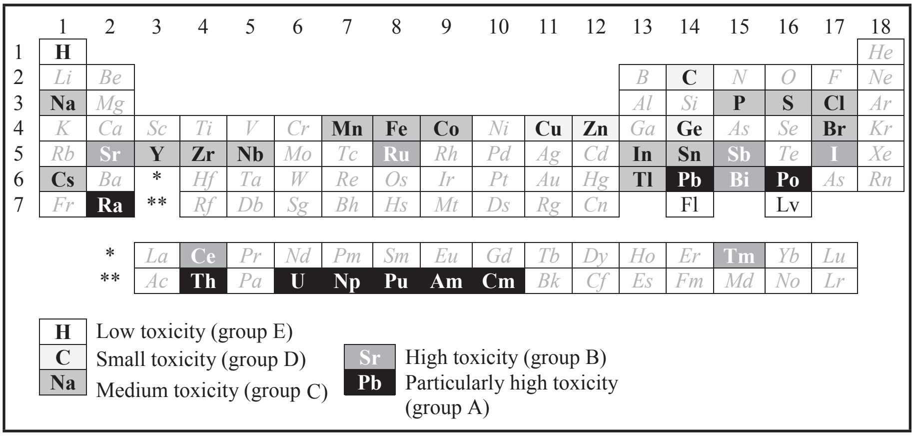
Some pollutants can form several soluble chemical species under alkaline conditions, so that the alkaline environment does not always result in low efficiency. For instance, copper can be removed under alkaline solutions with the addition of ammonia, since Cu^{2+} forms a stable complex with NH_3. EDTA also forms stable complexes in alkaline pH with many heavy metals such as Pb. In these cases, the alkaline front is key for the success of the treatment.

Other reactions take place during the electrokinetic remediation and also affect decisively the effectiveness of the process. The reactions of absorption/desorption affect the solubility of the pollutants and may retard their movement through the soil due to the retention on the surface of the soil particles. The reactions of precipitation affect the concentration in solution of the contaminants. Those reactions are induced by the presence of counterions (ions that forms an insoluble salt with the pollutant) and by the pH value as noted previously. Finally, the redox reactions affect the chemical speciation of the pollutants. The redox reactions can take place induced by the electric field into the soil among several soil constituents, or more frequently on the electrodes. In the anode the species are oxidized and in the cathode they are reduced. Thus, in the electrokinetic remediation of metal polluted soil, the heavy metal ions that reach the cathode can be electrodeposited and recovered as native metal.

8.5.2 Removal of radionuclides from contaminated soils

The origin of radioactive contamination is associated with atomic power plants, the production of nuclear fuel for nuclear reactors, and the processing of nuclear wastes. Other minor sources of radioactive contamination are associated with the management of some industrial and hospitality wastes that contain radioactive materials. Nuclear tests carried out in the past are another important source of radionuclide contamination in soils. The principal radioactive nuclides found in contaminated sites are ^{60}Co, ^{90}Sr, ^{90}Y, ^{106}Ru, ^{137}Cs, ^{144}Ce, ^{147}Pm, $^{238, 239, 240}Pu$, ^{226}Ra, and other radionuclides in minor concentration (Korolev, 2009). These radionuclides can be classified according to their toxicity in five groups as shown in Table 8.2. About 95% of the radionuclides

Table 8.2 Selected elements forming radionuclides classified by their toxicity



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H**																	*He*
2	*Li*	*Be*											*B*	**C**	*N*	*O*	*F*	*Ne*
3	**Na**	*Mg*											*Al*	*Si*	**P**	**S**	**Cl**	*Ar*
4	*K*	*Ca*	*Sc*	*Ti*	*V*	*Cr*	**Mn**	**Fe**	**Co**	*Ni*	**Cu**	**Zn**	*Ga*	**Ge**	*As*	*Se*	**Br**	*Kr*
5	*Rb*	**Sr**	**Y**	**Zr**	**Nb**	*Mo*	*Tc*	**Ru**	*Rh*	*Pd*	*Ag*	*Cd*	**In**	**Sn**	**Sb**	*Te*	**I**	*Xe*
6	**Cs**	*Ba*	*	*Hf*	*Ta*	*W*	*Re*	*Os*	*Ir*	*Pt*	*Au*	*Hg*	**Tl**	**Pb**	**Bi**	**Po**	*As*	*Rn*
7	*Fr*	**Ra**	**	*Rf*	*Db*	*Sg*	*Bh*	*Hs*	*Mt*	*Ds*	*Rg*	*Cn*		Fl		Lv		

*	*La*	**Ce**	*Pr*	*Nd*	*Pm*	*Sm*	*Eu*	*Gd*	*Tb*	*Dy*	*Ho*	*Er*	**Tm**	*Yb*	*Lu*
**	*Ac*	**Th**	*Pa*	**U**	**Np**	**Pu**	**Am**	**Cm**	*Bk*	*Cf*	*Es*	*Fm*	*Md*	*No*	*Lr*

H Low toxicity (group E)
C Small toxicity (group D)
Na Medium toxicity (group C)
Sr High toxicity (group B)
Pb Particularly high toxicity (group A)

Korolev (2009).

are found in contaminated sites in the upper soil layer due to the adsorption to soil particles and organic matter. Radionuclides can be found in soil, forming different chemical species and associated with the soil materials. The actual speciation or fractionation of radionuclides in a contaminated site depends on the soil composition. In general, radionuclides can be found in exchangeable form, 8–30%; in water soluble form, 2–10%; but most of the radionuclides are found bound to soil components, about 60–80%, which retard their transportation and dispersion in the environment (Korolev, 2009).

The electrokinetic technology has been tested as an efficient method for removing radioactive nuclides from contaminated soils (Korolev, 2009). The electrokinetic technology was applied to different clay soils, from sandy loam to clay, to test the ability of electrokinetics to remove several radionuclides: ^{90}Sr, ^{88}Sr, ^{137}Cs, ^{133}Cs, etc. ^{90}Sr and ^{137}Cs are the most toxic and dangerous for living organisms with a half-life of 28 and 30 years, respectively. These radionuclides were found in contaminated sites as free elements (dissolved) and adsorbed to soil particles. The electrokinetic technology was able to transport the ^{88}Sr isotope toward the cathode. The soil close to the anode shows the lowest concentrations of strontium that migrated toward the cathode, accumulating in the soil close to the cathode. At the end of the test, the free (dissolved) strontium was similar along the soil sample, whereas the adsorbed strontium showed an increasing profile along the soil sample. As a conclusion, the electrokinetic technology is able to transport the radionuclides but it is necessary to enhance the extraction and transportation of the radionuclides to achieve a significant removal.

Yu and Neretnieks (1997) tested and modeled the electrokinetic decontamination process to investigate the feasibility of using electrokinetic technology to remove ^{137}Cs and ^{90}Sr from the contaminated soil. The electrokinetic experimental setup consisted of 3-m-long columns with a model soil (bentonite clay) and a voltage gradient of 100V DC by electrodes connected to the soil. The results from the test and the mathematical model have shown that the efficiency of the electrokinetic treatment depends on the sorption and diffusion parameters. The treatment time will increase with increasing radionuclide sorption to the soil particles and with slower diffusion. For the model soil (bentonite clay) flushed with saline water that leads to less sorption, both ^{137}Cs and ^{90}Sr may be cleaned by the electrokinetic process within a few months of treatment.

Frizon, Lorente, and Auzuech (2005) have tested the electrokinetic technology for the removal of radionuclides from a cement-based material. The electrokinetic treatment is applicable to any solid porous materials as long as it contains enough interstitial water for the transportation of ions and electric current. Cs was used as a contaminant in a piece of mortar. The electric field was used first for the uniform contamination of mortar by electrokinetic transport, and in the second part of the work, the electric field was used for the removal of Cs. No electroosmosis was detected, so the transport of Cs was only due to electromigration. Electrokinetic decontamination extracted 96% of the initial Cs contamination after 3 weeks, when the material was initially contaminated with 100 mol/m^3 solution of cesium; 63–90% with the 1 mol/m^3 contaminating solution. At this stage, the results suggest that electrokinetics appears to be an effective method for decontaminating cement-based materials.

Despite the promising results of electrokinetic remediation of solid materials (soils or cement-based materials), the enhancement of the electrokinetic treatment for the effective remediation at large scale seems necessary. Several approaches to enhance the electrokinetic removal of radionuclides are discussed below. They include pH control on anode or cathode chambers, the use of chelating agents, and the combination of electrokinetics with other technologies such as soil flushing or soil washing.

8.5.3 Enhanced electrokinetic removal of radionuclides

The combination of electrokinetic treatment with soil flushing and the addition of chemicals in the anode and/or cathode to control the pH and to enhance the solubilization of the radionuclides result in much better removal of radionuclides from contaminated soils, sediments, and sludges.

The removal of cesium and cobalt from the contaminated soil around the TRIGA reactor in Korea using the electrokinetic technology was tested (Kim, Kim, Lee, Lee, & Kim, 2003). The alkaline environment on the cathode generated due to the electroreduction of water is responsible for the premature precipitation of radionuclides. In order to neutralize the OH$^-$ electrogenerated at the cathode, acetate buffer solution ($CH_3COONa + CH_3COOH$) was injected into the soil sample and acetic acid was periodically injected into the cathode reservoir to ensure a pH below 7. The results showed that ^{137}Cs and ^{60}Co were transported by electromigration rather than electroosmosis during the initial remediation period, and no precipitate was detected in the soil sample. After 10 days of treatment 25% of cesium in the soil was removed, whereas 94% of cobalt was removed.

NPO Radon organization (Moscow, Russia) has developed various methods to manage waste from various nuclear facilities (Perera, 2002; Prozorov, Shcheglov, Nikolaevsky, Shevtsova, & Korneva, 2000). The technologies tested include cementation, bituminization, and vitrification for the treatment of the liquid waste, whereas the solid waste can be treated by compaction and plasma incineration. The electrokinetic technology was also tested as a method for decontamination of solid materials. Electrokinetic treatment was based on ion transport under the effect of a DC electric field that can be used *in situ* in the contaminated sites, usually sites where solid or liquid radioactive waste was dumped. The influence of the different parameters such as voltage gradient, electric current intensity, and energy consumption on the dynamics of ^{137}Cs extraction was studied. Results have demonstrated that electrokinetic remediation is a very promising technology for the removal of radionuclides from loamy soil (Prozorov et al., 2000).

Korolev, Barkhatova, and Shevtsova (2007) applied the electrokinetic technology for the treatment of a loam soil contaminated due to an accidental spill of radioactive liquid waste with a specific ^{137}Cs activity of 80–200 kBq/kg. NPO Radon organization (Moscow, Russia) supplied the samples of contaminated soil. The experimental setup for the electrokinetic tests contains three compartments. One central compartment for the contaminated soil and one compartment at each end filled with a processing fluid, where the main electrodes were immersed. The electrode compartments and the soil compartment were separated by a drainage filter filled with polymer. Stainless steel (cathodes) and platinum-coated titanium (anode) plates were used as electrodes. Due to the limited removal results in the unenhanced electrokinetic tests, several chemicals (NH_4NO_3, KNO_3, water) were added to the anode compartment at a concentration of 1 mol/L, with the objective of improving the extraction and transportation of the radionuclides. The electrogenerated OH^- at the cathode was neutralized by the controlled addition of concentrated nitric acid, to avoid the premature precipitation of radionuclides in the soil close to the cathode. Test results showed that radionuclide ^{137}Cs removed from soil was accumulated in the catholyte along the test duration. The catholyte was removed periodically and substituted for fresh solution in order to avoid limitations in Cs removal due to concentration effects. Removed cesium in the cathode solution was collected. Almost 50% of initial cesium was removed when the facilitating agent in the anode was ammonium nitrate. The use of potassium nitrate resulted in the removal of 30%, and the use of water resulted in the removal of only 5% of the initial cesium. These results clearly confirm the important effect of anolyte and catholyte conditioning in the removal of radionuclides by electrokinetics.

Korolev (2009) designed new tests to increase the efficiency of electrochemical removal of ^{137}Cs by selecting an agent for transforming radioactive nuclides into a more mobile state. Simultaneously, research was aimed at lowering the soil acidity and selecting ecologically safe, deactivation conditions, which could cut down expenses for subsequent neutralization of the acidity, i.e., for complete remediation and restoration of polluted sites. Thus, the efficiency of using nitric and phosphoric acids in the anolyte in the removal of ^{137}Cs from soil was tested. These authors found that the use of a mixed solution of the two acids, 1 mol/L, and their ammonia salts in the anolyte was the most appropriate for the effective removal of Cs from the contaminated soil.

The results of these laboratory experiments demonstrated that ammonium cation is more efficient than potassium cation to desorb Cs from soil. Extraction of ^{137}Cs is 1.6 times more efficient by using ammonium nitrate solutions than using potassium nitrate solutions. The total extraction, in this case, of ammonium nitrate and potassium nitrate was approximately 50% and 30%, respectively, which is 5.4 and 3.3 times higher than without salt application. The highest Cs removal was achieved using as anolyte a mixture of phosphoric acid and ammonium phosphate. These leaching agents can be applied as the most efficient ones for electrokinetic cleaning of soils from radioactive nuclides.

Kharkats (1998) developed a theoretical model for the electrokinetic removal of radionuclides from soils, existing in an immobile form. This method is based on the application of a steady electrical field to a soil specimen placed between two electrodes. The system ensures the effective delivery of chemicals and complexing agents from the electrode chambers to the soil. The radionuclides interact with the complexing agents, forming stable chelates. Charged chelates are preferred in order to be removed by electromigration. The analysis presented shows that the character of the cleaning process depends substantially on the ratio between the rates of the complex formation reactions and the rates of the ionic transport processes. The model by Kharkats (1998) fits the behavior of Cs and Sr found in the experimental tests from Korolev et al. (2007), Korolev (2009), and Prozorov (2000).

8.5.4 Pilot-scale and field applications

Pilot-scale electrokinetic remediation equipment suitable to the geological characteristics of South Korean nuclear facility sites was developed for the remediation of radioactive soil (Kim et al., 2013; Kim et al., 2010; Kim et al., 2009). The optimal experiment conditions were chosen through pilot-scale electrokinetic remediation experiments. The total removal efficiency of ^{60}Co and ^{137}Cs from the radioactive soil of about 2000 Bq/kg was 95.8% by an electrokinetic remediation by the application of an electric current of 15 mA/cm^2 for 55 days. The remediation efficiency was affected by the initial concentration of contaminants, the soil particle size, and the enhancing chemical agents added to the soil to improve the solubility and transportation of radionuclides. As expected soils with larger particles are easy to remediate. The removal percentage is also higher at higher initial radionuclide concentrations. Nitric acid and acetic acid were used as facilitating agents. Nitric acid resulted in better removal than acetic acid. Furthermore, nitric acid had the advantage of reducing the electric power consumption.

Electrokinetic fences are applied for preventing radioactive nuclide diffusion from pollution foci into the environment (groundwater, soil, and other grounds), and they play a role of protective fences for the possible migration of radioactive nuclides.

Figures 8.7 and 8.8 show schemes of such electrokinetic protective fences. Figure 8.7 shows a section of an electrokinetic protective fence around a site contaminated with radioactive nuclides. The fence of Figure 8.7 is designed for a shallow contaminated site. The electric field is generated around the site by two parallel rows of anode and cathode wells. Thus, the electric field forces the transportation of the radionuclides toward the center of the contaminated site, avoiding the migration of radionuclides far from the site. Thus, contaminant radionuclides are maintained in

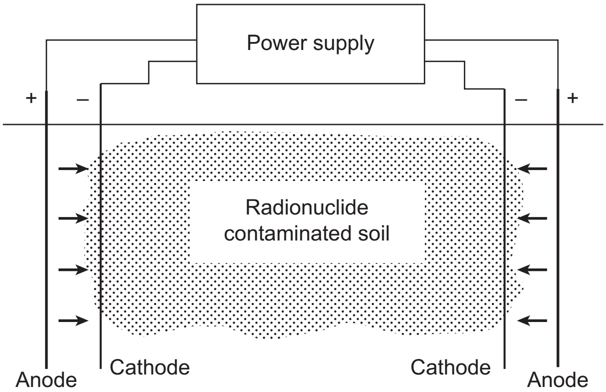


Figure 8.7 Electrokinetic fence around a contaminated soil site.

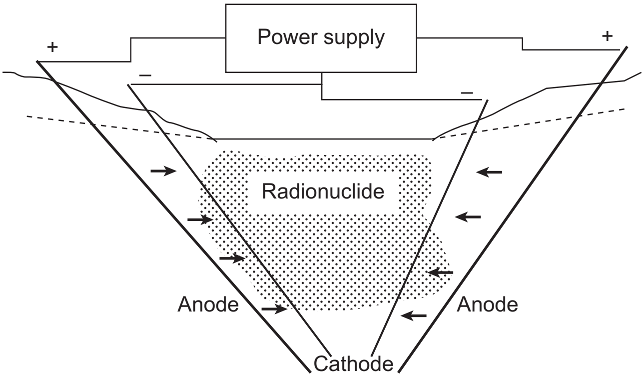


Figure 8.8 Electrokinetic fence around a flooded area with radionuclide contamination.

the limits of the contaminated area, avoiding any dispersion and the contamination of surrounding areas.

Figure 8.8 shows another scheme of an electrokinetic protective fence. This is applicable to contaminated sites where the radionuclides are located in the surface of the ground, for instance, an accumulating pond of liquid radioactive waste. There is a risk in such ponds of migration of the radionuclides downward, contaminating soil and groundwater with the subsequent dispersion of the radionuclides increasing the contaminated area. An inclined protective fence consisting of rows of anode and cathode wells should be constructed along the perimeter of this accumulating pond with the purpose of preventing this migration. The electric field generated by these protective fences will force the radioactive nuclides to migrate toward the center of the pond, avoiding the migration to the surrounding area. It will prevent pollution of adjacent soils and groundwater. The presented schemes of fences are applicable at emergency sites and in any other sites where radioactive pollution cannot be treated or removed.

Restoration of protective properties of artificial sorption fences created for radioactive nuclide migration from accumulating ponds is a no less important problem.

Usually clay grounds with high sorption ability and containing such minerals as smectite and illite are applied for constructing such fences. In addition, artificial protective fences made of other disperse grounds (from sand to loam) are applied; the sorption ability of such grounds is beforehand artificially enhanced with strengthening compounds, such as oxalic silica–alumina gel. These compounds decrease the filtration ability of the fence and raise its sorption characteristics.

8.6 Coupled technologies: electrokinetic treatment combined with other soil remediation technologies

Kim et al. (2013) designed a remediation system for radionuclide contaminated soil based on the combination of soil flushing and electrokinetic remediation. Pilot-sized washing-electrokinetic equipment suitable for the radioactive ash generated in Fukushima Japan was designed and constructed. The optimum operating conditions were determined in multiple tests at lab scale. The following parameters were optimized: facilitating agent chemical nature and concentration, and treatment time. The electrokinetic decontamination tests were carried out in 50 L pilot-scale equipment. The radioactive ash was first washed and then the residual Cs was removed by electrokinetics. When the initial ^{137}Cs concentration of radioactive ash was 41.8 Bq/g, the removal efficiency of ^{137}Cs in the radioactive ash after three washings was 89.1%. Then, the electrokinetic treatment reduced the ^{137}Cs concentration below 2.0 Bq/g in 10 days, reaching a global removal efficiency of 95.3% for ^{137}Cs. When the initial ^{134}Cs concentration of radioactive ash was 31.5 Bq/g, the removal efficiency of ^{134}Cs in the radioactive ash after three consecutive washings was 89.0%. Then, the time required to reach ^{134}Cs concentration below 2.0 Bq/g was 8 days in the electrokinetic treatment. The global removal efficiency was 94.4% for ^{134}Cs. The combined technology developed by Kim et al. (2013) removed 87–89% of ^{134}Cs and ^{137}Cs, respectively, from the radioactive ash after three consecutive washings. The resulting radioactive ash contaminated with 30–40 Bq/g of ^{134}Cs and ^{137}Cs needs an electrokinetic treatment of 8–10 days to reduce the radioactivity below 2.0 Bq/g.

8.7 Future trends

Electrokinetic remediation has been tested for the removal of radionuclides, reaching very promising results for large-scale operation. The addition of facilitating agents and the pH control on the cathode to avoid alkaline environment clearly increase the efficiency of the process. Considering the results from the literature, it is necessary to test new facilitating agents that can extract and keep in solution the radionuclides, so they can migrate under the effect of the electric field. However, the electromigration velocity will be limited by ionic mobility of the radionuclides and the physico-chemical characteristics of the soil. Further removal improvements can only be achieved by combining two remedial techniques. Thus, the combination of soil flushing and electrokinetics resulted in very promising results at lab and pilot-scale tests. Soil flushing removes the most soluble and easily extractable radionuclides from the soil. Then electrokinetics removes the residual radionuclides. Other combinations of techniques that have not been tested in the literature can be considered. For instance, phytoremediation can retain the radionuclide contaminants from soil, and electrokinetics can be superimposed during the plant growing process with the objective of mobilizing radionuclides to be more bioavailable for plants.

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In situ and *ex situ* bioremediation of radionuclide-contaminated soils at nuclear and NORM sites

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9.1 Introduction

The contamination of soils with radionuclides due to the many phases of the nuclear-fuel cycle is a major problem. These activities include mining and milling of the uranium, constructing and operating facilities for fabricating the nuclear fuel, and operating nuclear-power plants, as well as nuclear accidents, disposal of nuclear wastes (low- and intermediate-level waste (LILW), transuranic (TRU) wastes), including depleted uranium, reprocessing the spent nuclear fuel, and producing and testing nuclear weapons. Added to these problems are those inherent in phosphate mining, drilling for oil and gas, and disposing of their wastes. The radionuclides of concern from these activities include the actinides (Th, U, Np, Pu, Am), fission products (^{137}Cs, ^{90}Sr, ^{99}Tc, ^{129}I, ^{79}Se), activation products (^{60}Co, ^{63}Ni, ^{14}C, ^{3}H), and the naturally occurring radionuclides Th, U, and ^{226}Ra. These radionuclides are alpha, beta and/or gamma emitters, most with very long half-lives and high radiotoxicity. Remediating the contaminated soils requires removing these radionuclides and returning the clean soil to normal use or, if appropriate, immobilizing the radionuclides *in situ* so that they are stable and do not move into the environment. The latter process involves long-term monitoring and management of such sites that may or may not be accessible for public use, or until they pose no hazard to public health. In most cases, remediating large volumes of soils, albeit contaminated with low levels of radionuclides, is problematic in terms of the sheer volume of the waste, and the lack of appropriate technology to remove the radionuclides.

Bioremediation is the transformation or degradation of contaminants into nonhazardous or less hazardous chemical forms. Bioremediation is an attractive and promising green technology. Bacteria are commonly used, but other organisms, such as fungi, algae, or plants, have also been employed. Unlike organic compounds, radionuclides and toxic metals cannot be converted into innocuous compounds but must be removed or stabilized. Understanding the role of microbes in the environmental fate of radionuclides and the underlying mechanisms in microbe–radionuclide interactions is of great importance for developing effective methods of bioremediation for contaminated environments and biotechnology for treatment and managing hazardous wastes.

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Microbes play a major role in the biogeochemical cycling of metals and radionuclides. The electron transfer reactions are central to energy and the cycling of various elements in the environment. Microbial activity can affect the stability and the mobility of radionuclides in most soils. Depending on the radionuclide and the site-specific soil conditions, radionuclides can be solubilized or immobilized by the direct enzymatic or indirect nonenzymatic actions of microorganisms. Several radionuclides and metals are redox active and can be oxidized and reduced by microorganisms. Microbial reduction of certain radionuclides alters their solubility, thereby decreasing their mobility, bioavailability, and toxicity. Radionuclides initially present in soil in soluble form may be converted to an insoluble form or vice versa by the actions of microorganisms. Bioremediation methods include natural attenuation, biostimulation, and bioaugmentation. Natural attenuation depends on the intrinsic bioremediation potential, and involves little or no human intervention. In biostimulation, electron donors, electron acceptors, or trace element nutrients are injected into the soil to stimulate the growth and activity of indigenous microorganisms. Bioaugmentation involves deliberately adding microorganisms with the desired catabolic traits to accelerate metabolic conversions. These processes are exploited in designing *in situ* or *ex situ* bioremediation strategies involving the selective dissolution or immobilization of radionuclides.

9.2 Radionuclides in contaminated soils, sediments, and wastes

Contamination of the soils with radionuclides arises primarily from several sources: (1) the front and back end of the nuclear-fuel cycle (uranium mining and milling operations, nuclear-fuel fabrication facilities, nuclear-power plant operations, controlled release of gaseous radioactive components into the atmosphere, and reprocessing spent nuclear fuels); (2) the extraction of Th and rare-earth elements from monazite ore; (3) the operation of nuclear weapons production facilities; (4) disposal of low-, intermediate-, and high-level radioactive wastes; (5) the production of natural gas and oil, (6) the combustion of fossil fuels; (7) mining phosphate and applying fertilizer; (8) accidents at nuclear power plants; and (9) dirty bombs. The radionuclides in contaminated soils, sludge, and wastes may exist in various chemical forms, such as elemental, oxide, coprecipitates, ionic, inorganic, and organic complexes that regulate their mobility and stability in the environment. The mode of effectively remediating contaminated soils primarily is dictated by the nature of the chemical speciation, and the mineralogical association of the radionuclides with the solid phases.

9.2.1 Naturally occurring radionuclides

Naturally occurring radionuclide materials (NORMs) are those natural radioactive elements present in very low concentrations in the earth's crust. They include the long-lived radionuclides, such as uranium, thorium, radium and its decay product radon, and, in some instances, trace amounts of the short-lived polonium-210 (half-life of 138 days). Elevated concentrations of radionuclides often are found in certain sedimentary and igneous rocks and ores. Industrial activities that exploit the natural resources may lead to increased concentrations of radionuclides, often referred to as technologically enhanced naturally occurring radioactive material (TE-NORM), and thus results in products, by-products, residues, and wastes containing radionuclides. Such activities include the mining and processing of ores, the production of natural gas and oil, the combustion of fossil fuels, and the production of coal ash from burning coal in power plants.

9.2.1.1 NORM in the exploration of oil and gas

Enhanced concentrations of the radium-226 and -228 accumulate in oil field pits, tanks, lagoons, and sludge. Radon gas in natural-gas streams concentrate as NORM in gas-processing activities. Radon decays to lead-210, then to bismuth-210, polonium-210, and finally stabilizes as lead-206. Radon-decay elements occur as a shiny film on the inner surface of the inlet lines, treating units, pumps, and valves associated with the processing systems for propylene, ethane, and propane. The NORM waste may occur in a crystalline form, in carbonate matrix, or as white or brown solid scales or a thick sludge as solid, dry flaky substances.

9.2.1.2 NORM from phosphate mining

Phosphate fertilizers are obtained from phosphorites of sedimentary or magmatic origin. Sedimentary phosphate rock usually is strip-mined and contains high concentrations of ^{238}U (800–5200 Bq/kg), ^{230}Th (200–16,000 Bq/kg), ^{232}Th (5–170 Bq/kg), and ^{226}Ra (25–900 Bq/kg). Apatite $Ca_2[(PO4)_3(OH),F,Cl)]$, the predominant mineral, also contains trace amounts of ^{210}Po (Merkel & Hoyer, 2012). The mining and processing of phosphate fertilizers contaminate the surrounding soil and the application of the fertilizer over time tends to increase the concentration of radionuclides in agricultural soils, and thus transfer radionuclides through the food chain.

9.2.1.3 Uranium mining and mill tailing

Traditional uranium mining generates fine sandy tailings that contain virtually all the naturally occurring radioactive elements found in uranium ore. These are collected in engineered tailings dams and finally covered with a layer of clay and rock to inhibit the leakage of radon gas and ensure their long-term stability. Over the short term, the tailings material often is covered with water. After a few months, the tailings material contains about 75% of the radioactivity of the original ore; these are not classified as radioactive wastes. Uranium tailings are waste by-product materials left over from processing uranium-bearing ore. Uranium mill tailings also contain heavy metals, such as lead and arsenic. Large mounds of uranium mill tailings have been left at many old mining sites, and so remain a potential radiological and toxic metal hazard mainly due to the solubilization of ^{226}Ra, As, and Pb from ore minerals.

9.2.1.4 Weapons production and testing

Surface and subsurface contamination of actinides and fission products due to nuclear-fuel processing, weapons production, and weapons testing is a huge problem. The contamination of soils and sediments with actinides, such as Th, U, Pu, Np, and Am, and with the fission products ^{99}Tc, ^{90}Sr, ^{137}Cs, and ^{129}I was reported. Such sites occur in the United States (Bikini Atoll, the Rocky Flats, Colorado, Y-12 Plant, Oak Ridge, Tennessee, Fernald site, Ohio, Nevada Test Site, Nevada, Hanford, Washington, among others), the Myak facility and others in Russia, Sellafield in the United Kingdom, and also in Germany, France, Belgium, Belarus, and the Ukraine.

9.2.1.5 Accidents at nuclear-power plants

Widespread radioactive contamination of soil was caused by the accident at Chernobyl, and the nuclear disaster at the Fukushima Daiichi plant. The explosion and fire at Chernobyl threw hot particles of the nuclear fuel and fission products into the air. Approximately 100,000 km^2 of land was contaminated significantly by the fallout. The primary radionuclides of concern are the fission products ^{137}Cs and ^{90}Sr and minor amounts of the TRU elements Np, $^{239,\ 240}$Pu, ^{241}Am, and others embedded in a uranium oxide matrix. ^{137}Cs contamination at these sites is extensive and covers a large area with a range of concentrations, whereas actinide contamination is more localized to the accident area. The ^{137}Cs levels are very high in certain locales that it prevents reinhabitation at both Chernobyl and Fukushima. ^{137}Cs and ^{90}Sr will continue to be of greatest concern for several decades, while Pu isotopes and ^{241}Am will be of concern for hundreds and thousands of years, particularly in the immediate vicinity of the accident site.

9.2.1.6 Nuclear wastes

Nuclear wastes are classified as low-level wastes (LLWs), intermediate-level wastes (ILWs), transuranic wastes (TRUs), and high-level wastes (HLWs).

Low-level waste

LLW is generated from hospitals, industry, and the operation of nuclear power plants. It comprises paper, rags, tools, clothing, and filters that contain small amounts of mostly short-lived radionuclides. It does not require shielding during handling and transport and is suitable for burial in shallow land. To reduce its volume, it often is compacted or incinerated before disposal. It composes about 90% of the volume of waste, but only 1% of the radioactivity.

Intermediate-level waste

ILW contains higher amounts of radioactivity, and, in some cases, requires shielding. It includes resins, chemical sludge, metal reactor nuclear fuel cladding, and contaminated materials from decommissioning reactors. It may be solidified in concrete or bitumen for disposal. As a general rule, long lived waste from fuel and fuel reprocessing is disposed of in a geological repository.

Transuranic waste

TRU waste as defined by U.S. regulations is, without regard to its form or origin, a waste that is contaminated with alpha emitting transuranic radionuclides with half lives greater than 20 years and concentrations greater than 100 nCi/g (3.7 MBq/kg), excluding HLW. Elements that have an atomic number greater than uranium are called transuranics "beyond uranium." In the United States, it arises mainly from producing weapons, and consists of clothing, tools, rags, residues, debris, and other items contaminated with small amounts of radioactive elements, mainly plutonium. Under United States law, transuranic waste is categorized further into "contact handled" (CH) and "remote handled" (RH) on the basis of the radiation dose measured at the surface of the waste container. CH TRU waste has a surface dose rate not greater than 200 Röntgen equivalent person per hour (two millisieverts per hour (2 mSv/h)), whereas RH TRU waste has a surface dose rate of 200 Röntgen equivalent person per hour (2 mSv/h) or greater. CH TRU waste does not have the very high radioactivity of HLW, nor high heat generation, but RH TRU waste can be highly radioactive, with surface dose rates up to 1,000,000 Röntgen equivalent person per hour (10,000 mSv/h). The United States currently disposes of TRU waste generated from weapons-production facilities at the Waste Isolation Pilot Plant, in deep underground geological salt formations located in Carlsbad, New Mexico.

High-level waste

HLW arises from the "burning" of uranium fuel in a nuclear reactor; it contains the fission products and transuranic elements generated in the reactor's core. It is highly radioactive and hot, thus requiring cooling and shielding. HLW accounts for over 95% of the total radioactivity produced in generating electricity. Typically, HLW consists of spent fuel rods and separated waste from reprocessing the used fuel that normally is vitrified.

9.3 Characterization of radionuclides in contaminated soils and wastes

The chemical speciation and mineralogical association of radionuclides present in soils or wastes regulate their mobility and bioavailability. The radionuclides and toxic metals most commonly found in soils and wastes are americium, cadmium, cesium, chromium, cobalt, copper, lead, manganese, nickel, plutonium, technetium, thorium, strontium, uranium, and zinc. Typically, these contaminants are present in various forms, such as elemental, carbonate complexes, oxides, coprecipitates (metals coprecipitated with iron and manganese oxides), natural minerals, and soluble and insoluble organic complexes. In soils and wastes they may be present initially as soluble forms, or they may be formed after disposal by chemical and microbiological processes (weathering). Detailed information on the types and characteristics of the contaminants in soils and wastes is a prerequisite for selecting or developing appropriate bioremediation technology. The data needed include the chemical identity, concentration, speciation, and the mineralogical association of radionuclides and toxic metals. Chemical speciation is an important factor influencing the behaviors of metal ions in the environment. Chemical speciation refers to the chemical form in which a molecule or ion exists, whether it is a monomer or polymer, a dissolved aquo- or hydroxo- complex, or an insoluble oxide, and the like. Depending on the nature of the problem being studied, there can be multiple levels of information on speciation. These include (1) the identity of the element, (2) its physical state, (3) its oxidation state, (4) its molecular chemical formula, and (5) its detailed molecular structure. A variety of approaches can be used for assessing chemical speciation. Techniques such as solubility measurements, potentiometry, liquid–liquid partitioning, dialysis, chromatography, and optical spectroscopy have been employed for some time, and are considered classical methods. More recently, several more advanced spectroscopic techniques have been applied, including photoacoustic and thermal lensing, laser-induced fluorescence, magnetic resonance, and x-ray absorption spectroscopies. Each has its own particular sensitivity, specificity, cost, and benefit. Some methods can be used only for solid samples, whereas others can be used for both solid and liquid systems. In general, spectroscopic techniques, for instance, nuclear magnetic resonance and x-ray absorption fine structure spectroscopy, that yield detailed molecular structural information require relatively large concentrations of the target species (10^{-3} M), whereas techniques for obtaining only elemental composition, such as neutron activation analysis, can detect low concentrations (10^{-12} M).

The oxidation states of the redox-active radionuclides and the presence of the radionuclides as soluble or associated with carbonate, iron and manganese oxide, organic, silicate, and inert fractions provide information on the extent of the application of a particular *in situ* and *ex situ* remediation technology. For example, the radionuclides that are strongly bound to the soil matrix, such as the organic, silicate, and inert fractions, are far more difficult to remove and usually the process is very expensive.

9.4 Mechanisms of biotransformation of radionuclides

The activities of microbes are influenced by the presence of electron donors and acceptors. Microorganisms use oxygen as an electron acceptor under aerobic conditions; however, in the absence of oxygen, they can use nitrate, sulfate, metals, and carbon dioxide as alternate electron acceptors. The form of the metal (e.g., elemental, oxide, sulfide, ionic, inorganic complex, organic complex, coprecipitate), the availability of electron donors and nutrients (nitrogen, phosphorus), the presence of electron acceptors (Fe^{3+}, Mn^{4+}, NO_3^-, SO_4^{2-}, organic compounds), and the environmental factors (pH, Eh, temperature, moisture) affect the type, rate, and extent of microbial activity, and hence the transformation of radionuclides at contaminated sites. Oxidizing and reducing conditions influence the mobilization and immobilization of radionuclides and toxic metals. In an anaerobic environment, certain metals and radionuclides are reduced enzymatically from a higher oxidation state to lower one, thus affecting their solubility and bioavailability. For example, the reduction of $Fe^{3+} \rightarrow Fe^{2+}$ increases its solubility, while reducing $Cr^{6+} \rightarrow Cr^{3+}$ or $U^{6+} \rightarrow U^{4+}$ decreases their solubility. Many organic compounds form stable complexes with heavy metals and radionuclides, thus increasing their solubilization and leaching. Likewise, microbial metabolites and waste-degradation products can affect the solubility of heavy metals and radionuclides. Biodegradation of the metal–, radionuclide–organic complexes may engender the precipitation of the metal or radionuclide, and so retard its mobility.

The mechanisms of microbial transformations of radionuclides are reviewed extensively elsewhere (Mackasckie, 1991; Lovely, 1993; Lloyd & Lovely, 2001; Lloyd and Renshaw, 2005; Newsome et al., 2014; Francis, 1990, 2012; Banasack et al., 1999; Gadd, 2010). Briefly, the biotransformation of radionuclides includes one or more of the following mechanisms: (1) the oxidation–reduction of metals that affects their valence state and solubility; (2) changes in pH that affect the ionic state of the metals and their solubility; (3) solubilization, and leaching of elements by microbial metabolites and decomposition products, such as organic acid metabolites or the production of specific sequestering agents; (4) volatilization due to alkylation reactions (biomethylation); (5) immobilization leading to the formation of stable minerals or bioaccumulation by microbial biomass and biopolymers; (6) biotransformation of metal/radionuclide organic complexes, and (7) the remobilization of biosorbed or coprecipitated radionuclides due to mineralization. Of particular interest to the potential application to bioremediation are the oxidation–reduction reactions, solubilization, leaching, and the biodegradation of radionuclide–organic complexes.

9.4.1 Dissolution of radionuclides and metals

The direct and indirect actions of microorganisms occasion the dissolution of radionuclides and toxic metals. Direct action involves the dissolution of metals due to oxidation–reduction reactions. Indirect action entails dissolution due to the production of mineral acids, organic acid metabolites, and oxidizing agents, as well as by lowering the pH of the medium.

9.4.1.1 Direct action

Many microorganisms solubilize metals by (1) oxidation (increase in valence state) or (2) reduction (decrease in valence state). Direct action involves enzymatic reductive dissolution of the metal from a higher to a lower oxidation state, wherein the metal is used as the terminal electron acceptor. Microbial reduction and dissolution of iron and manganese oxides under anaerobic conditions have been studied extensively. For the most part, these redox reactions involve actively metabolizing bacteria. Reduction of metal ions also can occur passively when metals bind to reactive sites on the surface of, or within, microbial cells.

(i) Oxidative dissolution: Much of the information on the dissolution of metals deals with the oxidation of inorganic compounds, primarily from ore leaching by the autotrophic microorganisms *Thiobacillus ferrooxidans* and *T. thiooxidans*. The chemical and biochemical mechanisms involved in microbial leaching or biomining of metals have been extensively studied and are used commercially for extracting copper and uranium from ores. The role of *T. ferrooxidans* in extracting uranium from ore results from indirect and direct actions. The indirect mechanism is confined to its generating the oxidizing agent, ferric sulfate, and the solvent sulfuric acid and to the involvement

of Fe^{2+}/Fe^{3+} in mediating the oxidation of insoluble uranium oxide in a cyclical reaction to yield the soluble uranyl ion $UO_2 + Fe^{3+} \rightarrow UO_2^{2+} + Fe^{2+}$; in contrast, direct action involves the oxidation of $UO_2 \rightarrow UO_2^{2+}$ without using the Fe^{2+}/Fe^{3+} complex as the chemical electron carrier.

(ii) Reductive dissolution: Reductive dissolution of metals from a higher to a lower oxidation state due to enzymatic action by facultative and strict anaerobic microorganisms has attracted much attention because of its potential application in the *in situ* bioremediation of contaminants in the subsurface. Microbially mediated metal reductions play an important role in the biogeochemical cycles of metals. Using microbially mediated redox changes in metals for treating wastes and environmental remediation is attractive because the process can be carried out under mild conditions, does not produce hazardous secondary wastes, and potentially is applicable to a variety of waste forms. Examples of the enzymatic reductive dissolution of metals include the reduction of insoluble iron (Fe^{3+}) and manganese (Mn^{4+}) to their soluble forms Fe^{2+} and Mn^{2+}. Metal reduction can be mediated by actively metabolizing bacteria, or passively, wherein the metal is reduced when it interacts with binding sites both inside and outside the cell. These metals serve as alternate electron acceptors in the absence of oxygen for anaerobic respiration, or as an electron sink for the reoxidation of reducing equivalents. Bioreduction catalyzed by several microorganisms has been utilized in solubilizing Mn(IV) and Fe(III), and in extracting metals from ores.

9.4.1.2 Indirect action

The indirect dissolution of metals is due to the production of mineral acid from the oxidation of sulfide minerals by autotrophic bacteria, organic acids from the metabolism of organic compounds by heterotrophic bacteria, and the elaboration of metal-sequestering agents, such as siderophores. The mechanisms of bioleaching of metals from minerals by autotrophic microbes have been extensively investigated. An increase in heterotrophic microbial activity due to biodegradation of organic constituents of the soil or waste can affect the mobilization of radionuclides. Heterotrophic bacteria and fungi can release metals from various materials, including copper–nickel concentrates, low-grade copper ore, uranium from granites, and potassium from Lucite. Several mechanisms were proposed to explain the heterotrophic microbial solubilization of insoluble metals, including the production of organic acids, the formation of chelates, and the metabolism of metal-associated anions. Leaching of metals by heterotrophic organisms is due entirely to the chemical reactions of the excreted microbial metabolites and decomposition products. In many cases, a combined effect is important, for example, when organisms secrete organic acids that may have a dual effect in increasing metal dissolution by lowering the pH, and by complexation. A wide variety of heterotrophic microorganisms may be involved in solubilizing uranium from granitic rock where it generally occurs as an oxide (Bhurat, Dwivedy, Jayaram, & Dar, 1973). Such solubilization is caused by the production of organic acid metabolites, such as oxalic, isocitric, citric, succinic, hydrobenzoic, and coumaric acids via their carboxylic and phenolic groups (Berthelin & Munier-Lamy, 1983; Bloomfield & Kelso, 1973; Bloomfield & Pruden, 1975; Bloomfield, Kelso, & Piotrowska, 1971;

Bolter, Butz, & Arseneau, 1975). A *Bacillus* sp. able to reduce iron was shown to anaerobically mediate the solubilization of hydrous PuO_2 in the presence of a complexing agent, nitrilotriacetic acid (Rusin et al., 1994).

When microorganisms are grown in an iron-deficient medium, they elaborate specific iron chelators, such as siderophores. Iron-sequestering agents could play an important role in the complexation of radionuclides, and so increase their solubility. For example, the dissolution of plutonium dioxide was enhanced in the presence of Desferol, a polyhydroxamate chelate produced by microorganisms. *Pseudomonas aeruginosa* CSU, isolated from a Pu-contaminated pond at Rocky Flats, revealed several metabolic products that complexed uranium and thorium (Premuzic, Francis, Lin, & Schubert, 1985).

9.4.2 Immobilization of radionuclides and metals

Radionuclides and toxic metals are immobilized by (1) the bioaccumulation and biosorption by microbial biomass and biopolymers; (2) mineral formation; and (3) precipitation due to the enzymatic oxidation and reduction of metals. These processes received much attention because of their potential application in treating the secondary aqueous waste streams containing radionuclides.

(i) Bioaccumulation and biosorption. The ability of microorganisms and the polymers they secrete to scavenge metal ions has been studied intensively. Microbial bioaccumulation was reported for lead, silver, platinum, palladium, gold, mercury, gallium, cadmium, copper, and nickel, as well as the radionuclides cobalt-60, cesium-137, strontium-85, uranium, thorium, radium, americium, and plutonium. Microorganisms, living or dead, possess an abundance of functional groups on their cell surface that bind metal ions. Intracellular accumulation of metals was observed among all classes of microorganisms and usually occurs by an energy-dependent transport system. Polymers secreted by many actively metabolizing microbes also immobilize metals. Indeed, metal binding to cell surfaces and polymers is a promising technology for bioremediating contaminated surface and groundwaters. The mechanisms of metal binding by microbial cell walls and extracellular substances and the applications of these materials in bioremediation of radionuclide and toxic metal waste streams have been reviewed elsewhere (Beveridge & Doyal, 1989; Hughes & Poole, 1989; Volesky, 1990; Brierley, 1991; Francis et al., 2004; Pollmann et al., 2006).

(ii) Precipitation of metals by sulfate-reducing bacteria. Sulfate-reducing bacteria oxidize organic matter and reduce sulfate to sulfide in anaerobic environments. The hydrogen sulfide (H_2S) so produced reacts with metals to form water-insoluble, metal sulfide compounds. The precipitation of metals by sulfate-reducing bacteria in the natural environment and in treating waste water is well documented and is being exploited in engineered natural systems, such as constructed wetlands, to treat metal contaminants (Brierley, 1991).

(iii) Biocrystallization: Bacteria interact very strongly with metal ions and immobilize and concentrate them, eventually generating very small minerals. Microbial biofilms not only bind significant quantities of metallic ions naturally, they also serve as templates for the precipitation of insoluble mineral phases. In nature, bacteria

are constantly involved in producing minerals in soils and sediments. A *Citrobacter* sp. accumulates heavy deposits of metal phosphate, derived from an enzymatically liberated phosphate ligand. The cells exhibit no constraints on saturations and can accumulate several times their own weight of precipitated metal. This high capacity is attributable to biomineralization. For example, uranyl phosphate accumulates as polycrystalline HUO_2PO_4, at the cell's surface. The precipitation of uranium and other toxic metals by *Citrobacter* sp. was demonstrated with enzymatically liberated inorganic phosphate (Macaskie, Empson, Cheetham, Grey, & Skarnulis, 1992).

(iv) Immobilization due to reductive processes. The reduction of an element from a higher to a lower oxidation state or to elemental form affects its solubility, so resulting in the precipitation of several metals. For example, the following conversions by microorganisms have been reported: selenate, selinite, tellurate, and tellurite to elemental forms; vanadate to a vanadyl compound; molybdate and molybdenum trioxide to a molybdenum blue compound; arsenate to arsenite; mercuric chloride to elemental mercury; chromate ions to chromic ions that are precipitates at neutral pH; pentavalent and trivalent bismuth to an elemental form; lead dioxide to its divalent state; osmium tetroxide to the osmate ion; osmium dioxide and trivalent osmium to the metal; and hexavalent uranium to the tetravalent state; hexavalent Pu to the tetravalent form, petavalent neptunium to the tetravalent form, and heptavalent technetium to tetravalent form (Mohagheghi, Updegraff, & Goldhaber, 1985; Lovley, 1993; Woolfolk & Whitely, 1962; Kauffman, Laughlin, & Baldwin, 1986; Francis, Dodge, Gillow, & Cline, 1991a; Francis, Dodge, & Gillow, 1991b; Francis, Dodge, Lu, Halada, & Clayton, 1994; Francis, Dodge, & Gillow, 2008; Neu, Icopini, & Boukhalfa, 2005; Deo, Rittmann, & Reed, 2011). Basic information on the mechanisms of microbial transformations of radionuclides is useful in understanding the migratory behavior of radionuclides from the waste repository sites, in predicting their environmental fate and transport, in the long-term management of the contaminated sites, in remediation of contaminated sites, and in developing appropriate biotreatment technology, including the recovery and recycling of elements, the stabilization, volume reduction and minimization of wastes.

9.5 *Ex situ* and *in situ* remediation studies of contaminated soils

Radionuclide-contaminated sites can be remediated by using techniques designed to extract or segregate the contaminated fraction from the rest of the soil, either *in situ* or *ex situ*. *Ex situ* bioremediation involves excavating the contaminated material and its treatment in above-ground facilities located on site or offsite, whereas *in situ* remediation is undertaken at the site of contamination. *Ex situ* methods involve extraction separation, recovery of radionuclides, treatment of secondary waste streams, and the proper disposal of the solid wastes. The *ex situ* treatment processes are better understood; hence, they are relatively easy to implement, monitor, and control. The treatment of radionuclide-contaminated soils, sediments, and wastes involves excavation followed by *ex situ* treatment or disposal. The common *ex situ* treatment for excavated soils is solidification/stabilization.

In situ remediation technologies have several advantages over *ex situ* methods as they are cheaper, and less disruptive because no excavation is required. In addition, the exposure of site workers to hazardous contaminants is minimal. *In situ* bioremediation methods are suitable for mitigating widespread pollution, that is, present in dilute concentrations, or otherwise inaccessible. However, *in situ* treatment methods for radionuclide-contaminated soil have not been fully explored because of their radioactivity and the uncertainty in containing the radionuclides over the long term.

Radionuclides can be extracted by exposing the contaminated soil to a solution containing extracting agents (washing the soil, and its *in situ* flushing). Soil washing removes metals by chemical or physical treatment in aqueous suspension. Soil washing is an *ex situ* process that requires soil excavation prior to treatment. Chemical treatment involves adding extraction agents that react with the contaminant and leach it from the soil. The contaminated fraction of soil and/or process water is separated from the remaining soil, and disposed of or treated. It includes soil decontamination as well as treating the impregnated extracts or the secondary waste by biological means.

Bioleaching uses microorganisms directly to solubilize metal contaminants, or as a result of interactions with the metabolic products, or both. Bioleaching can be used *in situ* or *ex situ* to aid in removing metals from soils. This process is being adapted from the mining industry for use in the remediation of metals.

To date, the majority of the technologies that have been investigated for remediating radionuclides are *ex situ* technologies. Much of the contaminated soils are removed and stored, or depending on the radioactivity and its concentration, they are disposed of at a LLW or ILW facility. If the concentrations are low but the large volume of the waste makes it prohibitively expensive to dispose of as LLW then chemical and biological treatments are employed to selectively remove the radionuclides from the soil and return it to normal use; thereafter, secondary treatment of the liquid waste to concentrate the extracted radionuclides and dispose them as appropriate is an attractive option.

The microbial transformations of selected radionuclides of interest in contaminated soils, sediments, and wastes relevant to *in situ* and or *ex situ* bioremediation technologies are summarized below.

9.5.1 Thorium biotransformation and remediation studies

Thorium is a natural radioactive element predominantly found in a single isotopic form, viz. ^{232}Th. It is an alpha emitter with a half-life of about 14 billion years. Thorium is nearly three times more abundant than uranium in the Earth's crust, and is present in minerals such as thorite ($ThSiO_4$), thorianite ($ThO_2 + UO_2$), and monazite. Thorium is extracted from monazite along with the rare-earth metals. Unlike uranium, information is lacking on the impact of thorium mining and processing. Mining and refining it may lead to the contamination of soil and water. Thorium is only stable at its +4 oxidation state. It readily undergoes hydrolysis in water and forms colloids and polynuclear species.

Microbe–thorium interactions have received little attention, possibly because thorium is not used currently in commercial nuclear reactors. However, there is a growing interest worldwide in building thorium-based reactors. The role of microbial activities in the dissolution and immobilization of thorium is unknown.

The biosorption of thorium by a *Pseudomonas* strain (Kazy, D'Souza, & Sar, 2009) and by the fungi *Rhizopus arrhizus* and *Aspergillus niger* was about 116–180 mg/g biomass; furthermore, it was shown that Th^{4+} coordinates with the nitrogen of the fungal chitin cell (Tsezos & Volesky, 1981, 1982; White & Gadd, 1990). The biosorption of Th by a dry biomass of *Sargassum filipendula* was 2.59 µg Th/g in a fixed-bed reactor (Picardo, Ferreira, & Da Costa, 2009). Coprecipitation for removing Th from water was explored using exopolymeric substances produced by a soil bacterium *Bradyrhizobium* (*Chamaecytisus*) strain BGA-1 (Diaz-Marrero, Santamaria, Hernabdez, & Corzo, 2004). Various species of bacteria, actinomycetes, and fungi were screened for the accumulation of thorium ions from water; the maximum accumulation was observed in the cells of *Micrococcus luteus* (Nakajima & Tsuruta, 2004). Alginate polymers were effective in removing and recovering Th (IV) from solution; the alginate polymers removed 169 mg Th/g.

Several metabolic products capable of complexation with Th were elaborated when *Pseudomonas aeruginosa* was grown in medium containing Th (Premuzic et al., 1985). Desouky, El-Mougith, Hassanien, Awadalla, and Hussien (2011) reported that the metabolic bioproducts from *Aspergillus ficuum* and *P. aeruginosa* extracted thorium (Th^{4+}), uranium (UO_2^{2+}), and rare-earth elements from a thorium–uranium concentrate. *P. aeruginosa* produced an element-specific ligand (siderophore) that changed the pH and enhanced the chelation of Th^{4+} and UO_2^{2+}. The siderophore generated at pH 5.3 can bioleach and complex with 68% of uranium and 65% of thorium. Also, *A. ficuum* produced different kinds of organic acids that leached 30% of uranium and 29% of thorium in addition to 20% of lanthanum, 33% of cerium, and 2.5% of yttrium as rare-earth elements at pH 3.0 (Desouky et al., 2011). Organic acid metabolites, such as citric acid, produced by *A. niger* form stable complexes with Th (Bobtelsky & Graus, 1954). These studies clearly showed that microbial activities can affect the solubility of Th and demonstrated their potential use in remediating Th-contaminated soils.

9.5.2 Technetium biotransformation and remediation studies

Technetium-99 is a beta emitting radionuclide with a half-life of 2.1×10^5 years. It is released into the environment from nuclear power reactors, nuclear wastes, reprocessing facilities, and from testing nuclear weapons. It exists in as many as 19 isotopes, and in multiple oxidations states (0, +3, +4, +5, +6, +7). Of these, the stable heptavalent pertechnetate ion (TcO_4^-) and the quadrivalent Tc(IV) ion are of environmental concern. Pertechnetate (TcO_4^-) ion is the most stable and soluble ion in aqueous environments (Yoshihara, 1996).

Technetium can undergo oxidation–reduction reactions under environmental conditions. It can be reduced chemically and biologically. The reduction and precipitation of pertechentate anion are carried out anaerobically by a wide variety of microorganisms (Lolyd & Mcaskie, 1996; Henroit, 1989; Pignolet, Auvray, Fosny, Capot, & Moureau, 1989; Francis, Dodge, & Meinken, 2002a) and that bacteria are able to enzymatically reduce soluble Tc(VII) to insoluble Tc(IV) under anaerobic conditions

(Lolyd & Mcaskie, 1996). A *Halomonas* strain isolated from a seawater removed Tc(VII) by aerobically reducing it to Tc(IV) (Fujimoto & Morita, 2006).

$$\mathbf{Tc(VII)_{aq}} \xrightarrow[\text{Fermenters, sulfate reducres}]{\text{Dissimilatory metal reducers}} \mathbf{Tc(IV)_{S}}$$

The predominant chemical species identified include TcO_2, $TcO(OH)_2$, and TcS_2, depending on the type of microorganism involved. In addition, microorganisms can mediate the reduction of Tc(VII) to Tc(IV) indirectly by generating ferrous iron and sulfide. For example, the sulfate reducers reduce pertechnetate to insoluble TcS_2. Other organisms are known to generate Tc oxide (TcO_2) and oxyhydroxide species [$TcO(OH)_2$] anaerobically. In culture medium, Tc is associated with the cells and with macromolecules as reduced Tc–organic complexes. Pignolet et al. (1989) observed that Tc was bound to high-molecular-weight cellular constituents in pure and mixed cultures of bacteria isolated from marine sediments. Henrot (1989) reported the association of Tc with bacterial polysaccharides in anaerobically grown bacteria, and stated that the reduction of pertechnetate was metabolically linked, and not due to changes in the redox conditions. About 70% of the total Tc was associated with the bacteria and/or precipitated. The remaining Tc in soluble form was associated with organics. The anaerobic reduction of soluble Tc(VII) to Tc(IV) by *Clostridium* sp. precipitated Tc. The reduced Tc was associated with the cell biomass, as well as being associated with organic metabolic products in solution. Also, the reduced Tc(IV) formed a soluble Tc DTPA complex when DTPA was added to the medium of *Clostridium* species (Francis et al., 2002a).

$$\mathbf{Tc(VII)_{aq}} \xrightarrow{\textit{Clostridium}\ \text{sp.}} \mathbf{Tc(IV)\text{-}organic\ complex}$$

Technetium adsorption by soils and sediments has been attributed to microbial activity. Landa, Thorvig, and Gast (1977) reported that 8 out of 11 soils tested adsorbed 98% of the pertechnetate within 2–5 weeks, and that sterilizing the soil eliminated this adsorption. Tagami and Uchida (1996) investigated the influence of microbial activity on plant-available Tc under aerobic and anaerobic (waterlogged) conditions in soil amended with 0, 0.05%, and 0.5% glucose and compared them with sterile soil. They found that Tc was bound to the soil as a result of changes in the redox caused by microbial action. Sheppard, Sheppard, and Evenden (1990) noted the negligible sorption of TcO_4^- in aerobic soils, and substantial sorption of reduced Tc in anaerobic environments, especially in the presence of organic matter; they suggested that reduced Tc may be transported as a complex with organic ligands. Peretrukhin, Khizhnyak, Lyalikova, and German (1996) showed that Tc was sorbed on to the sediments of a lake in Russia by the action of sulfate-reducing bacteria. Biogenic hydrogen sulfide converted the readily soluble sodium pertechnetate to poorly soluble Tc(VII) and Tc(IV) sulfides.

The Tc(IV) forms complexes with naturally organic compounds, such as acetate, oxalate, citrate, and humic acids, and with the synthetic chelating agents ethylenediaminetetraacetate (EDTA) and DTPA that can increase their solubility. The nature and stability of the Tc–organic complexes is not understood. Moreover, the ability of the bacterium to metabolize Tc–organic complexes, such as Tc–DTPA and Tc–citrate, is not known. These studies suggest that Tc may be present as insoluble or soluble forms or as colloids, depending on the type and extent of bacterial activity in subsurface environments; hence, the potential exists for the transport of reduced Tc in these forms.

However, the reduced Tc(IV) in soils and sediments can be remobilized by reoxidation to Tc(VII), depending on the nature of the oxidant present in the systems (Gu, Dong, Liang, & Wall, 2011).

9.5.3 Radium biotransformation and remediation studies

Radium is a naturally occurring radionuclide formed by the decay of uranium in the environment. In nature, radium occurs in trace quantities in uranium ores. All isotopes of radium are highly radioactive, but ^{226}Ra is the most stable isotope. It has a half-life of 1601 years, and is an alpha emitter with accompanying gamma-radiation. Microorganisms indirectly can affect the environmental mobility of radium.

At many uranium mining and milling sites, soluble radium is released and must be removed from the effluents prior to their discharge. Coprecipitation, by adding barium chloride ($BaCl_2$) to sulfate-rich tailing effluents, is the method employed for removing radium as $(Ba,Ra)SO_4$. The precipitate is allowed to settle, resulting in a radioactive sludge, and supernatant free of Ra^{2+} ready for discharge to the environment (McCready, Bland, & Gonzales, 1980).

9.5.3.1 Radium coprecipitation with barium sulfate

At many uranium mining and milling sites, soluble radium is removed as a coprecipitate with $BaSO_4$ by adding $BaCl_2$ to sulfate-rich tailing effluents. The resulting $(Ba,Ra)SO_4$ precipitate is allowed to settle, yielding a radioactive sludge and supernatant that is sufficiently low in $^{226}Ra^{2+}$ to be discharged. The disposal of radioactive sludges must ensure that $^{226}Ra^{2+}$ does not leach into the groundwater because microbes might transform the stabilized radioactive wastes into mobile compounds. For example, Ra, coprecipitated with $BaSO_4$, was solubilized anaerobically by sulfate-reducing bacteria (Fedorak et al., 1986).

$$(Ba,Ra)SO_4 \xrightarrow{\text{Sulfate-reducing bacteria}} {}^{226}Ra^{2+} + Ba^{2+} + H_2S$$

$BaSO_4$ was solubilized under anaerobic conditions by bacteria (Bolze, Malone, & Smith, 1974). High Ba^{2+} concentrations in aquifers have been attributed to sulfate reduction by *Desulfovibrio vulgaris*. Thus, McCready and Krouse (1980) showed that *D. vulgaris* could release H_2S, $^{226}Ra^{2+}$, and Ba^{2+} from a $(Ba,Ra)SO_4$ sludge. Studies of such sludges from two Canadian uranium mine and mill sites revealed that after adding usable carbon, SO_4^{2-} was reduced to S^{2-}, with a concurrent release of $^{226}Ra^{2+}$, Ba^{2+}, and Ca^{2+} due to enhanced anaerobic microbial activity. Levels of dissolved $^{226}Ra^{2+}$ reached approximately 400 Bq/L after 10 weeks of incubation. Thus, for ultimately disposing of these sludges, conditions must be maintained that minimize the activity of the indigenous sulfate-reducing bacteria to ensure that $^{226}Ra^{2+}$ is not released.

Aerobic treatment of the effluents from uranium mills containing toxic amounts of Mn^{2+} and ^{226}Ra with *Arthrobacter* sp. precipitated 92% of the Mn^{2+} as the hydrous oxide of manganese; along with it, about 95% of the ^{226}Ra was coprecipitated (Mathur & Dwivdey, 1988). However, under anaerobic conditions, Mn and ^{226}Ra can be remobilized by the bacterial reduction of manganese oxide (Mn(IV) to Mn(II); this phenomenon must be taken into consideration for waste disposal, particularly under anaerobic conditions, such as in landfills and subsurface disposal facilities where conditions become anoxic.

These studies show that the disposal of wastes containing radionuclides and metals coprecipitated with iron and manganese oxides may entail the extensive leaching of iron, toxic metals, and radionuclides due to enhanced anaerobic microbial activity.

9.5.4 Polonium biotransformation and remediation studies

Polonium-210 is a very rare highly radioactive, toxic element that occurs naturally in association with U and Th minerals. It has a short half-life of 138 days, and is chemically similar to bismuth and tellurium. It is found in uranium ores at about 0.1 mg per metric ton (1 part in 10^{10}), i.e., approximately 0.2% of the abundance of radium. Different isotopes of Po are produced in the decay of ^{238}U, ^{235}U, and ^{232}Th. It is the last radioactive member of the ^{238}U decay series, and can be measured in very low quantities using alpha spectroscopy. ^{210}Po can be an environmental pollutant caused by uranium-containing phosphorite–phosphate and phosphogypsum–phosphoric acid production. Polonium exists as +2 and +4 oxidation states. Sulfate-reducing bacteria mobilize the Po contained in phosphogypsum due to reduction of the sulfate in the gypsum under anaerobic conditions. Organic ligands produced by aerobic bacteria are also known to mobilize Po by forming Po–organic complexes.

Immobilization of Po by sulfate-reducing bacteria is due to H_2S production and the precipitation of Po as polonuim sulfide (PoS). Bacterial uptake of Po extracellularly or intracellulary has been reported (Larock, Hyun, Boutelle, Burnett, & Hull, 1996). Such immobilization in nature must be considered as transient if, on the death of these cells, the Po becomes redissolved in the bulk phase.

Because of the chemical similarity of Po to S, studies were begun to determine whether bacteria, particularly those species active in sulfur cycling, could account for the selective solubilization and mobilization of Po. Possible sources of Po are the U-rich phosphate rock and phosphogypsum (gypsum), a by-product in manufacturing phosphoric acid. Experiments involving the interaction of bacteria with this waste gypsum demonstrated the solubilization of Po. Sulfate-reducing bacteria particularly were effective at mediating Po release, provided that the sulfide levels did not rise above 10 μM, in which case Po apparently was coprecipitated as a metal sulfide. Conversely, the ability of sulfate-reducing bacteria to effectively remove dissolved Po when sulfide levels are high suggests that these bacteria may serve as an effective bioremediation tool in reducing Po levels in groundwater.

The biomethylation of Po by microbes to dimethyl polonide in the presence of methylcobalamine was observed. The loss of Po was noted from cultures of bread mold and nonsterile groundwater in Florida. Volatile Po has been trapped from the headspace of cultures inoculated with sediments and pure cultures of bacteria, and the volatile Po compound has been identified as dimethyl polonide (Bahrou et al., 2012).

9.5.5 Cesium biotransformation and remediation studies

Cesium is a metal that occurs naturally in various minerals in a nonradioactive stable form, or as produced from uranium and plutonium during fission in nuclear reactors that is radioactive and unstable. The most common radioactive forms of cesium are ^{137}Cs and ^{134}Cs. Cesium-137 contamination of the environment is much more significant than that of ^{134}Cs; it mainly is contained in the topsoil layer. Cesium-137 was introduced into the environment from the fallout from atmospheric tests of nuclear weapons in the 1950s and 1960s (much of it now has decayed), nuclear-reactor waste, spent nuclear-fuel wastes from reprocessing plants, and accidental releases, such as the Chernobyl accident in the Ukraine and in Fukushima, Japan. Cesium-137 undergoes radioactive decay, with the emission of beta particles and relatively strong gamma-radiation, to barium-137m, a short-lived decay product, which, in turn, decays to a nonradioactive form of barium. The half-life of ^{137}Cs is 30.17 years.

Cesium is a structural analog of K. Much of the Cs deposited on the litter layer leaches into mineral soil and remains associated with the soil's mineral phases, and expectedly, perhaps only a small fraction will be bioavailable. ^{137}Cs resides predominantly on "strong" sites on clay interlayers. Cleaning up of contaminated soils generates a large volume of radioactive waste. In some instances, large contaminated areas might be mitigated by burying and covering the contaminated substances with concrete, soil, or rock to prevent the contamination from spreading further into the environment. Stripping out ^{137}Cs from contaminated soil efficiently and without destroying the soil organic content dramatically could lower the volume of waste and the cost of disposal.

Cesium bound to interlayer sites is not readily exchanged by other cations, and generally is considered fixed (Comans, Haller, & De Preter, 1991). A strong surface association between Cs and the soil's solid phase occurs at frayed edge sites (FES) of micaceous phyllosilicate minerals. Plant root and microbial exudates may enhance Cs bioavailability in the rhizosphere by accelerating weathering at the frayed edges of phyllosilicate minerals, and releasing Cs sorbed to frayed edge and interlayer sites, so making the ion available for uptake. Many studies documented the significance of exudates from plant roots and rhizosphere microorganisms to phyllosilicate mineral-weathering processes in the soil environment (Wendling, Harsh, Palmer, Hamilton, & Flury, 2004; Wendling et al., 2005a,b; Staunton & Levacic, 1999; Kim, McDonald, & Jordan, 1997; Robert & Berthelin, 1986; Berthelin, 1983). Oxalate affected Cs interactions with illite (Wendling et al., 2004).

Biogeochemical processes in the rhizosphere can greatly alter the interactions between contaminants and soil minerals. Cesium desorption from illite in the presence of exudates from bacteria found in the rhizosphere of crested wheatgrass

(*Agropyron desertorum*) reveals the potential contribution of bacteria to illite weathering in the rhizosphere of crested wheatgrass. Exudates from three strains of bacteria belonging to the genera *Bacillus*, *Ralstonia*, and *Enterobacter* significantly enhanced Cs desorption from illite. In addition, Cs desorption increased with increasing concentrations of the *Bacillus* exudate. Cesium desorption from illite as a function of both exudate type and concentration was positively correlated with Al dissolution, suggesting that the Al-complexing ability of the exudates played an important role in enhancing Cs desorption. The density of FESs on illite increased after treatment with bacterial exudates, whereas the Cs/K selectivity of FES decreased. These results suggest that exudates from bacteria isolated from the rhizosphere can enhance Cs desorption from frayed edges of illite and, therefore, can alter Cs availability in micaceous soils. Soil decontamination using microbes is an option that is being considered. Cesium-137 mimics that of sodium and potassium, which are readily absorbed by the cells. Cesium-accumulating bacteria isolated from soil display the rod–coccus growth cycle and contain mesodiaminopimelic acid, mycolic acids, and tuberculostearic acids (Tomioka, Uchiyama, & Yagi, 1992). Because monovalent cation uptake is usually energy dependent, cesium accumulation by bacterial strains may be energy dependent. Therefore, the mechanism of cesium removal by these strains is not simple adsorption. The optimum pH for Cs uptake by the strains *Rhodococcus erythropolis* CS98 and *Rhodococcus* sp. strain CS402 was 8.5. Rubidium and cesium assume part of the role of potassium in the growth of both strains. Potassium and rubidium inhibited Cs accumulation by these strains. It is likely that both strains accumulated Cs through a potassium transport system (Tomioka, Uchiyama, & Yagi, 1994). Recently, adsorption of cesium by unicellular green algae was reported (Shimura et al., 2012). Nevertheless, the nature of Cs association with the cells (extra- or intracellular) remains unclear, as does the long-term fate of bioassociated Cs. Very high radiocesium activities have been observed in the fruiting bodies of several fungal species since the Chernobyl accident (Dighton & Horrill, 1998).

Sasaki, Shirato, Tahara, Sato, and Takenaka (2013) demonstrated that the terrestrial cyanobacterium *Nostoc (N) commune* can absorb high levels of radioactive cesium. This species is a heterocystous blue-green algae that forms jelly-like clumps of polysaccharides. Radioactive material is presumed to be deposited in them, simplifying their removal from the environment. Furthermore, this species reportedly grows under high radiation exposure. Sasaki et al. (2013) monitored the accumulation of radioactive material in the *N. commune*. In Nihonmatsu City, Fukushima Prefecture, *N. commune* accumulated 415,000 Bq/kg dry weight ^{134}Cs and 607,000 Bq/kg dry weight ^{137}Cs. The concentration of cesium in the *N. commune* tended to be high in areas where the soil's radioactivity was high. A cultivation experiment confirmed that *N. commune* absorbed radioactive cesium from polluted soil. These data demonstrated that radiological absorption using *N. commune* might be suitable for decontaminating polluted soil. Because this species is a heterocystous blue-green algae that forms jelly-like clumps, it can be easily collected from the soil's surface. Furthermore, its weight decreases by about 90% when it is dried. Radiological absorption by *N. commune* may be a viable strategy for decontaminating polluted soil.

Radiocesium is known to be bioavailable in forest ecosystems for a long time, and it is necessary to intervene with the cycling process to decontaminate the forest soils. Ecological processing to recycle radioactive Cs in a forest ecosystem is a viable approach for enhancing the decontamination of radio-Cs. Mushrooms accumulate high concentrations, and although the mushroom biomass in a forest ecosystem is small, the fungal mycelium in detritus and soil is large, and thus fungi contain substantial amounts of radio-Cs. It is well known that concentrations of some nutrients, such as nitrogen and phosphorus increase, whereas potassium decreases during the decomposition of leaf litter. Nobuhiro, Yao, Taizo, Yoichiro, and Masanori (2013) recorded the concentrations of radio-Cs during the decomposition of leaf litter on a forest floor where ^{134}Cs and ^{137}Cs, respectively, in the surface soil were 5700 and 6800 Bq/kg. They placed 16 g (dry wt) of the newly fallen mixed deciduous leaf litter (half of which was oak, *Quercus serrata*) from a deciduous forest about 50 km from Fukushima NPP into 25 × 25 cm litter bag. The ^{137}Cs concentration in the fresh litter was ca. 1000 Bq/kg in December 2011. During the process of decomposition on the forest floor, the Cs in the litter increased exponentially and exceeded 10,000 Bq/kg after 6 months, indicating that Cs and K show contrasting dynamics during the early decomposition phase. An increase in fungal biomass in the early stage of litter decomposition also was observed. Therefore, this upward movement of Cs from the humus and soil layer points to the fungal translocation of nutrients from outside the litter's substrate. Retrieving the litter after 6 months showed a loss of removed 18% of ^{134}Cs.

In the long term, secondary contamination by the wash off of ^{137}Cs from contaminated soils, and its remobilization from sediments, continues at a much lower level. Soils with high organic content may release much more radiocesium to surface waters than the mineral soils. Although the physical processes (radionuclide removal, mixing with soil) and chemical processes (soil liming, fertilization) involved in environmental remediation technologies are well understood, many of the biological processes that could be used in remediating contaminated soils are not fully understood.

9.5.6 Strontium biotransformation and remediation studies

Strontium-90 is a high-yield fission product. It is a beta emitter with a half-life of 29.1 years. The biochemical behavior of strontium is similar to that of calcium and, therefore, it tends to concentrate in the bones and teeth. Strontium-90 is an important radionuclide contaminant at nuclear facilities and nuclear-accident sites. In the natural environment, strontium exists solely as Sr^{2+}. The geochemical behavior of strontium is similar to that of Ca^{2+} and Sr speciation is not influenced directly by changes in redox conditions. However, processes such as biosorption, bioaccumulation, and bioprecipitation have been investigated for developing bioremediation strategies for removal or immobilization of Sr from contaminated water or sites.

In soils, ^{90}Sr is bound as an exchange complex to clay minerals, or exists as a fixed component of the soil's organic matter, iron (hydr)oxides, or insoluble carbonate or phosphate. Microorganisms can affect the association of various forms of Sr in soils by (1) dissolution of the carbonate and phosphate phases, clays, and other minerals due to the production of organic acids and sequestering agents; (2) reductive dissolution of iron and the release of Sr associated with the iron oxides, (3) biodegradation of the organic carbon associated with the Sr fractions; and (4) immobilization due to precipitation reactions, i.e., the formation of strontium carbonate (Anderson & Appanna, 1994), microbial formation of strontium calcite phase at a groundwater discharge zone (Ferris, Fratton, Gerits, Schultze-Lam, & Sherwood loolar, 1995), and by biomass/exopolymers.

Bioaccumulation of Sr as a structural analogue for Ca was reported for several microorganisms (Page & Doran, 1981; Strandberg, Shumate, & Parrot, 1981; Faison, Cancel, Lewis, & Adler, 1990). Consequently, there is considerable interest in using microorganisms to remove radioactive Sr from waste streams. Sr-binding activity in *Microccous luteus* is localized on the cell envelope, and is sensitive to pretreatment. Bound Sr can be displaced by chelating agents, divalent cations, or H^+ (other monovalent cations are less effective at displacing Sr). Strontium binding in *M. luteus* is reversible, though both ion exchange, mediated by acidic cell surface components, and intracellular uptake may be involved (Faison et al., 1990). Biosorption of strontium was reported by bacterial and algal cultures (Shimura et al., 2012). In addition, accumulation of strontium into barite in the form of $(Ba,Sr)SO_4$ was shown for the selective removal of strontium using unicellular freshwater green algae (Krejci et al., 2011). Strontium was accumulated as $SrSO_4$ crystals in the vacuole of the desmids.

Microbially induced calcium carbonate precipitation (MICP) was offered as a promising approach for the cleanup of radionuclide-contaminated sites, particularly for Sr bioremediation (Fujita, Taylor, Wendt, Reed, & Smith, 2010; Thorpe et al., 2012; Achal, Pan, & Zhang, 2012). MICP is driven by microbial metabolism, and can be implemented using four different mechanisms: bacterial ureolysis, sulfate reduction, fermentation of fatty acids, and denitrification. Among them, only denitrification does not produce toxic by-products. Incorporating strontium into calcite ($CaCO_3$) in artificial groundwater was studied using urease-producing bacteria (Warren et al., 2001; Fujita et al., 2004). MICP via biological denitrification is a more environmentally friendly and promising approach because it does not add additional pollutants such as NH_4, as in the case of a urease-based approach. It can easily be performed under anoxic conditions, and has greater carbonate yield per mole of electron donor, facilitating the formation of $SrCO_3$ precipitates. Nitrate often is present as a cocontaminant with radionuclides in contaminated environments. Hence, Thorpe et al. (2012) investigated Sr^{2+} sorption and precipitation during denitrification in sediment microcosm experiments, and found that it caused the pH to increase (>9), resulting in decreased Sr^{2+} solubility.

9.5.6.1 Microbiologically induced calcite precipitation

The overall reactions involved in the bioremediation process include the urease-producing NH_4^+ and HCO_3^-, desorption of Ca^{2+} and/or Sr^{2+} from solid surfaces by the NH_4^+- and HCO_3^--promoted precipitation of $CaCO_3$, and coprecipitation of ^{90}Sr (Wu et al., 2011). Indigenous or introduced microorganisms induce the *in situ* $CaCO_3$ precipitation. The following chemical reactions are proposed.

Urease-driven strontium precipitation

Microbially catalyzed hydrolysis of urea produces ammonia and bicarbonate, and increases the pH.

$$NH_2(CO)NH_2 + 3H_2O \xrightarrow{\text{Urease}} 2NH_4^+ + HCO_3^- + OH^-$$

Bicarbonate promotes the precipitation of $CaCO_3$ in the presence of dissolved calcium with the formation of calcite.

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3 + H_2O + CO_2$$

The precipitation of $CaCO_3$ is influenced by the concentration of Ca, dissolved inorganic carbon, pH, and the presence of nucleation sites. Bacterial cells serve as nucleation sites and precipitation of $CaCO_3$ on bacterial cell surfaces has been reported (Ferris, Fyfe, & Beveridge, 1987; Fujita, Ferris, Lawson, Colwell, & Smith, 2000).

Ammonium ions promote the exchange of sorbed Sr.

$$\text{Solid - }Sr^{2+} + 2NH_4^+ \rightleftharpoons \text{Solid} - (NH_4^+) + Sr^{2+}$$

Sr coprecipitates into calcite and thus is removed from the aqueous medium.

$$xSr^{2+} + (1-x)\,Ca^{2+} + 2HCO_3^- \rightleftharpoons Ca_{(1-x)}Sr_xCO_3 + H_2O + CO_2$$

Fujita et al. (2000, 2004) used ureolytic bacteria that precipitate calcium carbonate to immobilize strontium. Strontium was integrated into the calcite structure through substitution for calcium by forming strontium–carbonate minerals that have very low solubility (Fujita et al., 2000, 2004). The effects of adding molasses and urea were tested for stimulating microbial hydrolysis of urea in the Eastern Snake River Plain Aquifer, Idaho (Fujita et al., 2008). Diluted molasses was injected three times over 2 weeks to promote microbial growth. Thereafter, one injection of urea in a single-well experiment caused the total number of cells to increase by one–two orders of magnitude. Quantitative polymerase chain reaction assay revealed that numbers of urease genes (ureC) rose by 170 times above preinjection levels. The researchers recovered calcite precipitates after injecting the urea. Overall, the data indicated the viability of manipulating biogeochemical processes to promote the *in situ* immobilization of metals or radionuclides. The environmental conditions conducive to carbonate precipitation are not unique to any specific microorganism.

Denitrification-driven strontium precipitation

Denitrification involves the reduction of NO_3^- to N_2 and is driven by the presence of an electron donor (i.e., acetate). The microbial denitrification produces the alkalinity and carbon dioxide (CO_2) required for the MICP. Denitrification of nitrate produces almost 2 mol of CO_3^{2-} per mole of acetate (1.6 mol of nitrate).

$$8/5\ NO_3^- + CH_3COO^- \xrightarrow{\text{Denitrifiers}} 4/5\ N_2 + 2\ CO_2 + 13/5\ OH^- + 1/5\ H_2O$$

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

$$Sr^{2+} + HCO_3^- + OH^- \rightleftharpoons SrCO_3(s) + H_2O$$

Denitrifying bacteria are ubiquitous in the environment. The anoxic conditions of aquifer sediments of subsurface environments are ideal as bacteria use NO_3^- as an electron acceptor instead of O_2. Therefore, denitrification-driven MICP can be an effective bioremediation approach for immobilizing radionuclides *in situ* or *ex situ*. This can be achieved by adding an exogenous electron donor (i.e., acetate) if nitrate is a cocontaminant.

Immobilization of Sr as $SrCO_3$ by bacteria was reported (Anderson & Appanna, 1994). *Pseudomonas fluorescens* grown in a medium containing Sr–citrate metabolized citrate and precipitated Sr as crystalline $SrCO_3$ due to the production of CO_2 from citrate metabolism. This study demonstrated the potential of Sr for microbial immobilization in contaminated environments.

^{90}Sr contamination is a major problem at several sites; at some, ^{90}Sr has migrated deep underground, thus complicating site remediation. A method based on mixing a solution of calcium citrate and sodium phosphate in soil was developed to immobilize ^{90}Sr in contaminated soils (Moore et al., 2004). As the indigenous soil microorganisms mineralize the citrate, calcium is released and forms hydroxyapatite. Treating soils with a sodium phosphate/calcium citrate solution results in the formation of hydroxyapatite with CO_3^{2-} substitutions, with a formula of $(Ca_{4.8}Na_{0.2})[(PO_4)_{2.8}(CO_3)_{0.2}]$ (OH). The average Sr uptake was 94.7% for soil treated with apatite; in desorption experiments, the apatite-treated soil released an average of 4.8% of it. These results show the potential of forming apatite in soil via soluble reagents for retarding radionuclide migration: injecting a Ca–PO_4–citrate solution (with a Ca–citrate solution complex); the *in situ* biodegradation of citrate resulting in apatite $[Ca_6(PO_4)10(OH)_2]$ precipitation and coprecipitation of ^{90}Sr in pore fluid and solids in the treatment zone; adsorption of ^{90}Sr by the apatite surface; apatite recrystallization with ^{90}Sr substitution for Ca (permanent); and the radioactive decay of ^{90}Sr to ^{90}Y to ^{90}Zr.

Studies also demonstrated that citrate biodegradation/apatite precipitation occur in several sediments, resulting in the sequestration of U, Tc, Sr, and Pb. The solids are initially amorphous; however, laboratory tests show that they age to form crystalline apatite in a period of several weeks.

9.5.7 Iodine biotransformation and remediation studies

Radioactive iodine (^{129}I) is a long-lived fission product produced in significant amounts in nuclear power reactors. It has a half-life of 1.57×10^7 years and will be present in radioactive wastes and on their storage in geological disposal facilities. Radioactive iodine is released into the environment from geological repositories, from spent nuclear-fuel reprocessing plants, and in accidents at nuclear power plants.

The predominant chemical forms of iodine (I_2) in the environment are iodide (I^-) and iodate (IO_3^-), both of which are highly soluble and mobile in the environment. Iodate is the most stable form of iodine in seawater. Iodate can be reduced to iodide in the surface waters of seas, and this reduction appears to be linked to biological activity. Major mechanisms that govern the iodine cycle are the atmospheric volatilization of organic iodine compounds, the accumulation of iodine in living organisms, the oxidation and reduction of inorganic iodine species, and the sorption of iodine by soil and sediments. Microorganisms are known to influence the chemical behavior of iodine through various processes, such as volatilization in the form of organic–iodine compounds (i.e., CH_3I), the oxidation of iodide (I^-) to iodine (I_2), the reduction of iodate (IO_3^-) to iodide (I^-), and via bioaccumulation (Amachi, 2008).

Incubating soil samples with varying levels of oxygen, water, and biomass levels demonstrated the immobilization of iodine. Pure cultures of bacteria and fungi isolated from the soil incorporate radioiodine (Bors & Martens, 1992). Sorption of radioiodine was higher in soils that contained organic substances or biomass compared to clay minerals; the sorption process was irreversible (Bors & Martens, 1992). Thus, growth and metabolic activities of microorganisms could have important effects on the mobility of iodine in the natural environment.

In terrestrial environments, iodine concentrations accumulated in soils at ~5 mg/kg worldwide, which is much higher than those of their parent materials, such as rocks and plants (0.05–0.5 mg/kg) (Amachi, Fuji, Shinoyama, & Muramatsu, 2005). Such high iodine accumulation in soils and sediments was attributed, at least in part, to microbial effects, although the mechanism of the accumulation process is not fully understood. Here, one possible explanation is that the iodide ion (I^-) is transported actively into the bacteria isolated from the marine sediment, which accumulate iodide >5000-fold (Amachi et al., 2005). Iodide adsorption by the Gram-positive soil bacterium *Bacillus subtilis* showed that positively charged single sites on the cell wall were responsible for iodide sorption on to the bacterial surface with a concentration of 3.54 ± 3.80 mmol iodide per gram of bacteria. The uptake and accumulation of iodide in washed cell suspensions of marine bacteria increased when glucose was added, whereas iodate was not accumulated by the bacteria (Amachi et al., 2005). The adsorption of iodine by unicellular green algae was reported (Shimura et al., 2012). Although a wide variety of terrestrial and marine bacteria have the potential for fixing iodine in the environment, there is very little information on the biochemical mechanisms of microbial transformations of iodine, and on the chemical speciation and stability of the bioaccumulated iodine in bacteria.

9.5.8 Uranium biotransformation and remediation studies

Uranium occurs naturally in the earth's crust and is present in ores as uraninite and pitchblende as ^{238}U (99.27%), ^{235}U (0.72%), and ^{234}U (0.005%). It also occurs in secondary mineral phases associated with silicates, phosphates, carbonates, and vanadates. Uranium exists in four oxidations states (VI, V, IV, III); of these U(VI) and U(IV) are the predominant forms in the environment. Widespread uranium contamination of soil and water has resulted from front and back ends of the nuclear-fuel cycle, and from weapons production, nuclear research, coal combustion, mining, and application of phosphate fertilizers. In oxic environments, uranium primarily exists as soluble uranyl (U(VI) species. In anaerobic environments, U(VI) is reduced to the less soluble immobile form U(IV). Microorganisms play a significant role in the biogeochemical cycling of uranium by oxidation–reduction reactions, and thus regulate the solubility and environmental mobility.

9.5.8.1 Uranium dissolution

Autotrophic and heterotrophic microorganisms are known to solubilize uranium and their potential has been investigated for extracting and recovering uranium from ores. The iron- and sulfur-oxidizing bacteria catalyze the dissolution of uranium from ores and mill tailings. *T. ferrooxidans* solubilizes uranium from ore by indirect action due to its generation of Fe^{2+}/Fe^{3+} and sulfuric acid (Munoz, Gonzalez, Ballester, & Blazquez, 1993). Ferric iron and manganese oxide also can facilitate the oxidative dissolution of precipitated U(IV) to U(VI). Heterotrophic microorganisms indirectly solubilize uranium by producing CO_2, sequestering agents such as siderophores and organic acid metabolites, as well as by lowering the pH of the medium (Francis, 1990).

9.5.8.2 Uranium immobilization

Soluble U(VI) is immobilized by facultative and strict anaerobes. They include dissimilatory metal reducers, sulfate reducers, and fermenters. The reduction of uranium was reported in axenic cultures of iron-reducing bacteria, fermentative bacteria, sulfate-reducing bacteria, cell-free extracts of *Micrococcus lactilyticus*, and in wastes by *Clostridium* sp.

$$\mathrm{U(VI)_{aq}} \xrightarrow[\text{Fermenters, sulfate reducers}]{\text{Dissimilatory metal reducers}} \mathrm{U(IV)_{s}}$$

Studies showed that the biological reduction of U(VI) also could result in the formation of mononuclear U(IV) phases associated with C/N/O-, P-, or S-containing ligands, but the exact nature of these mineral phases is unidentified.

Determining the nature of the chemical species, such as the oxidation states, the organic and inorganic complexes, and the mineralogical association of uranium in contaminated soils is important in assessing its long-term environmental mobility and stability. Several conventional techniques were used to determine the speciation of uranium, for example, hydrogen consumption, direct measurement of U(VI) in solution, conversion of insoluble species such as U(IV) to soluble U(VI) by acidification and oxidation, extraction from the aqueous phase using solvents, such as thenoyltrifluoroacetone, and the separation of U(VI) and U(IV) by ion-exchange resin. These methods are not reliable generally because they involve extensive sample preparation that can affect its oxidation state. X-ray spectroscopic techniques require very little manipulation of the sample and provide more accurate information on the oxidation state of elements than conventional methods. The speciation of uranium in microbial cultures has been followed by x-ray absorption near edge fine structure (XANES) and x-ray photoelectron spectroscopy (XPS) to show the reductive precipitation of soluble U(VI) to insoluble U(IV) by the anaerobic bacteria. Uranium was reduced only in the presence of growing or resting cells. Organic acid metabolites, the extracellular components of the culture medium, and heat-killed cells failed to anaerobically reduce uranium (Francis et al., 1994; Gao and Francis, 2008). The change in free energy for reducing manganese and iron was −83.4 and −27.2 kcal/mol CH_2O, respectively, and for reducing hexavalent uranium to the tetravalent state, the change was −63.3 kcal/mol, and to the trivalent state, it was 52.2 kcal/mol. Uranium reduction should occur in the sequence Mn(IV) > U(VI) > Fe(III).

Contamination of soil and groundwater by uranium has been observed at or near sites where it is mined or processed. Several bacteria are known to reduce U(VI), but our understanding of the biochemistry of this process is incomplete (Wall & Krumholz, 2006). The direct implication of microorganisms in the reduction of uranium is of considerable interest because of its potential application in bioremediating contaminated sites, in pretreating radioactive wastes, and in processes critical to the performance of nuclear-waste repositories. *In situ* and *ex situ* bioremediation strategies are based on the microbial reduction of soluble U(VI) to insoluble U(IV). Numerous studies demonstrated that such reduction of uranium (VI) to uranium (IV) in groundwater and aquifer sediments is a viable *in situ* bioremediation option for immobilizing uranium. These studies highlighted the fact that indigenous bacteria can reduce uranium present in the natural environment but that microbial activities are limited by the availability of suitable electron donors. Therefore, to stimulate the *in situ* microbial reduction of U(VI) to U(IV), electron donors such as acetate, ethanol, or lactate are injected at the contaminated sites.

9.6 *In situ* and *ex situ* immobilization of uranium by anaerobic bacteria

Immobilization or stabilization of radionuclides is accomplished by chemically or biologically converting them to insoluble and environmentally stable forms. Microbial reduction of soluble hexavalent U(VI) to a tetravalent form U(IV), such as the uraninite (UO_2) precipitate, is a promising technology to remediate uranium-contaminated groundwater and soil. Field studies revealed that U(VI) can be reduced and immobilized simply by amending the contaminated site with organic substrates, such as glucose or acetate. However, complete reduction of U(VI) to U(IV) may not be always possible due to the nature of the chemical form, the mineralogical association of uranium, and the conditions favorable for mediating the biogeochemical processes in contaminated sites.

Stabilizing uranium in wastes by enhancing anaerobic microbial activity was demonstrated by exploiting the unique metabolic capabilities of the dual-action anaerobic bacterium *Clostridium* sp. to solubilize and precipitate uranium in a sludge and sediment sample (Francis et al., 1991b). Sludge was collected from a uranium-process waste stream after the biodenitrification of nitric acid uranium waste water, and the sediment from a contaminated pond that received uranium-process waste water at the Y-12 Plant at Oak Ridge, Tennessee. Table 9.1 shows the chemical characteristics of the sediment and sludge samples. Both samples contained varying levels of the major elements, Al, Ca, Fe, Mg, K, and Na, and toxic metals, As, Cd, Cr, Co, Cu, Pb, Mn, Hg, Ni, U, and Zn. The concentrations of uranium in the sediment and sludge samples respectively were 920 and 3100 ppm. The sediment contained high levels of Cr, Cu, Mn, Hg, and Zn. In comparison, the sludge was high in Ca and low in Fe and Mn, and contained higher amounts of Cd, Cr, Pb, and Ni. In addition to those elements listed in Table 9.1, analysis of the sediment sample by x-ray fluorescence showed the presence of titanium, gallium, bromine, strontium, rubidium, yttrium, and zirconium. Selenium, a common element present in waste from uranium mining, was not detected in these samples. The sediment had a high ash content, and appreciable amounts of organic carbon and nitrogen; x-ray diffraction analysis showed high levels of SiO_2. The sludge was low in organic carbon and nitrogen but high in ash and sulfate; the latter resulted from adding sulfuric acid and ferric sulfate in the waste-treatment process.

Table 9.1 Characterization of Oak Ridge sediment and sludge samples

Constituents	Sediment	Sludge
Physical, %		
Moisture	60.8 ± 0.1[a]	56.7 ± 0.4
Ash	79.8 ± 0.0	65.3 ± 0.0
Chemical, % dry weight		
Carbon	12.0 ± 0.1	1.35 ± 0.0
Nitrogen	0.44 ± 0.0	0.12 ± 0.0
Sulfate sulfur	0.99 ± 0.03	2.57 ± 0.05
Major metals, % dry weight		
Aluminum	5.34 ± 1.8	5.21 ± 0.02
Calcium	3.21 ± 0.01	24.1 ± 1.2
Iron	4.66 ± 0.17	0.50 ± 0.01
Magnesium	1.05 ± 0.10	1.30 ± 0.09
Potassium	1.19 ± 0.02	0.05 ± 0.0
Sodium	0.09 ± 0.01	1.87 ± 0.04
Toxic metals, mg/gdw		
Arsenic	19.8 ± 2.3	1.3 ± 0.0
Cadmium	13.3 ± 0.1	93.5 ± 0.3
Chromium	421 ± 6	396 ± 9
Cobalt	81.3 ± 12.1	38.7 ± 10.5
Copper	394 ± 2	371 ± 1
Lead	195 ± 12	267 ± 18
Manganese	629 ± 9	244 ± 4
Mercury	342 ± 4	10.6 ± 1.1
Nickel	188 ± 2	1260 ± 5
Selenium	<1.0	<1.0
Uranium	647 ± 42	2700 ± 200
Zinc	1030 ± 40	1000 ± 30

[a] ±1 standard error of the mean.

Francis et al. (1991b), manuscript in preparation.

The mineralogical association of cadmium, chromium, copper, manganese, nickel, lead, uranium, and zinc in the sludge and sediment was determined by a selective extraction procedure (Francis et al., 1991a; Tessier, Campbell, & Bisson, 1979); Figure 9.1 shows these associations of uranium in the sludge and sediment. The inert (predominantly silicates) and the organic fractions respectively contained 301 and 293 μg/g of uranium, and the Fe–Mn oxide fraction contained 162 μg uranium/g dry wt. Nearly half of the total uranium (1600 μg) in the sludge was associated with the carbonate fraction (Figure 9.1). The association of uranium with other fractions was as follows: exchangeable, 400 μg; iron oxide, 216 μg; organic, 516 μg; and inert, 80 μg/g dry wt. Comparing the total uranium obtained by digesting the entire sample with the sum of the selective extractions showed good agreement within ±10% (±1 SEM).

Clostridia are ubiquitous in soils, sediments, and wastes, and could be very useful in pretreating and stabilizing uranium in radioactive wastes. To determine the anaerobic microbial transformations of uranium sludge and sediment, samples were incubated anaerobically with and without nutrients in an N_2 atmosphere. The unamended samples did not show significant microbial activity nor produced organic acid metabolic products. However, the amended samples showed an increase in total gas, CO_2, H_2, CH_4, and organic acids; pH was lowered by about 2.5 units. This change was due to the generation

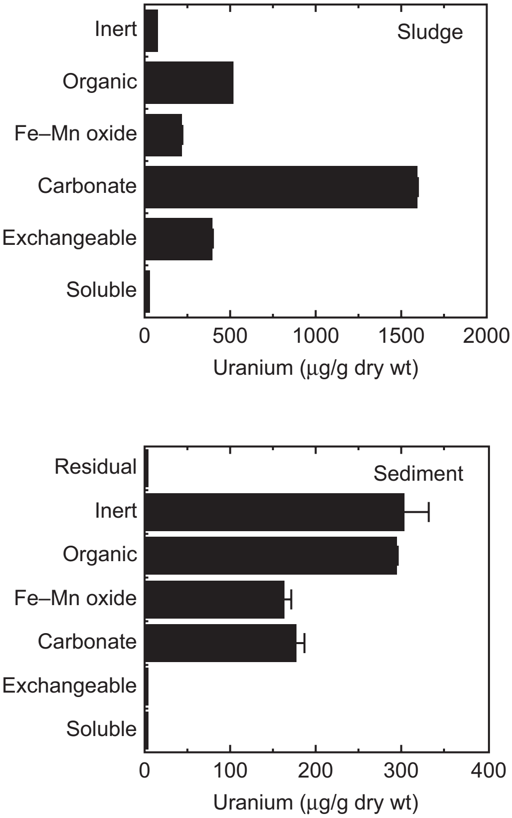

Figure 9.1 Mineralogical association of uranium in Y-12 sludge and sediment.

Francis et al. (1991b), manuscript in preparation.

of organic acid metabolites from glucose fermentation. The organic acids were acetic, butyric, propionic, formic, pyruvic, lactic, isobutyric, valeric, and isocaproic acids. A significant amount of gas was produced due to glucose fermentation by anaerobic bacteria, as well as from the dissolution by the organic acids of $CaCO_3$ in the sludge. A decrease in sulfate concentration was observed only in amended samples.

This treatment process removed a large fraction of soluble nontoxic metals, such as Ca, K, Mg, Mn^{2+}, Na, and Fe^{2+}, and enriched and stabilized Cd, Cr, Cu, Ni, Pb, U, and Zn with the remaining solid phase due to the direct and indirect actions of the bacteria (Francis et al., 1991a). Metals associated with the exchangeable, carbonate, and iron oxide fractions were solubilized indirectly via the production of organic acid metabolites, whereas dissolution of iron oxides and metals coprecipitated with iron oxides was due to direct enzymatic reduction of iron. The uranyl ion associated with the exchangeable, carbonate, and iron oxide fractions was released into solution by direct and indirect actions of the bacteria, and subsequently, was reduced enzymatically to insoluble U(IV) (Figures 9.2–9.4). XANES analysis of uranium in the untreated

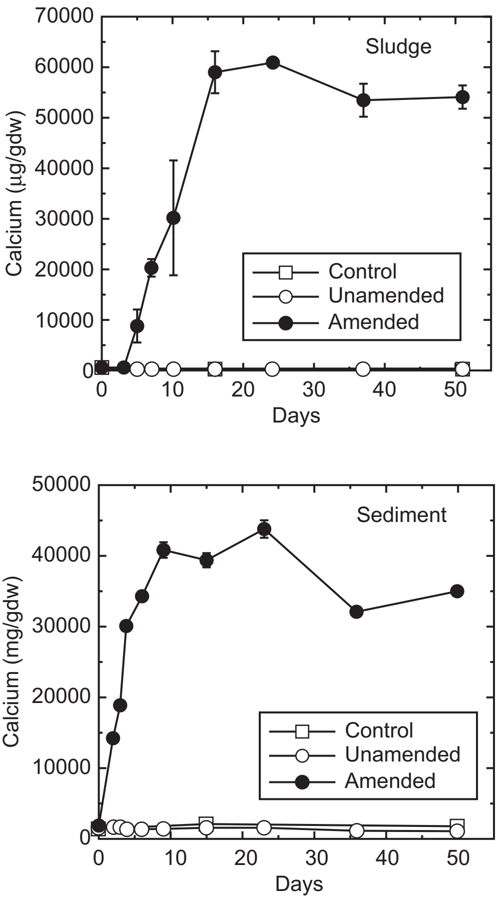

Figure 9.2 Dissolution of calcium from Y-12 sludge and sediment by indirect action of the bacteria due to production of organic acids and lowering the pH of the medium.

Francis et al. (1991b), manuscript in preparation.

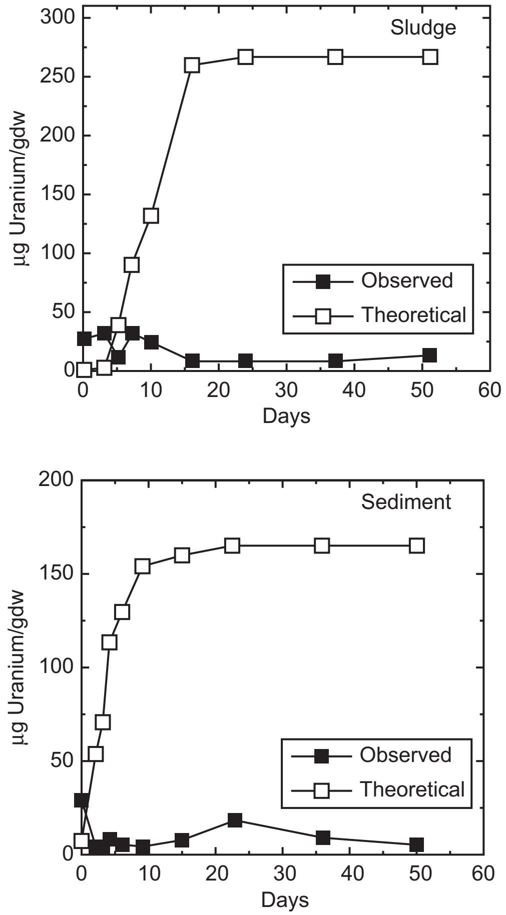

Figure 9.3 Dissolution and precipitation of uranium from Y-12 sludge and sediment. U(VI) associated with carbonate fraction is solubilized due to indirect action; with the iron oxide due to reductive dissolution of Fe(III) to Fe(II) and the released U(VI) is reduced to U(IV) by enzymatic action.

Francis et al. (1991b), manuscript in preparation.

(control), the treated sludge, and sediment samples showed the partial reduction of U(VI)→U(IV) in the sludge, and its complete reduction in the sediment (Figure 9.4). Uranium was predominantly associated with the carbonate fraction, and to a lesser extent, with the oxide, organic, and inert fractions; after microbial activity, its concentration increased for all three fractions. Analysis of the mineralogical association of the metals in the wastes after microbiological action showed that many of the metals were redistributed with stable mineral phases, such as the organic and silicate fractions (Figure 9.5). An overall reduction in the volume and mass of the waste after microbial action was apparent due to the removal of the bulk soluble nontoxic components from the waste, such as Ca, Na, and Fe.

This biotreatment process (Figure 9.6) can be applied to mixed wastes containing radioactive elements and toxic metals generated from defense, energy, and industrial operations wastes to chemically convert the radionuclides and toxic metals to more stable forms. Reducing the mass of the wastes means that more material can be stored or disposed of, can be handled easier, and can be transported. It also facilitates

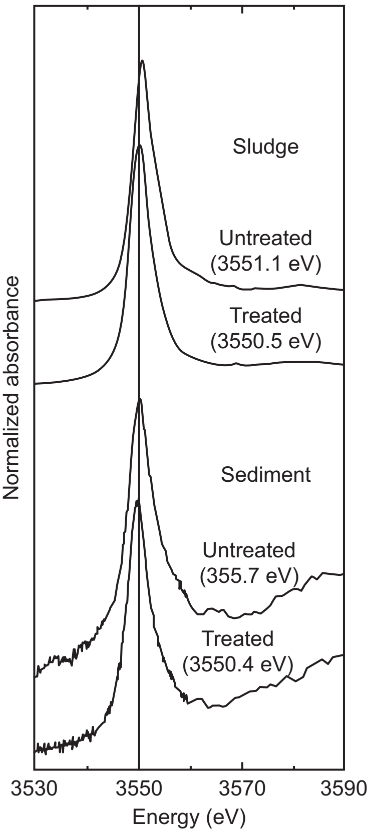

Figure 9.4 XANES analyses of the sludge and sediment from the Y-12 Plant, Oak Ridge, Tennessee, at the Mv edge before and after bacterial activity. The sludge contained 2070 ppm uranium and the absorption maximum for the untreated sample was 3551.1 eV, indicating that the uranium was predominantly in the hexavalent form. After bacterial treatment there was a shift in the absorption maximum to 3550.5 eV, which is slightly higher than that of tetravalent uranium (3550.4 eV), but much less than that of U(VI), indicating reduction to U(IV). The sediment contained 647 ppm of uranium and the untreated sample showed an absorption maximum at 3550.7 eV, which corresponds to a mixture of U(IV) and U(VI). The sediment was rich in organic matter and reducing. In the bacterially treated sample the peak shifted to 3550.4 eV, which was identical to that of U(IV), indicating that the uranium was reduced to the tetravalent form.

Dodge & Francis, manuscript in preparation.

changing the radionuclides and toxic metals to more stable forms so that the material can be processed chemically for disposal in shallow or deep geological formations.

9.6.1 Remobilization of uranium

Under anaerobic conditions, some host metal (hydr)oxides (e.g., Mn^{4+} and Fe^{3+}) can be reduced either chemically or enzymatically to soluble forms. Microbially mediated reductions play an important role in the biogeochemical cycles of metals, and can also lead to the remobilization of sorbed metals, such as Cd, Cr, Ni, Pb, and Zn to iron and manganese oxides (Francis & Dodge, 1990). Further, the remobilization of bioreduced U(IV) can be reoxidized to U(VI) by Fe(III) and Mn(IV) with the formation-soluble uranyl carbonate.

Although the U(IV) solids and U(VI)-bearing Fe or Al minerals are relatively stable, the presence of organic complexing agents and dissolved organic matter also may affect the long-term stability of uranium in contaminated sites. The bioreduced U(IV) precipitates can be oxidized and then subjected to dissolution or remobilization by various oxidants, such as dissolved oxygen, ferric iron, and nitrate, or through complexation by organic ligands. Naturally occurring organic ligands, such as siderophores, citrate, phthalates,

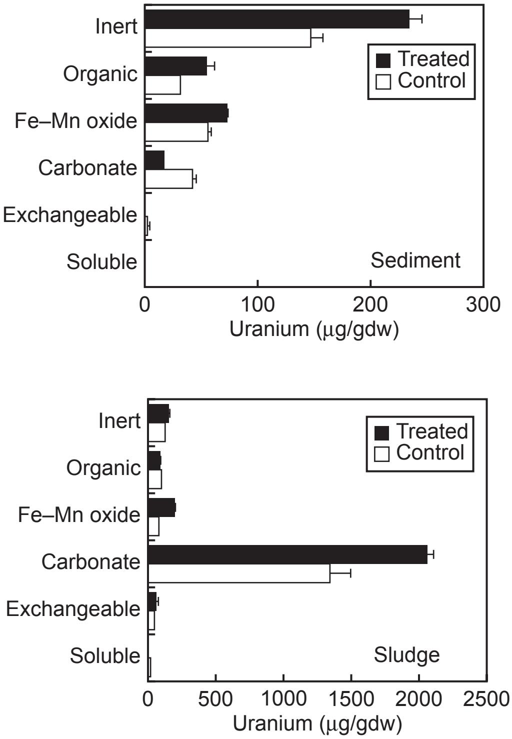

Figure 9.5 Mineralogical association of uranium in sediment and sludge before and after anaerobic microbial action.

Francis et al. (1991b), manuscript in preparation.

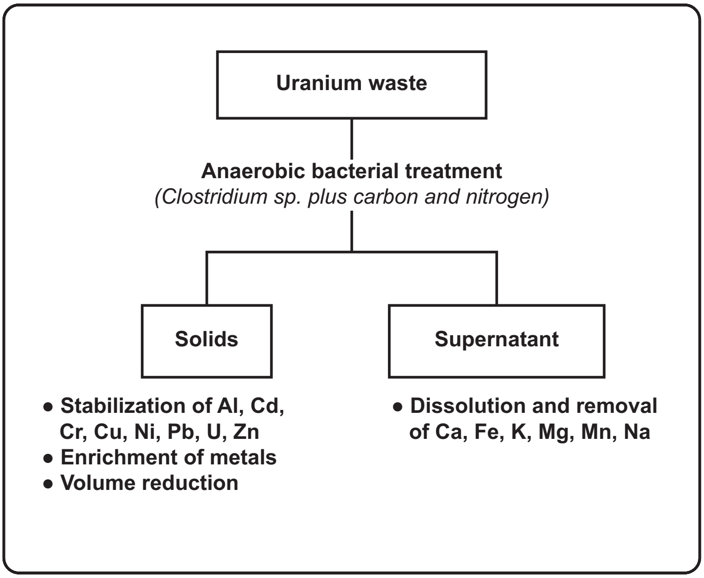

Figure 9.6 Stabilization of uranium in wastes, soils, and sediments by anaerobic bacterial treatment. Substantial amounts of bulk nontoxic elements Ca, Fe, K, Mg, Mn, and Na were solubilized from the waste, reducing the mass by ~20% in batch studies. Further reduction can be achieved by optimization of process parameters. Stabilization and reducing the volume reduce disposal costs.

Francis et al. (1991); Francis (1994).

humic substances, and synthetic chelating agents, such as EDTA, can mobilize both reduced U(IV) and oxidized U(VI) by forming soluble complexes. Remobilization of biologically immobilized U(IV) by naturally occurring organic ligands is a major concern in the long-term stability of uranium following *in situ* remediation (Francis & Dodge, 2008; Dodge & Francis, manuscript in preparation; Vazquez et al., 2009; Gu et al., 2005; Luo & Gu, 2009, 2011).

9.7 *Ex situ* remediation of uranium-contaminated soils, sediments, and wastes

For decontamination, radionuclides must be removed and recovered from the contaminated site, so that the site is restored. Various soil-washing techniques were developed, including physical methods, such as wet screening, attrition scrubbing, or chemical methods consisting of treating with organic and inorganic acids, salts, bases, and chelating agents. For example, the following chemicals have been used to extract radionuclides and toxic metals: nitric acid, hydrochloric acid, phosphoric acid, sulfuric acid, sodium carbonate, ammonium carbonate, sodium hydroxide, oxalic acid, citric acid, EDTA, and DTPA. Many of the inorganic chemicals used are corrosive, which irreparably damages the soil. Furthermore, all chemical extraction methods generate secondary waste streams that entail additional problems of hazardous waste disposal.

9.7.1 Bicarbonate extraction

Carbonate extraction of soils is an attractive procedure because U(VI) forms a very stable complex with carbonate $[UO_2(CO_3{}^{-2})_3{}^{-4}]$, and carbonate generates a waste stream with lower concentrations of secondary soil constituents consisting of iron, aluminum, calcium, and silica than acid extractions. Bicarbonate is environmentally benign and has no deleterious effects on the soil's structure.

A process for remediating and recovering uranium from contaminated soils was developed using bicarbonate extraction (Phillips, Landa, & Lovley, 1995). It consists of two steps: (1) extraction of uranium from contaminated soils using bicarbonate, and (2) reductive precipitation of U(VI) in bicarbonate extracts by sulfate-reducing bacteria *Desulfovibrio desulfuricans*. The extraction efficiency of bicarbonate ranged from 20% to 94% of the nitric acid-extractable uranium. However, the kinetics of uranium extraction by bicarbonate varied among ores, acid tailings, mixed tailings, and alkaline tailings. In the second step, uranium in the bicarbonate extracts was recovered as uraninite particles by dissimilatory microbial reduction of soluble U(VI)–carbonate complexes. Microbial reduction is more effective in removing uranium from bicarbonate extracts than physiochemical methods, such as ion exchange. The precipitated uranium recovered as uraninite is either reused or disposed of as waste. The bicarbonate extract is recycled to retrieve more uranium.

9.7.2 Citric acid extraction

Citrate is a naturally occurring organic complexing agent well known for its ability to form strong complexes with uranium (Rajan & Martell, 1965). It also is known to effectively remove metals from soils and wastes (Jackson, Lim, & Zelany, 1986). It is environmentally friendly, exhibits relatively consistent removal efficiency, and is cost-effective. Citric acid forms different types of complexes with the transition metals and actinides, and has been used to extract plutonium from contaminated soils (Nishita, Havg, & Rutherford, 1977), to decontaminate the components of nuclear reactors (U.S. Patent Nos. 4,839,1000; 4,729,855; 4,460,500; 4,587,043; 4,537,666; 3,664,870, and 3,103,909), and to extract metals and radionuclides, such as arsenic, barium, cadmium, cesium cobalt, copper, chromium lead, nickel, zinc, strontium, thorium, and uranium, from contaminated soils, wastes, and municipal solid-waste incinerator ash (Francis & Dodge, 1994; Francis, Mattus, Elless, & Timpson, 1993; Peters, Li, Miller, Patton & Martino, 1995).

A bisequential extraction procedure using citric acid in combination with dithionite followed by ammonium carbonate extraction with potassium permanganate removed uranium at levels of 450–540 mg/kg, to levels <50 mg/kg in Fernald soils. The first extraction is based on the citrate–bicarbonate–dithionite procedure, developed by Jackson et al. (1986) to remove sesquioxides from layer silicates. The basic principle is reducing the ferric oxides to ferrous forms, which weakens the crystalline characteristics of the mineral phase, and results in the reductive dissolution of ferric iron. Citrate is used to chelate the ferrous iron and prevent its precipitation. The bicarbonate maintains a pH (7.3) that favors a strong reducing environment created by adding dithionite, a strong reductant. The higher pH of this extraction environment also removes significantly less calcium and magnesium from dolomite and calcite (carbonate minerals) than citric acid or sulfuric acid. The second extraction (that uses ammonium carbonate and potassium permanganate) is intended to oxidize the remaining U(IV) to U(VI) to form the strong uranyl carbonate complex (Francis et al., 1993). In 4-h batch-type stirred reactor tests, citric acid extracted ~95% of uranium from Fernald's storage pad soil, and ~60% from incinerator site soil. The extraction of uranium from both soils by citric acid was highly dependent on pH; the most effective extraction occurred at a pH value of 4.

Citric acid is a good extractant because at low pH values it promotes the dissolution of carbonate minerals and iron and aluminum sesquioxide coatings on soil particles; i.e., the two mineral phases may act as contamination sites for uranium in soils. Consequently, large quantities of calcium, magnesium, iron, and aluminum are present in citric acid effluents, which make the removal of uranium more difficult and the disposal of the waste stream more voluminous and complex than extracting with carbonate.

Citric acid has several advantages over sulfuric acid leaching: (1) it biodegrades rapidly to carbon dioxide and water, making the treatment and disposal of the effluent more environmentally benign; (2) it is inexpensive, and even may be obtained as an industrial waste product; and (3) it offers a buffered system in contrast to sulfuric acid wherein the pH of the extraction suspension varies widely as the carbonates are neutralized.

9.7.3 Remediation of uranium contaminated soils and wastes by citric acid

In this process, uranium and toxic metals are extracted from wastes or contaminated soils with the complexing agent, citric acid. Then, the citric acid extract first is biodegraded to recover the toxic metals, followed by photochemical degradation of the uranium–citrate complex that is recalcitrant to biodegradation. The toxic metals and uranium are recovered in separate fractions for recycling or disposal. Using this combined chemical and microbiological treatment is more efficient than present methods and should result in considerable savings in the costs of cleanup and disposal.

9.7.3.1 Metal citrate complexes

Citric acid, a natural organic compound, is a multidentate ligand that forms stable complexes with various metal ions (Glusker, 1980; Rajan & Martell, 1965). The type of complexes it forms is shown in Figure 9.7. The biodegradation of these complexes depends on the type of metal complex formed with citrate; bidentate ones readily are biodegraded whereas the tridentate and binuclear complexes are recalcitrant (Francis, Dodge, & Gillow, 1992).

9.7.3.2 Biodegradation of metal–citrate complexes

The rate and extent of biodegradation of several metal–citrate complexes by microorganisms varies. For example, *Pseudomonas pseudoalcaligenes* degraded

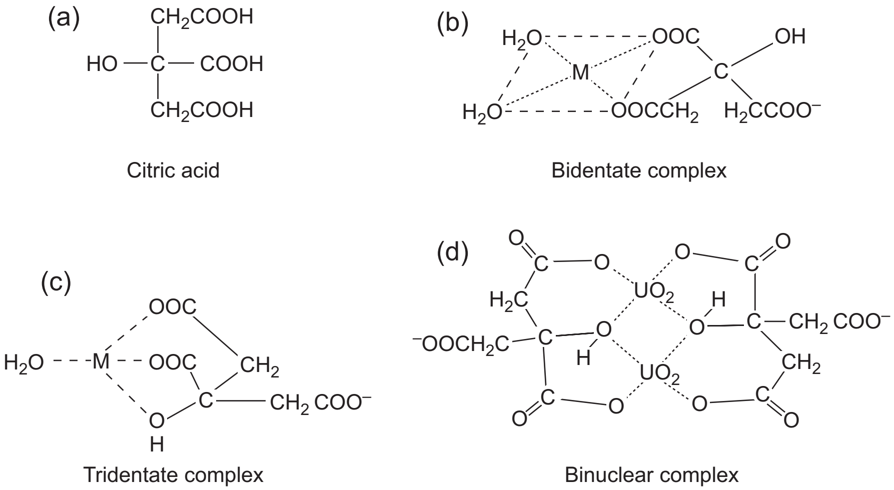

Figure 9.7 Metal citrate complexes. (a) Citric acid, a natural organic compound capable of forming different types of complexes with metals. It forms (b) bidentate, (c) tridentate, (d) binuclear, and polynuclear complexes depending on the metal.
Francis et al. (1992).

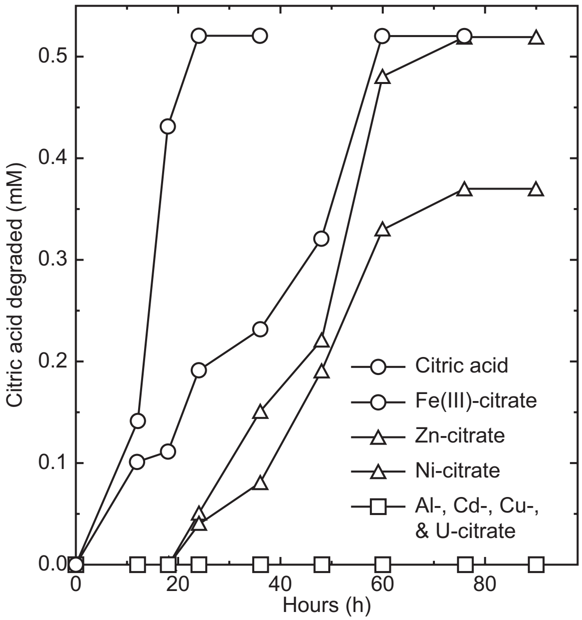

Figure 9.8 Biodegradation of metal–citrate complexes by *Pseudomonas fluorescens*. Biodegradation is influenced by the type of complex formed between the metal and the citric acid. Bidentate complexes (Ca–, Fe(II)–, Ni–, Zn–citrate) are readily degraded. Tridentate (Cd–, Cu–citrate), binuclear (U–citrate), and polynuclear (U–citrate) species are recalcitrant. Francis et al. (1992); Joshi-Tope and Francis (1995).

Mg–citrate at a much lower rate than Ca–, Fe(III)–, and Al(III)–citrate (Madsen & Alexander, 1985). Studies with a *Klebsiella* sp. showed that citric acid and Mg–citrate were readily degraded, whereas Cd–, Cu–, and Zn–citrate were resistant (Brynhildsen & Rosswall, 1989). Both studies also revealed that metal toxicity was not responsible for the lack of, or the lower rate of degradation of certain metal–citrate complexes but offered no other explanation. Biodegradation studies with *P. fluorescens* showed that bidentate complexes of Fe(III)–, Ni–, and Zn–citrate were readily biodegraded, whereas complexes involving the hydroxyl group of citric acid, the tridentate Al–, Cd–, and Cu–citrate complexes, and the binuclear U–citrate complex were not (Francis et al., 1992; Figure 9.8). The presence of the free hydroxyl group of citric acid is the key determinant in effecting such biodegradation. The lack of degradation was not due to their toxicity, but was limited by the transport and/or the bacterial metabolism of the complex. No relationship was observed between biodegradability and stability of the complexes. The tridentate Fe(II)–citrate complex, although recalcitrant, was readily biodegraded after oxidation and hydrolysis to the bidentate Fe(III)–citrate form, denoting the structure–function relationship in the metabolism of the complex (Francis & Dodge, 1993). Although uranyl citrate was recalcitrant to biodegradation it was readily photodegraded by light (Dodge and Francis, 1994; Figure 9.9).

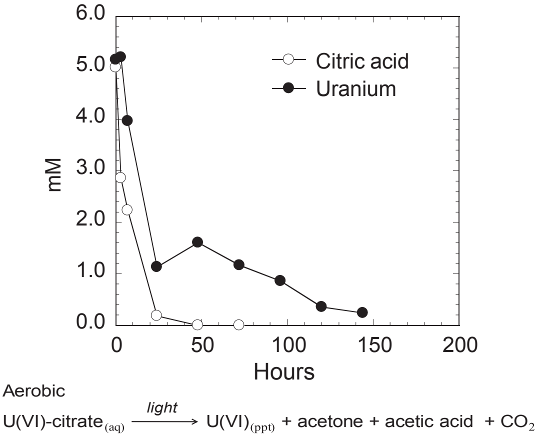

Figure 9.9 Photodegradation of the 1:1 U–citrate complex. Exposure of uranyl citrate complex to visible light (400–700 nm) showed photodegradation of citric acid to acetic acid and carbon dioxide, with precipitation of uranium as uranium trioxide ($UO_3 \cdot 2H_2O$).

Dodge and Francis, 1994.

9.7.3.3 The citric acid process

Although citric acid is an effective chelating agent for removing metals and radionuclides from contaminated soils, the ultimate disposal of the citric acid–metal extract is a concern. Francis and Dodge (1994) developed a process to recover the metals and radionuclides from the extract (Figure 9.10), in which the extract undergoes microbiological degradation, followed by photochemical degradation under aerobic conditions. Several metal–citrate complexes are readily biodegraded, and the metals are recovered in a concentrated form, along with the bacterial biomass. Uranium that forms a binuclear complex with citric acid is not biodegraded. The supernatant containing this complex is separated, and on exposure to light, it rapidly degrades, forming an insoluble, stable polymeric form of uranium. Uranium is recovered as a precipitate ($UO_3 \cdot 2H_2O$) in a concentrated form for recycling or for disposal (Figures 9.9 and 9.10). This treatment process, unlike others which use alkaline or acidic reagents, does not create additional hazardous wastes for disposal, and causes little damage to the soil that then can be returned to normal use.

9.7.3.4 Extraction of radionuclides and metals from soils and wastes

Uranium-contaminated soil samples were obtained from the Fernald site in Ohio, the RMI site, Ahstabula, Ohio, and uranium-contaminated sediment and sludge samples from the West End Treatment Facility, at the U.S. Department of Energy, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; they were analyzed for total uranium, mineralogical association, and speciation. The concentrations of U in the soils varied from 473 to 1880 ppm (Table 9.2). RMI soils also contained Tc.

Ten grams of soil or sludge from the Oak Ridge Y-12 plant containing uranium was extracted with 100 mL of 0.4 M citric acid for 5 h in the dark. The citric acid extract and the solids were separated and analyzed for metals. In this sample, aluminum, beryllium, cobalt, chromium, manganese, nickel, antimony, tin, zinc, and zirconium were extracted with >50% efficiency; uranium and thorium were extracted

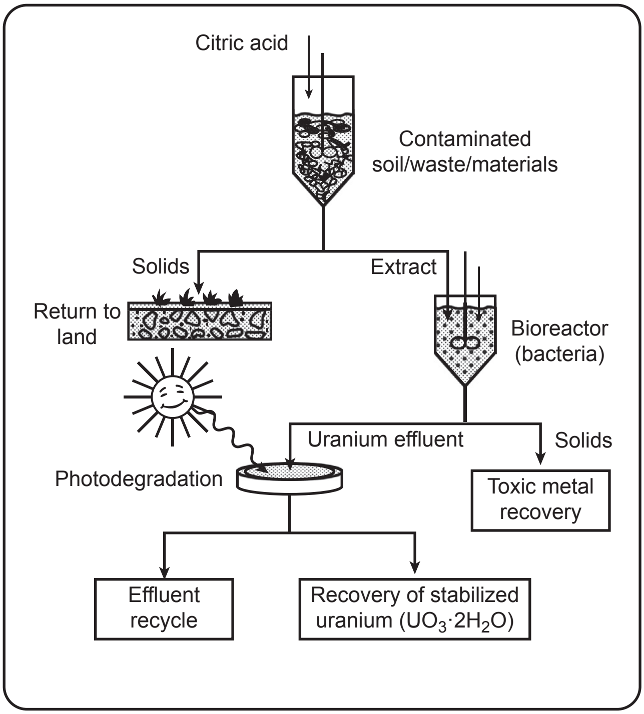

Figure 9.10 Citric acid process for treating uranium- and toxic metal-contaminated soils, sediments, and wastes.
Francis and Dodge (1994, 1998).

with 87% and 94% efficiency, respectively. Silver, copper, lead, and vanadium were not extracted, probably due to the type of their association with stable mineral phases (Francis, 1998). For example, copper predominantly was associated with the organic fraction and a small amount with the iron oxide and inert fractions. Table 9.2 lists the efficiency of extraction of uranium from Oak Ridge Y-12 plant sludge and sediment, and various soils from the Fernald and RMI sites, Ohio.

9.7.3.5 Biodegradation of citric acid extracts containing metals

Citric acid extracts were amended with 0.1% NH_4Cl, K_2HPO_4, and KH_2PO_4, the pH was adjusted to 6.5, and the extract was inoculated with a culture of *P. fluorescens* (ATCC 55241). The bacteria degraded citric acid at a rate of 0.5–0.7 mM/h; there was little change in concentration of uranium, suggesting that the uranium–citrate complex was not biodegraded (Figure 9.11(a–d)). Other metals present in the extract, viz. Al, Ba,Ca, Fe, Cu, Mn, Ni, Pb, Sr, Ti, and Zn, were removed from it through the biodegradation of their respective citrate complexes, or precipitated from solution due to changes in the pH as a result of citrate degradation and were recovered along with the biomass (Figure 9.12).

Table 9.2 **Analyses of contaminated soils and wastes and extraction of uranium by citric acid**

Sample	Technetium (pCi/g)	Uranium (ppm)	Citric acid (M)	Uranium extracted (%)
Ashtabula, OH				
RMI No. 27117	120 ± 7[a]	1880 ± 20	0.5	83
RMI No. 27227	109 ± 15	698 ± 19	0.5	64
RMI No. 27230	144 ± 47	725 ± 38	0.5	69
Fermco, OH				
Soil No. 4 02585	NA	473 ± 10	0.5	86
Storage pad soil[b]	NA	450	0.4	99
Y-12 plant, Oak Ridge, TN				
Sludge	NA	2410	0.4	87
Pond sediment	NA	920	0.1	33

NA = not analyzed.
[a] = ±1 standard error of the mean.
[b] Data from C.W. Francis et al. (1993).
Francis and Dodge (1998), unpublished results.

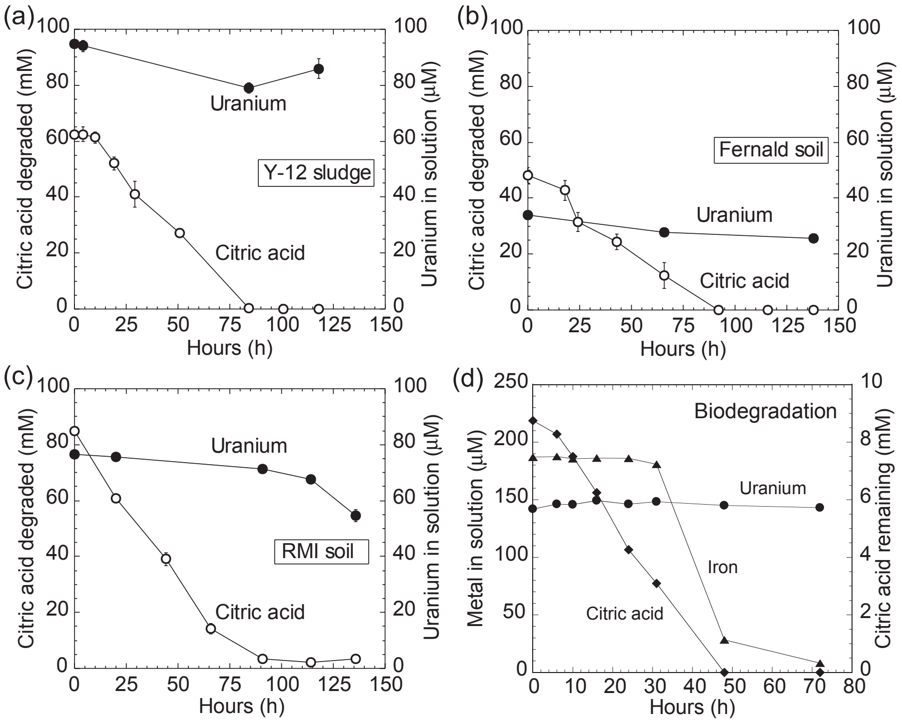

Figure 9.11 (a) Biodegradation of sludge citric acid extract (*Francis & Dodge, 1994, 1998*). (b) Biodegradation of citric acid extract of Fernald soil (*Francis & Dodge, 1994, 1998*). (c) Biodegradation of RMI Soil citric acid extract (*Francis & Dodge, 1994, 1998*). (d) Biodegradation of citric acid decontamination solution of uranium-contaminated steel (*Francis et al., 2005*).

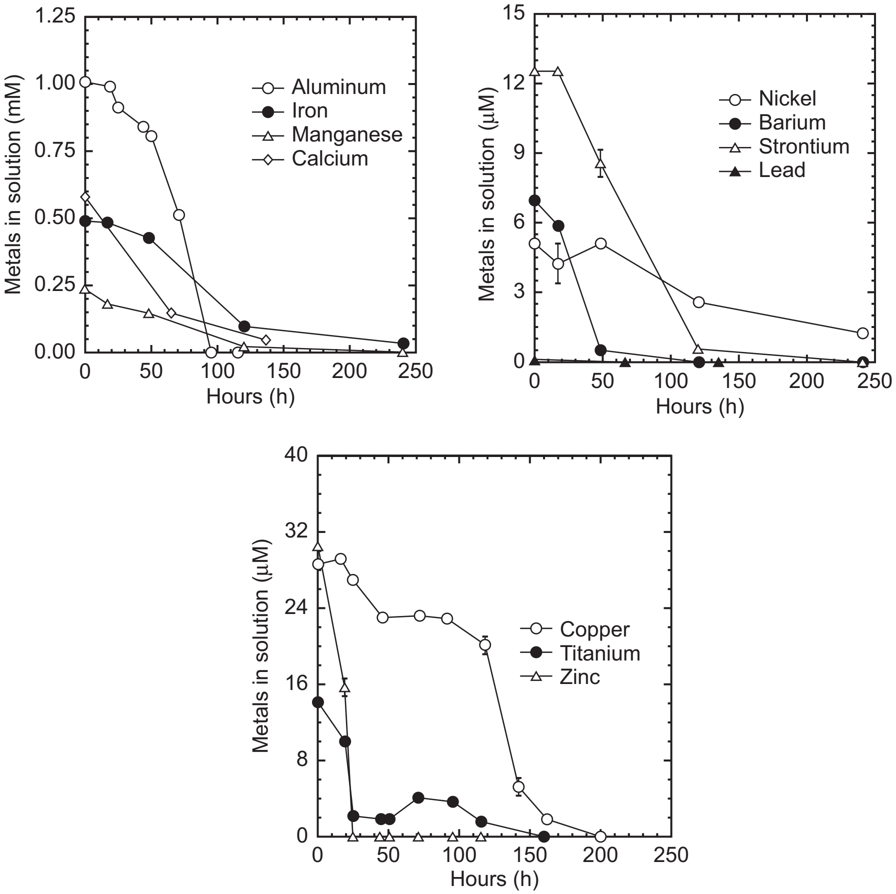

Figure 9.12 Fate of other metals during the biodegradation of the citric acid extract from sludge.

Francis and Dodge (1994, 1998).

9.7.3.6 *Photodegradation of uranium–citrate extracts*

The pH of the supernate from the biodegradation treatment primarily containing the uranium–citrate complex was adjusted to pH 3.5 with HCl, and then exposed under high-output fluorescent growth lights to degrade the complex and recover uranium (Figure 9.13). The uranium precipitated out of solution as a polymer soon after it was exposed to light; after 50 h, ~85% of the uranium was removed. The uranium precipitate was identified as ($UO_3 2H_2O$) by EXAFS (Figure 9.14). The uranium precipitate was almost insoluble at near-neutral pH, but soluble in acidic pH (<3.5). The solids remaining after extraction with citric acid were washed with deionized water and dried in an oven overnight at 105 °C to determine the weight loss due to removing the citric acid. Extracting the metals from the waste reduced its weight by 47%. These results show that (1) uranium was extracted from the mixed waste with >85% efficiency using

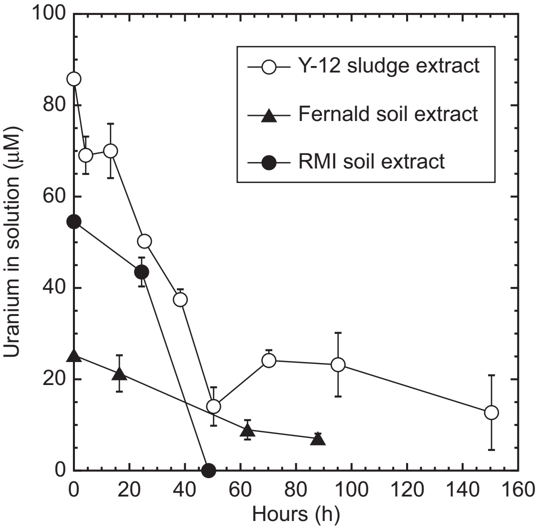

Figure 9.13 Photodegradation of uranyl citrate in citric acid extracts after the biodegradation of citric acid and metal citrates.

Francis and Dodge (1994, 1998).

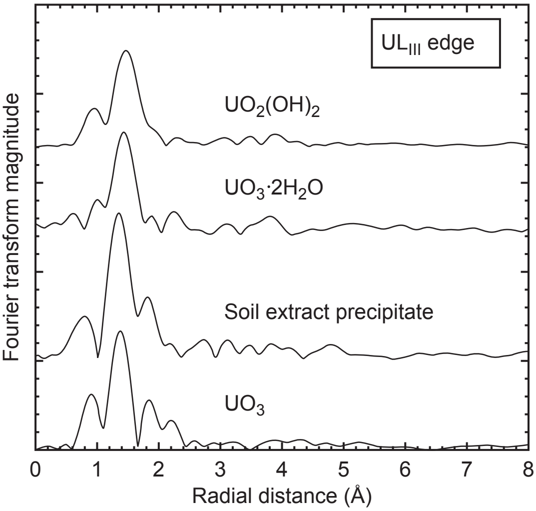

Figure 9.14 Extended x-ray absorption fine structure (EXAFS) spectrum of uranium precipitate (schoepite) recovered from the photodegradation of citric acid soil extract after biodegradation.

Francis and Dodge (1998).

0.4 M citric acid; (2) other metals such as chromium, cobalt, manganese, nickel, strontium, thorium, zinc, and zirconium also were extracted; (3) the uncomplexed excess citric acid and several metal–citrate complexes (Co, Ni, Zn, and Zn) except the binuclear uranium–citrate complex were readily biodegraded by *P. fluorescens*, and the metals were recovered with the bacterial biomass; and (4) the uranium–citrate complex was photodegraded, allowing the uranium to form a polymer that was recovered as a concentrated solid. Thus, the toxic metals and uranium are recovered separately in a concentrated form for recycling or for disposal.

This process has significant potential applications: (1) it can be applied to a variety of materials and waste forms; (2) mixed waste is separated into radioactive and hazardous wastes; (3) uranium is separated from the toxic metals and recovered for recycling or disposal; (4) it does not generate secondary-waste streams; (5) it causes little damage to the soil; and (6) environmentally and economically important metals are removed in a concentrated form. Using combined chemical, photochemical, and microbiological treatments of contaminated materials will be more efficient than the present methods and result in considerable savings in the costs of cleanup and disposal.

9.7.4 **In situ** ***leaching***

In situ soil flushing is used to mobilize metals by leaching the contaminants from soils so that they can be extracted without excavating the contaminated materials. An aqueous extracting solution is injected into, or sprayed onto, the contaminated area to solubilize and mobilize the contaminants. The extractant can be applied by surface flooding, sprinklers, leach fields, vertical or horizontal injection wells, basin infiltration systems, or trench infiltration systems. After coming into contact with the contaminated material, the extractant solution is collected using pump-and-treat methods for its disposal or its treatment and reuse. Extracting agents used for *in situ* soil flushing and washing include acids/bases, chelating agents (oxalate, citrate, EDTA, DTPA), oxidizing/reducing agents, and surfactants/cosolvents. Water alone can be used to remove water-soluble contaminants. The applicability of *in situ* soil flushing technologies to contaminated sites will depend largely on site-specific conditions, such as hydraulic conductivity, that influence the ability to contact the extractant with contaminants, and to effectively recover the flushing solution with collection wells.

9.7.4.1 In situ *leaching of uranium*

Conventional mining involves removing mineralized rock (ore) from the ground, breaking it up, and treating it to remove the minerals. *In situ* leaching (ISL), also known as solution mining, or *in situ* recovery, involves leaving the ore where it is in the ground, and recovering the minerals from it by dissolving them, and then pumping the pregnant solution to the surface where the minerals are recovered. Consequently, there is little surface disturbance and no tailings or waste rock are generated. However, the ore body must be permeable to the liquids used, and located such that the liquids do not contaminate the groundwater away from the ore body. ISL can also be applied to other minerals, such as copper and gold, for uranium- and other radionuclide-contaminated soils. ISL techniques were developed where it is a controllable, safe, and environmentally benign method of mining, operating under strict operational and regulatory controls. Due to the low capital costs (relative to conventional mining), it often proves to be an effective method of mining low-grade uranium deposits.

9.7.4.2 Uranium recovery

The native groundwater from the host aquifer initially is extracted by submersible pumps, after which uranium complexing reagents (acid or alkaline) and an oxidant (hydrogen peroxide or oxygen) are injected into the well field. The leach liquors pass through the ore to oxidize and dissolve the uranium minerals *in situ*. Depending on the type of leaching environment, the uranium will be complexed as uranyl sulfate, predominantly $UO_2(SO_4)_3{}^{4-}$ under acid leach conditions, or a uranyl carbonate, predominantly $UO_2(CO_3)_3{}^{4-}$, in a carbonate leach system. This then is precipitated with an alkali, e.g., as sodium– or magnesium–diuranate. In either case, the pregnant solution from the production wells is pumped to the treatment plant where the uranium is recovered in a resin/polymer ion-exchange system, or liquid-ion exchange one (World Nuclear Association, UK).

9.8 Plutonium biotransformation and remediation studies

Plutonium occurs in several oxidations states, i.e., Pu(III), Pu(IV), Pu(V), and Pu(VI) in the environment, and its solution chemistry is very complex. However, Pu(IV) is the predominant, most stable form in contaminated soils. Due to high ionic charge, it can undergo hydrolysis and convert to a polymeric form at $pH>2$. Although Pu is considered relatively immobile, its transport was observed at several DOE sites, even at very low concentrations. The chemical speciation of Pu can be influenced by the soil's pH, redox conditions, organic content, mineralogy, and microbial activities (Francis, 2007). The chemical form of Pu varies in contaminated sites, and is dependent on environmental conditions prevailing there, and on the waste stream. $PuO_2(s)$ was the predominant form at Rocky Flats, Colorado (Clark, Janecky, & Lane, 2006), whereas Pu was associated with mineral or organic colloids at the Nevada Test Site and Rocky Flats site (Kersting et al., 1999; Xu et al., 2008). Microbial activities affect redox conditions, and thus, the oxidation state of Pu in the environment (Neu et al., 2005). Information is limited on the influence of microbes on the solubility of Pu (Deo & Rittmann, 2012; Deo et al., 2011). The bacterial reduction of Pu(VI) and Pu(V) to Pu(IV) was shown to immobilize soluble Pu. The microbial reduction of Pu(VI/V) potentially can produce a highly insoluble form of Pu(IV). However, amorphous Pu(IV) can be further reduced anaerobically to the more soluble Pu(III) by *Clostridium* sp. (Francis et al., 2008); by *B. subtilis* in the presence of the chelating agent NTA (Rusin et al., 1994); and by *Geobacter metallireducens* and *Shewanella oneidensis* with EDTA (Boukhalfa et al., 2007).

Francis, Dodge, and Ohnuki (2007) detailed the aerobic biotransformation of Pu(IV)–citrate by *P. fluorescens,* finding that citrate was degraded rapidly while a polymeric form of Pu(IV) formed. Adding Pu(VI) to *B. subtilis* cells and kaolinite clay engendered the formation and association of Pu(IV) predominantly with bacterial cells (Ohnuki et al., 2007). The reductive transformation of Pu(VI) to Pu(IV) was observed only in the presence of *B. subtilis* cells; kaolinite clay alone did not cause any changes in the oxidation state of Pu. The remobilization of Pu and other radionuclides was observed in Pu-contaminated soils from the Nevada Test Site caused by enhanced microbial activity under aerobic and anaerobic conditions and affected the concentration of Pu in the solution phase (Francis et al., 2007).

9.8.1 *Effect of microbial activity on Pu mobilization from contaminated soils*

The characterization of Pu at contaminated sites shows that its environmental form varies according to the site and the waste stream. For example, at Rocky Flats, Colorado, the predominant form appears to be as $PuO_2(s)$, while, at the Nevada Test Site (NTS), Pu was associated with mineral oxides; at Oak Ridge, Tennessee, it is associated with organic matter. Pu generally is considered to be relatively immobile; however, its transport to varying distances in low concentrations as colloids was observed at Rocky Flats, Los Alamos National Laboratory, and the NTS. Plutonium in surface waters at the Rocky Flats site was associated with organic macromolecules. Studies with Pu-contaminated soils show that Pu and other radionuclides are remobilized due to enhanced aerobic or anaerobic microbial activity (Francis and Dodge, unpublished results). Several bacteria and fungi grown in the presence of Pu produced extracellular Pu complexes that raised the concentration of Pu in soil-column eluates relative to that of the controls. Elution through soil effectively removed positively charged Pu complexes. The increased mobility of Pu in soil reflected the formation of neutral and negatively charged Pu complexes. In the presence of known microbial metabolites and synthetic ligands (i.e., DTPA, EDTA, and EDDHA), Pu(VI) was reduced to Pu(IV) before complexation, suggesting that the latter valence state would be the dominant one associated with organic complexes in soils.

9.8.2 *Characterization of Pu in contaminated soil*

Plutonium contaminated soil (HP-11) obtained from Area 11 soil of the Double Track test shot area at the NTS had a gross activity of 50 nCi/g. The individual alpha components of the total activity were determined and are given in Table 9.3. The beta-emitter Pu-241 also was detected but not quantified. The minerals present in the soil were determined using μ-x-ray diffraction on beamline X7A at the National Synchrotron Light Source; the predominant ones were various forms of iron oxides and aluminosilicates. The uranium was present in the soil as a hexavalent form associated with the minerals schoepite ($UO_3{\cdot}2H_2O$) and liebigite ($Ca_2UO_2(CO_3)_3{\cdot}11H_2O$).

9.8.3 *Mobilization of Pu, Am, and U in NTS soil due microbial activity*

Figure 9.15 illustrates the effect of bacterial activity on the mobilization of radionuclides in NTS soil. Under anaerobic conditions, glucose was metabolized with a decrease in pH to 4.8 and an increase in alpha activity in solution. However, the appearance of the actinide in solution was concomitant with the decrease in pH (Figure 9.15). In addition, the alkalinity of the soil suggests that its mobilization may be due to the dissolution of carbonate species present in the soil.

Adding citric acid to the soil showed the metabolism of citric acid and an increase in both alpha and beta activity in solution. However, with time there was a sudden decrease in alpha and beta activity (data not shown) that coincided with the complete

Table 9.3 Alpha activity and concentration in NTS soil

	NTS soil	
Isotope	**(nCi/g)**	**(μg/g)**
U 233/234	<0.18	$<6.1\times10^{-2}$
U 235/236	<0.15	$<3.6\times10^{1}$
U 238	<0.14	$<4.2\times10^{2}$
Am 241	3.8 ± 0.7	1.1×10^{-3}
Pu 238	0.44 ± 0.02	2.6×10^{-5}
Pu 239/240	69.2 ± 6.5	1.1×10^{-1}
Total	<75	ND

ND = not determined.
Francis and Dodge, manuscript in preparation.

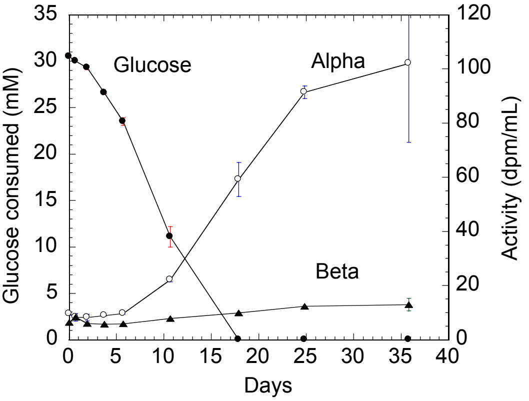

Figure 9.15 Mobilization of actinides due to microbial activity.
Francis and Dodge, unpublished results.

utilization of citric acid by the bacteria. There was only a slight decrease in pH to 7.7 in the bacterially active sample. This observation suggests that citric acid forms a soluble complex with the actinide, and that its removal due to bacterial metabolism releases the actinide that then is precipitated. These results also suggest that the type of carbon source will have a different effect on microbial mobilization of actinides.

9.9 Summary

Microorganisms play a major role in the environmental mobilization and immobilization of radionuclides. Such microbial processes are being exploited to extract or stabilize radionuclide-contaminated soils. However, the biochemical mechanisms of biotransformation of the various chemical forms of radionuclides found in contaminated soils are not fully understood, and consequently, *in situ* or *ex situ* bioremediation of contaminated soils has not been deployed. Based on our current understanding of uranium biogeochemistry, it appears that microbial reductive precipitation of uranium is an attractive *in situ* bioremediation process that can be developed further provided that reducing conditions can be maintained to limit the reoxidation and remobilization of sequestered uranium. Alternatively, extracting uranium from contaminated soils by carbonate or citric acid is a potentially promising *ex situ* process that was validated in laboratory and batch studies. The microbially induced calcite precipitation of strontium via bacterial ureolysis as an *in situ* process was demonstrated in laboratory- and simulated field-scale studies. The short half-life of ^{90}Sr (29 years) and the long-term stability of calcite make this coprecipitation process very attractive for sequestering the radionuclide that it would permit sufficient time for radioactivity to decay.

Acknowledgments

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Physical, chemical, and biological treatment of groundwater at contaminated nuclear and NORM sites

10

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10.1 Introduction

Many different treatment processes can potentially be used to remove radionuclides from groundwater. The specific radionuclides that need to be treated will determine which treatment processes are feasible to meet a given discharge limit. All of these treatment processes were originally developed to remove non-radioactive contaminants, such as heavy metals and toxic organics. Most of the information about design and operation of these processes that was developed for the common contaminants can be directly applied to treating radionuclides. One important consideration is that the radionuclides are normally present at much lower concentrations than are other contaminants. The performance of many of the treatment processes are concentration dependent, such as the solubility limit during precipitation or the loading on ion exchange resins. In some cases, the concentration of natural, non-radioactive isotopes of contaminant radionuclides will be much higher than the radionuclide concentration and will determine the performance of the treatment process. The details of a wide variety of treatment processes are described in this chapter, and then the application of the processes to specific radionuclides is described.

10.2 Physical treatment methods

Physical treatment processes for groundwater include filtration, reverse osmosis (RO), and air stripping. These processes are routinely used for treatment of traditional contaminants (heavy metals, toxic organics, etc.) from groundwater and process wastewaters, so equipment and methods of design and operation are readily available, and can, in most cases, be directly applied to treatment of radionuclides.

10.2.1 Filtration

Filtration is the removal of solid particulates from a liquid using porous media, including porous membranes (surface filters) of various types, or beds (columns) of solid particles (sand, anthracite, garnet, etc.), also called depth filters or media filters.

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Membrane filters can be single sheets (typically used in laboratory applications) or cartridges formed from sheets (pleated or spiral wound). The filter membranes are manufactured to have specific pore sizes, to remove particles, molecules, or ions down to a given size, for example 50, 0.5, or 0.05 μm. The smaller pore size filters will remove more particles but typically plug faster. The most common filter membranes, called particle filters, range down to about a 10-μm pore size. Microfilters range from 0.1 to 10 μm in pore size, whereas ultrafilters range down to about 0.01 μm. All of these filters remove particulates, or very large molecules in the case of ultrafilters, whereas RO filters (described below) remove dissolved ions. Membrane filters are normally discarded after they plug. Depth filters are normally backwashed to remove accumulated particles and used for multiple cycles. Depth filters can use a single size of medium or two or more sizes. Smaller media sizes will remove smaller particulates from the water, but depth filters do not have a sharp cut-off size like membranes do. Using two or more sizes of media can increase the time between backwashes by spreading the particles removed from the water through more of the media depth. Larger media sizes are used in the top part of the bed, with smaller sizes on the bottom. In order to maintain the correct size distribution after backwashing, the larger media need to have a lower density than the smaller sizes. A typical arrangement would be to have larger particles made from anthracite and smaller particles made from sand, called a dual-media filter column. After backwashing, the smaller sand particles settle faster and end up in the bottom of the column again, whereas the larger anthracite particles end up on top of the sand.

For treating groundwater, particulate filters would typically be used as a pretreatment step prior to another treatment process, such as RO or ion exchange treatment, or as the final treatment step in a precipitation process, to remove any precipitated solids that escape the clarifier. A filter by itself would not normally be capable of adequately treating groundwater to remove radionuclides, although some radionuclides will sorb to particulates in the contaminated groundwater and be removed by a filter.

10.2.2 Reverse osmosis

RO uses a very fine pore size (<0.001 μm) filter to retain ionic contaminants while allowing the water to pass through. The RO filter elements can be spiral-wound membranes, hollow fibers, or tubes. Osmosis is a natural process that causes water or ions to diffuse from areas of high concentration to areas of lower concentration. RO uses pressure to move water in the opposite direction, from an area of low water concentration (the retentate, which contains a higher concentration of ions), through an RO filter, to an area of higher water concentration (permeate, which is purer water). The pressure applied across the RO filter must be sufficient to overcome the osmotic pressure, due to the concentration gradient, plus overcome the resistance of the filter membrane. The RO filter retains essentially all of the ions, so it is not selective for radionuclides or other contaminants that must be treated, but also retains the common ions in groundwater, such as calcium and magnesium. The common ions, which are normally present in much higher concentrations than other contaminants, will usually control the osmotic pressure.

The increasing concentration of the common ions in the retentate, as water is pushed through the RO filter, can lead to precipitation, which can plug the filter membrane. Precipitation, also called scaling, must be controlled to protect the membrane. Possible control measures include acidifying the water, precipitating the ions prior to RO treatment, adding anti-scaling chemicals, or combinations of these treatments. Keeping the feed water slightly acidic can assist in preventing scaling; however, the membranes can be damaged by too low a pH, so controlling the pH of the feed water in the range of 4.5–5.5 is typical (Eckenfelder, 1989, p. 366–376). A particulate filter is normally used in front of the RO system to reduce the amount of solids reaching the RO filter. The layer of solids that collect on the RO membrane can be reduced by periodic backpulsing (using permeate or clean water) to push the solids away from the filter. Occasional use of enzymatic detergent or other cleaning agents followed by water rinsing can restore permeate production if backpulsing becomes ineffective. The RO membranes should last for up to 2–3 years in properly operated systems (Sammon, 1983).

RO membranes are normally deployed as cross-flow filters, where the high velocity of the wastewater along the filter keeps the flow turbulent which helps control the thickness of the solids on the filter and reduces plugging of the filter. The amount of pure water that can be produced, and consequently the amount of concentrated retentate water left, depends on the chemistry of the feed water, any pretreatment processes used, and the anti-scaling chemicals added. For groundwater, a retentate volume of 10–20% of the feed water volume would be typical. The retentate stream contains essentially all of the contaminants that were in the feed water, and must be disposed of by some other treatment method. The lower volume and higher contaminant concentration of the retentate will reduce the cost of final treatment and disposal, but this cost reduction must more than offset the cost of the RO process for it to be economically viable.

10.2.3 Air stripping

In air stripping, the wastewater is contacted with air, causing the volatiles to transfer into the gas stream. Air stripping is applicable only for volatile contaminants that have a relatively low solubility in water, such as radon. Stripping of contaminants from water is a common method for treating groundwater at remediation sites, but is usually applied to organic contaminants such as benzene. Because of widescale use, there is a substantial amount of information about design and operation of these systems, and much of this information can be applied to removing volatile radionuclides. Common types of equipment used for air stripping include packed towers and spray towers. The groundwater to be treated would flow down through the column, flowing either over the packing in a thin layer or as small droplets in a spray tower, counter-current to the air stream. The equipment should be designed and operated to distribute the water evenly and to provide a large surface area of liquid to interact with the air stream, which flows up through the column. The air stream, which contains the volatile contaminants, would be vented from the top of the column. Depending on the concentration of contaminants in the air stream and local regulations, the air stream may need to be treated to remove the contaminants prior to discharge.

The distribution coefficient (*H*) is the equilibrium concentration of the contaminant in the gas phase divided by the corresponding liquid concentration, which varies with temperature. If the solute is a gas at the operating conditions (such as radon), this coefficient is often referred to as the Henry's law constant. Larger *H* values lead to higher efficiencies in air-stripping columns. Taller columns and higher air flows also improve contaminant removal, but increase the capital or operating costs of the system. The flow rate that a column can process is directly related to the cross-sectional area of the column. Increasing the temperature of the water can also improve contaminant removal, at the cost of higher energy use. Since the temperature of groundwater does not change much from summer to winter, and because the heat capacity of the water is much higher than for the air, the performance of an air stripper usually does not change much as the air temperature changes through the year (Nyer, 1985, p. 47–54).

10.3 Biological treatment methods

Biological treatment processes normally use bacteria to degrade organic compounds, either aerobically or anaerobically. Other organisms, such as algae or plants, are used in a very limited number of situations. Some inorganic compounds, such as ammonia and nitrate, can also be treated by bacteria. Groundwater can be treated either *ex situ*, by pumping groundwater to a treatment process, or *in situ*, by adding nutrients or oxygen to the groundwater to promote treatment of contaminants in the groundwater. Sorption of inorganic ions, such as heavy metals and radionuclides, can occur, but biological treatment is not normally used as a method to treat radioactively contaminated groundwater unless treatment for biodegradable organics is also required. Other treatment processes may be required following biological treatment to reduce the radionuclide concentration to below required discharge limits. Treating radioactively contaminated water in a biological treatment system can greatly influence the requirements and cost of disposing of excess sludge, which will contain some radionuclides.

Biological treatment has been used in *in situ* porous barriers to remove radionuclides from groundwater, typically as part of a multilayer system (Conca et al., 2002). Biological treatment can also be used to produce chemically reducing conditions within a porous barrier, which can precipitate radionuclides, such as uranium and technetium, that are soluble in oxidized form but insoluble when chemically reduced (Watson et al., 2013).

10.4 Chemical treatment methods

Sorption-type processes (adsorption and ion exchange) are the most commonly used methods for treatment of radionuclides from groundwater. In adsorption processes, the contaminant is adsorbed on the surfaces of a porous particle, including the surfaces within the pores of the particles. Ion exchange is similar, except that the contaminant replaces another ion (counter ion) that was originally associated with the active site on the ion exchange material. Precipitation is a common method for treating industrial wastewaters. Many metals, including metallic radionuclides, will form insoluble hydroxides (precipitates) if the pH of the water is increased. Other chemicals, such as sulfide or carbonate ions, can be added in some cases to further reduce the solubility of the target contaminants.

10.4.1 Ion exchange

Ion exchange media include natural and man-made inorganic materials, such as zeolites, and manufactured organic resins, typically porous beads of polystyrene with some divinyl benzene cross-linking, with various functional groups (active sites) attached. The resins are typically 0.5–1 mm in diameter. Common functional groups include sulfonic ($-SO_3^-$) and trimethylammonium ($-N^+(CH_3)_3$), which would be a strong acid cation resin and a strong base anion resin, respectively. The sulfonic groups on the cation resin would originally have either sodium or hydrogen ions associated with the sulfonic groups, called sodium form or hydrogen form resin. The trimethylammonium sites would have either chloride or hydroxide ions associated with the amine. These counter ions would be replaced by contaminant ions from the groundwater as the resin is used. There are also several different types of functional groups that are selective for specific types of contaminants, such as iminodiacetic ($-CH_2N(CH_2CO_2^-)_2$), which is selective for heavy metals, thiol ($-S^{2-}$), which is selective for any metal ions that form insoluble sulfides (e.g., Hg, Cd, Ag), and polyfunctional (diphosphonic and sulfonic acid) groups (Diphonix Resin), which is selective for multivalent cations, such as uranium and plutonium. These specialty resins are more expensive than the common ion exchange resins, but in some situations they can treat much larger volumes of groundwater before needing to be replaced or regenerated.

Zeolites are a class of porous aluminosilicate minerals with many different chemical formulas and crystal structures, and are the most common type of inorganic ion exchange media used for removing radionuclides from water. More than 200 unique zeolite structures have been identified, and more than 40 naturally occurring types of zeolite have been identified (International Zeolite Association, 2013). Natural zeolites are mined and then crushed into small particles for use in wastewater treatment, as molecular sieves or as catalysts, among many other uses. Synthetic zeolites are made by crystallization from a silica–alumina solution as it is made more basic. Control of the crystallization conditions plus the use of molecular templates determine which zeolite structure is produced. Synthetic zeolites can be almost purely one zeolite structure, whereas natural zeolites will contain mixtures of zeolite structures and other minerals in addition to the predominant zeolite type. Total ion exchange capacity for zeolites ranges from 2 to 5.5 meq/g (GSA Resources, 2013).

Zeolites function as cation exchangers, with additional selectivity due to the atomic/molecular-sized holes in the zeolite framework that favor some cations over others. For example, Chabazite zeolite has a much higher affinity for cesium and strontium ions than for the much more common sodium, calcium, or magnesium ions. Chabazite can remove radioactive cesium and strontium from groundwater while letting the more common ions pass through, greatly increasing the amount of water that can be treated before the zeolite is spent and must be replaced.

A number of other inorganic sorbents have been developed for removing specific radionuclides. Sodium nonatitinate and monosodium titinate have been tested at Savannah River National Laboratory for removing strontium from high-pH, high-salt wastewater (Hobbs, Blume, & Thacker, 2000). Crystalline silicotitanate (CST) is highly selective for cesium over sodium, and is available commercially from UOP (Des Plaines, Illinois) as IONSIV IE-911, but it is much more expensive than zeolites. CST was used at Oak Ridge National Laboratory to remove radioactive cesium from more than 115,000 L of high-pH, high-salt wastewater that was stored in underground tanks. Zeolites are not effective for removing cesium from high-sodium concentration solutions, so the high cost of the CST was not a deterrent in this case (Walker et al., 1998). CST is also very effective in removing cesium and strontium from groundwater, with strontium breakthrough occurring after treating 10 times more water than for a comparable zeolite column and cesium breakthrough of at least 20 times more; however, zeolite would probably still be more economical in this situation (Bostick & DePaoli, 2000). Natural and modified clay products have been tested for treating radionuclides, particularly cesium (Mulyutin et al., 2012), but they have not been used in full-scale treatment systems for groundwater. Natural clay in soils tends to sorb cesium and can keep it from migrating with the groundwater.

Ion exchange medium is normally used in flow-through columns, with the water flowing down through a fixed bed of the medium. Contaminants in the water start loading onto the medium at the top of the bed, displacing the ions that were originally associated with the active sites. The portion of the bed that is actively removing contaminants from the water is called the loading zone. The height of the loading zone depends on the kinetics of the particular ion exchange material used and the velocity of the water through the bed. As the medium at the top of the bed becomes fully loaded, the loading zone slowly moves down the column until it reaches the bottom of the bed and the concentration of contaminants in the water exiting the bottom of the column (effluent) starts to increase. When the effluent concentration exceeds the limit of what can be discharged, the ion exchange medium needs to be regenerated or replaced. Most organic ion exchange resins can be regenerated, with acid, base, or salt solution. Regeneration would produce a relatively low-volume solution containing a high concentration of the radionuclides that were removed from the water. This solution must then be treated and disposed of. Inorganic ion exchange media cannot normally be regenerated, so the loaded medium is disposed of as solid radioactive waste. In many cases, the loaded organic resins are also disposed of rather than being regenerated, because of the difficulty and cost of treating the radioactive regenerant solution for disposal.

Listings of the relative selectivity of different ions for various ion exchange media are available from manufacturers and other sources. For strong acid cation resins, for example, ions with higher charges and higher atomic weights are normally preferred, so Sr^{2+} and Cs^{+} ions would readily replace Na^{+} ions if the concentration difference is not too high. However, Cs^{+} ions would not normally displace Ca^{2+} ions, so a cationic resin would have a low capacity for treating radioactive cesium in groundwater that contains moderate concentrations of Ca^{2+}. The loading and selectivity of inorganic and organic ion exchange materials can be difficult to predict for a complex groundwater, so the design of a system typically requires experimental data to determine the optimum adsorbent and to define design and operational parameters (Watson, 1995).

The performance of an ion exchange system is strongly influenced by the composition of the groundwater to be treated. Batch equilibrium tests can be used to determine the loading of the contaminant on the medium (Q) at various liquid concentrations (C). The resulting isotherm relationship can be used to predict the expected loading of the contaminant onto each candidate sorbent for a particular groundwater. The ratio of Q/C is called the equilibrium distribution coefficient (K_d). The theoretical capacity of each ion exchange material (Q_{max}, expressed as equivalents per unit volume or weight) is normally available from the manufacturer, but the actual loading that can be expected for removing dilute contaminants from groundwater will be much lower than the theoretical capacity. The highest loading on the medium would occur at the top of the column, where the loading on the ion exchange material is in equilibrium with the initial radionuclide concentration in the groundwater. The material at the bottom of the column would have a lower loading and would be in equilibrium with the effluent concentration from the column. For groundwater that contains a mixture of radionuclides, each one would have a different K_d, and each radionuclide would break through the column at a different time.

Small-scale flow tests, or short-term well-mixed batch tests, can predict the minimum contact time needed to achieve a given contaminant removal, which will provide an estimate of the height of the loading zone. For efficient use of the ion exchange medium, the column height should be much larger than the height of the loading zone. By using two columns in series (lead–lag configuration), the medium in the first column can be fully loaded while the effluent from the second column still meets the discharge limits. When the lead column is fully loaded, the medium is replaced or regenerated, and then placed in the lag position, with the original lag column moved to the lead position. The partially loaded medium in the new lead column can then be fully loaded, while the new lag column removes any contaminants in the effluent from the lead column.

10.4.2 Adsorption

Adsorption is similar to ion exchange, except that there is not necessarily a counter ion already associated with the active site that is displaced by the contaminants. Activated carbon is the most common adsorbent used in wastewater treatment, and is frequently used to remove low-volatility organic contaminants from water. Activated carbon can also be used to remove contaminants from air streams. Activated carbons are made from a wide variety of carbonaceous materials, including coal, wood charcoal, petroleum coke, and coconut shells. Activated carbons have very high surface areas and numerous pores of various sizes. They are available as powders or granules. (Perrich, 1981). Activated carbon has some affinity for heavy metals, including radionuclides, but the capacity is usually fairly low, so they are not normally used for treating metal contaminants in groundwater, except for mercury. If activated carbon is used to treat groundwater that contains organic contaminants in addition to radionuclides, the loading of some radionuclides on the carbon will greatly increase disposal costs and will probably preclude reactivation of the carbon.

Activated alumina is a porous, granular, aluminum oxide medium that can remove anionic species from groundwater, including fluoride, arsenic, selenium, and uranium. Apitite (calcium phosphate) and other phosphate rocks have been tested as adsorbents for metals ions including americium, plutonium, and strontium (Conca et al., 2002).

The design and operation of adsorption systems for treating groundwater are similar to those using ion exchange resin. Small-scale batch and/or column tests can provide adsorption isotherm and kinetic data. A loading zone will develop at the top of an adsorbent column, and slowly move down the column, and breakthrough of the contaminant will occur when the loading zone reaches the bottom of the column (Watson, 1995).

10.4.3 Precipitation

Precipitation of contaminants is normally accomplished by increasing the pH of the groundwater, using caustic (NaOH), lime ($Ca(OH)_2$), or caustic soda (Na_2CO_3), to minimize the solubility of the contaminants that need to be removed from the water. Other chemicals, such as sulfide, can also be added to further reduce contaminant solubility. The contaminants are removed as a sludge by settling and/or filtration. Solubility data are available for most pure compounds, which can be used as a guide to the least soluble form of a contaminant (e.g., hydroxide, carbonate, sulfide), but these data cannot reliably be used to predict the actual solubility of a compound in a complex groundwater. Laboratory testing is required to determine the optimal treatment conditions for a particular water and contaminant. Since the characteristics of the groundwater strongly influence the solubility of the contaminants, the laboratory tests should use samples of the actual groundwater rather than simulants, if possible. The results from the laboratory tests should directly predict the results for a large-scale treatment facility, as long as the water chemistry, contact time, and mixing characteristics are the same. Trace concentrations of some compounds in the water, such as complexing agents, can have a strong effect on the solubility of contaminants.

The solubility of most contaminants decreases as the pH is raised, but the solubility of some metals, called amphoteric (Al, Cr, Zn), will increase again at very high pH. The addition of coagulants, such as iron or aluminum salts, will frequently reduce the concentration of the target contaminants in the treated water. The iron or aluminum forms hydroxide flocs that help to trap smaller particles that precipitate and can also provide sorption sites to further reduce the concentration of some contaminants. Organic polyelectrolytes can also be used to help produce larger floc particles that settle faster.

Precipitation reactions are normally carried out in stirred tank reactors with separate clarifiers or in combined reactor clarifiers. There is usually a well-mixed region where the precipitation chemicals are added, a slow-mix zone where floc formation is promoted, and then a clarification zone where the treated water is separated from the precipitated floc particles. The precipitate sludge is dewatered using a filter or centrifuge and then solidified for disposal. The clarified water may be filtered to remove any floc particles that leave the clarifier.

10.5 Application of treatment processes to specific radionuclides

10.5.1 Cesium

The two common radioactive isotopes of cesium (Cs) are ^{134}Cs and ^{137}Cs, which are both produced by uranium fission and do not occur naturally. The half-lives are 2.1 years for ^{134}Cs and 30.3 years for ^{137}Cs, so the ^{137}Cs is most likely to be of concern. Cesium is chemically similar to sodium and potassium, which are normally present in much higher concentrations than cesium. The concentration of natural, nonradioactive, Cs is normally very low in groundwater.

Zeolites are the most common means of removing Cs from contaminated groundwater, since zeolites have a much higher affinity for Cs than Ca, Mg, or Na. Total ion-exchange capacity ranges from 2 to 5.5 meq/g; however, only a small fraction of these sites would be occupied by cesium ions in spent zeolite. For groundwater containing 76 mg/L Ca, 9 mg/L Mg, 9 mg/L Na, 1.6 mg/L K, 0.1 mg/L Sr, and 0.0003 mg/L Cs being treated with a column of Chabazite zeolite, initial breakthrough (1%) of Cs occurred after treating 23,000 bed volumes of groundwater (Bostick & DePaoli, 2000). The average Cs loading on the zeolite was 0.0007 meq/g at initial Cs breakthrough. Of the common ions found in groundwater, potassium has the strongest negative impact on Cs loading. The zeolites also have high selectivity for strontium, as described below. Zeolite cannot be regenerated, so the spent zeolite, which could contain high concentrations of Cs, must be disposed of as a solid radioactive waste.

CST has a very high selectivity for Cs and a total ion-exchange capacity of about 2.5 eq/L. CST is available commercially as IONSIV® IE-911 (UOP Molecular Sieves, Mt. Laurel, New Jersey). In a small-scale test using the same groundwater described above, there was no measurable breakthrough of Cs after treating 61,000 bed volumes of groundwater. Predicted 1% breakthrough, based on batch isotherm test results would be about 130,000 bed volumes (Bostick & DePaoli, 2000). CST has some affinity for potassium, with 50% breakthrough occurring after treating 14,600 bed volumes, but very little affinity for calcium, magnesium, or sodium. CST cannot be regenerated, so the spent sorbent, which could contain very high concentrations of Cs, must be disposed of as a solid radioactive waste. The expense of CST normally precludes using it in situations where zeolites would be effective.

Natural clay has an affinity for cesium. Clay-based products have been tested at laboratory scale for removing cesium from water. In many cases the clay in soil retains any cesium in the groundwater, so the concentration of soluble cesium is very low in the groundwater.

Transition metal hexacyanoferrates (HCF), such as cobalt-HCF and copper-HCF, have a high affinity for Cs. A granular version of an HCF is available as CsTreat® from Fortum Corp. (Espoo, Finland), which can be used in a flow-through column (Harjula, Lehto, Esko, & Paavola, 1994). The material is particularly effective in high-salt solutions, where zeolites do not work.

A strong acid cation resin would have lower affinity for Cs than for common cations such as Ca and Mg; therefore, the capacity of the resin for Cs would be low, since most of the active sites would be occupied by the common cations. The specialty ion exchange resins, such as iminodiacetic and thiol, do not have any selectivity for cesium.

RO will remove Cs from water, along with all of the other ions. The cesium in the retentate will remain soluble. The retentate could be solidified for disposal, but the volume is likely to be large (10–20% of the feed water volume). Zeolite could be used to remove Cs from the retentate. The lower flow rate and higher Cs in the retentate would reduce the size of the column required, and would increase the Cs loading on the zeolite; however, the savings from reduced zeolite purchase and disposal costs would need to offset the cost of the RO treatment.

Cesium is soluble in water under almost all conditions, so precipitation is not a viable option for treating Cs.

Bacteria and plants have some ability to concentrate Cs from water, mostly due to transport mechanisms for accumulating potassium, which is required by the organisms; however, the extent of Cs uptake varies widely (Avery, 1995). Biological treatment to remove Cs from groundwater is not likely to be very effective.

10.5.2 Metals

Various metallic radionuclides are possible but uncommon contaminants in groundwater. They include fission products, such as cerium-144 (half-life = 285 days) and europium-152 (half-life = 13.5 years), and activation products, such as cobalt-60 (half-life = 5.27 years) and iron-55 (half-life = 2.73 years). These metal ions would behave similarly in most treatment processes, so they are grouped together. Naturally occurring or contaminant heavy metals can also be present in groundwater, normally at much higher concentrations than for the radioactive metals. The nonradioactive metal concentrations will normally determine the performance of any treatment system.

Complexing ion exchange resins, such as iminodiacetic ($-CH_2N(CH_2CO_2^-)_2$), have very high affinity for heavy metals over common cations such as Ca and Mg. One of the complexing ion exchange resins would normally be the preferred option for treating low concentrations of heavy metals in groundwater. Very low effluent metal concentrations and long run times for ion exchange columns would be expected. If high concentrations of metals are present, precipitation should be considered, either alone or as a pretreatment prior to ion exchange. Strong acid–cation exchange resins would also have affinity for these metal ions, so they would preferentially load on the resin compared to Ca and Mg. Zeolites have limited selectivity and capacity for heavy metals; however, some loading may occur as a byproduct of treating ^{137}Cs and ^{90}Sr in the groundwater if metallic radionuclides are also present.

Most metallic radionuclides have low solubility at higher pH, so precipitation would be an effective treatment, particularly for groundwater that contains higher concentrations of metals. The pH for minimum solubility is typically different for each of the metals, so a compromise value will need to be selected if multiple metals are present. Laboratory-scale testing would be needed to determine the optimum pH for a given groundwater. Adding iron or aluminum salts prior to pH adjustment will frequently reduce the concentration of the target contaminants in the treated water. The iron or aluminum forms hydroxide flocs that help to trap smaller particles that precipitate, and can also provide sorption sites to further reduce the concentration of the metallic radionuclides. Adding sulfide ions will reduce the solubility of many metals.

RO will remove metal ions, including radioactive metals, from water, along with all of the other ions. Precipitation could be used to treat the retentate. If soluble contaminants, such as ^{137}Cs, are present, additional treatment steps may be required.

A variety of metals can accumulate in bacteria, so some removal of metals, including radioactive metals, from groundwater would be expected during biological treatment. Removals of 10–94% for chromium, nickel, and zinc were measured for sewage treatment plants (Stoveland, Astruc, Lester, & Perry, 1979). Achieving reliable treatment to an allowable discharge limit may be problematic.

10.5.3 Radium

Radium occurs naturally in very low concentrations from the decay of uranium and thorium, ^{226}Ra from ^{238}U and ^{228}Ra from ^{232}Th. Thorium is more abundant than uranium, so ^{228}Ra is generally present in higher concentrations; however, uranium complexes are soluble in water in oxidizing conditions and can move with the groundwater. If reducing conditions are encountered, the uranium can precipitate, forming concentrated secondary deposits. Groundwater in the vicinity of these secondary deposits would contain high concentrations of ^{226}Ra (Cothem & Rebers, 1990). The half-life of the radium isotopes are 1599 years for ^{226}Ra and 5.76 years for ^{228}Ra. There are no stable isotopes of Ra. The natural concentration of Ra in groundwater can vary widely, depending on the local concentration of uranium and thorium. The chemistry of radium is similar to calcium, magnesium, and strontium. Radium-226 is a byproduct of uranium mining, either left in ore that is leached with carbonate to recover the uranium or leached from the ore along with the uranium if sulfuric acid is used. Some of the ^{226}Ra is recovered for commercial use.

Strong acid–cation exchange resins have a much higher affinity for Ra over Na and a slightly higher affinity for Ra over Mg and Ca. Radium is likely to break through an ion exchange column only slightly after Ca and Mg, so the amount of groundwater that can be treated before regeneration or disposal of the resin is required will mostly be driven by the concentration of Ca and Mg in the water. Removal of over 90% of the Ra from groundwater can be achieved by cation exchange (Brinck, Schliedelman, Bennett, Bell, & Markwood, 1976).

Zeolites have an affinity for Ra, similar to strontium and barium ions (Chalupnik, Franus, & Gzyl, 2013). The concentration of natural Sr, and Ba if present, would be much higher than the Ra concentration and would determine the amount of water that could be treated prior to Ra breakthrough.

Radium is insoluble at high pH, so precipitation can be used to treat groundwater. The addition of barium ions prior to increasing the pH will further reduce the Ra concentration, due to co-precipitation with the barium. The addition of sulfate ions along with the Ba can further improve Ra precipitation, to even below the true solubility of $RaSO_4$, apparently due to adsorption of the Ra on the surface of the $BaSO_4$ particles (Doerner & Hoskins, 1925).

RO will remove Ra from water, along with all of the other ions. Precipitation could be used to treat the retentate. The lower volume and higher contaminant concentration in the retentate would improve the efficiency of the precipitation process, compared to treating the original groundwater; however, these savings would need to offset the cost of the RO treatment.

10.5.4 Radon

Radon (Rn) is an inert gas that is produced from the decay of radium (Ra) isotopes, which are the longest half-life radionuclides in the uranium and thorium decay chains. Radon has a short half-life, maximum of 3.8 days, so it is only present in groundwater that contains Ra. All isotopes of Rn are radioactive. Since uranium and thorium are present at low concentrations in many types of rock, Rn can be present naturally in groundwater. Groundwater that contains elevated concentration of Ra will also contain higher concentrations of Rn, unless the Rn has been somehow vented from the groundwater.

Radon has a Henry's Law Constant of 4.1 at atmospheric pressure, so it can be readily removed from groundwater by air stripping (Drago, 1998). Radon removals of well over 90% can be expected for counter-current air strippers with more than 3 m of packing and with air:water volumetric flow ratios of 5 or more (Drago, 1998). A well-designed and well-operated air stripper should be able to achieve 99% radon removal. Aeration as part of a biological treatment system or in an aerated storage tank can also remove radon. Depending on the initial radon concentration in the groundwater and local regulations, treatment of the effluent air stream may be required. A column of granular activated carbon can remove radon for an air stream. If off-gas treatment is required, an economic assessment will be needed to determine whether direct treatment of the water using activated carbon or air stripping with off-gas treatment is less expensive.

Radon can also be removed from groundwater by adsorption on activated carbon. Typically a down-flow packed column of granular activated carbon is the most efficient method to deploy activated carbon, but adding powdered activated carbon to the mix tank of a precipitation process would also be effective for removing radon. If radium or other radionuclides are being treated using precipitation, the addition of powdered activated carbon would provide radon treatment in the same equipment. Radon removal approaching 99% can be achieved using a column of granular activated carbon (US EPA, 2013).

10.5.5 Strontium

Strontium-90 (^{90}Sr) is a common fission product of uranium and has a half-life of 29.1 years. All of the other radioactive isotopes of Sr have fairly short half-lives and are not normally a concern in groundwater; however, if present, they would all behave the same as ^{90}Sr in any treatment system. Trace levels (0.1–3 mg/L) of natural Sr are common in groundwater (Skougstadt & Horr, 1960), and these concentrations would be much higher than likely concentrations of ^{90}Sr; therefore, the natural Sr concentration will normally determine the performance of any treatment system.

Zeolites are a common method for removing Sr from contaminated groundwater, since they have a much higher selectivity for Sr compared to Ca, Mg, or Na. Total ion-exchange capacity ranges from 2 to 5.5 meq/g; however, only a small fraction of these sites would be occupied by Sr ions in spent zeolite and an even smaller fraction would contain ^{90}Sr. For groundwater containing 76 mg/L Ca, 9 mg/L Mg, 9 mg/L Na, 1.6 mg/L K, 0.1 Sr mg/L, and 0.0003 mg/L Cs being treated with a column of Chabazite zeolite, initial breakthrough (1%) of Sr occurred after treating 5000 bed volumes of groundwater (Bostick & DePaoli, 2000). The Sr loading on the zeolite was 0.014 meq/g at initial Sr breakthrough. The amount of water that was treated prior to Sr breakthrough was much lower than for Cs breakthrough because the total concentration of Sr in the groundwater was much higher than the total Cs concentration, but the Sr loading on the zeolite was much higher than for Cs, for the same reason.

CST has some selectivity for Sr and a total ion-exchange capacity of about 2.5 eq/L. In a small-scale test using the same groundwater described above, 1% breakthrough of Sr occurred after treating 15,000 bed volumes of groundwater, three times better than for Chabazite zeolite (Bostick & DePaoli, 2000). The expense of CST normally precludes using it in situations in which zeolites would be effective. CST has some affinity for potassium, but very little affinity for the other common cations in groundwater (Ca, Mg, and Na).

Sodium nonatitinate and monosodium titinate have been tested at Savannah River National Laboratory for removing strontium from high-pH, high-salt wastewater (Hobbs et al., 2000). These sorbents are less effective for removing strontium from neutral, low-salt wastes such as groundwater, and have not been used for this purpose.

Cation exchange resins have a much higher affinity for Sr over Na and a slightly higher affinity for Sr over Mg and Ca. Strontium is likely to break through an ion exchange column only slightly after Ca and Mg, so the amount of groundwater that can be treated before regeneration or disposal of the resin is required will mostly be driven by the concentration of Ca and Mg in the water.

RO will remove Sr from water, along with all of the other ions. Precipitation could be used to treat the retentate, as long as soluble contaminants, such as ^{137}Cs, are not present. The lower volume and higher contaminant concentration would improve the efficiency of the precipitation process, compared to treating the original groundwater; however, these savings would need to offset the cost of the RO treatment. If precipitation will not remove all of the contaminants, the retentate could be solidified for disposal, but the volume is likely to be large (10–20% of the feed water volume).

Strontium is fairly insoluble at high pH, so precipitation is a common technique for reducing ^{90}Sr concentrations in groundwater. Reductions of 95% can be expected for a well-designed precipitation system (Lucero et al., 1998). The Ca and Mg in the water will also be removed by precipitation. Adding carbonate, for example by raising the pH of the water using soda ash, will normally further reduce the solubility of Sr. If precipitation by itself will not reduce the ^{90}Sr concentration to below the discharge limit, it could be used as a pretreatment step prior to ion exchange. Since most of the Ca, Mg, and Sr are removed during precipitation, the ion exchange media (resins or zeolites) would be able to treat much more water before regeneration is required. If ^{137}Cs is present in the groundwater, it will not be removed by the precipitation process, but zeolite treatment of the effluent would remove the ^{137}Cs and any residual ^{90}Sr.

Strontium can accumulate in organisms along with Ca, so some removal of Sr from groundwater would be expected during biological treatment; however, achieving reliable treatment to an allowable discharge limit is unlikely.

10.5.6 Technetium

Technetium is a fission product of uranium and does not occur naturally, and there are no non-radioactive isotopes of Tc. Technetium-99 (half-life = 2.1×10^5 years), is the most common isotope found in water. The oxidized form of technetium, the pertechnetate anion (TcO_4^-), is very soluble and mobile in groundwater. The reduced form of technetium (TcO_2) is insoluble.

Ion exchange, using a strong base anion resin, is the most common method for removing Tc from groundwater. Pertechnetate ions have a higher affinity for the active sites on anion resins than do sulfate ions and a much higher affinity than the other common anions in groundwater, such as chloride, carbonate, or nitrate. High sulfate concentration in the groundwater can affect the loading of Tc, but the other anions would have minimal effect. Laboratory-scale and pilot-scale treatment tests were conducted using groundwater from the Hanford Site in Washington State, which contained about 15,000 pCi/L ^{99}Tc and 1 mg/L uranium (US DOE, 1995). Strong base anion exchange resins successfully removed both contaminants from the groundwater. Breakthrough of Tc occurred after about 3000 bed volumes of groundwater had been treated. There were indications from these tests that U had started displacing Tc from the resin, indicating that U had a higher affinity. Full-scale pump and treat operations began at the site in September 1995 using Dowex 21K strong base anion exchange resin. The results were similar to the pilot-scale tests (Myers, Gustafson, & Wittreich, 1996). Because of their high affinity for Tc, the anion exchange resins can be difficult to regenerate. The loaded resins would normally be disposed of as solid radioactive waste.

Activated carbon can adsorb Tc from slightly acidic water, with maximum adsorption occurring at a pH of 2–4. The exact mechanism is not known, but may involve chemical reduction of the soluble pertechnetate ion to TcO_2 on the surface of the carbon (Holm, Gafvert, Lindahl, & Roos, 2000). The technique has been used to concentrate Tc from water samples as part of analyzing the Tc concentration.

Technetium can be chemically reduced and precipitated using ferrous salts. The Fe^{2+} is oxidized to Fe^{3+}, whereas the soluble pertechnetate is reduced to insoluble TcO_2. The Fe^{3+} precipitates to form iron hydroxide, which helps trap the TcO_2 solids (McBeth, 2011). A number of other chemical reducing agents are known to convert TcO_4^- to insoluble TcO_2 (Kim et al., 2005; Brownridge, Dunbabin, & Sharpe 2001). Stannous chloride is commonly used, but other reducing agents, such as sodium borohydride and sodium dithionite, are also effective. Zero valent iron (iron filings or turnings) can chemically reduce pertechnetate ions to insoluble TcO_2. A laboratory-scale test using a column packed with steel wool treated 1200 bed volumes of a high-pH water, with moderate concentrations of dissolved salts (Na_2CO_3 and $NaNO_3$) and 0.1 mg/L ^{99}Tc, without breakthrough. The steel wool was oxidized to iron hydroxide while the pertechnetate was reduced to TcO_2, which was trapped in the iron hydroxide layer. However, there was a continuous leakage of ^{99}Tc at about 3% of the influent concentration. The steel wool was highly deteriorated by the end of the test (Bostick et al., 1995).

Anaerobic bacteria can chemically reduce pertechentate ions to insoluble TcO_2 (Lloyd, Cole, & Macaskie, 1997). Standard aerobic biological treatment would not be expected to affect Tc concentrations significantly.

10.5.7 Transuranics

Transuranics include isotopes such as neptunium-237, plutonium-238, plutonium-239, and americium-241. They are produced in nuclear reactors from neutron activation of uranium isotopes, directly or in multiple steps. They are all radioactive, with varying but usually long half-lives. Minute amounts of ^{237}Np and ^{239}Pu occur naturally in uranium ore. Transuranic contamination of groundwater is unusual, but can occur at nuclear research and processing sites.

Ion exchange is a common method for removing transuranics from aqueous solutions. The transuranics typically occur as cations in water, with an oxidation state of 3+ or 4+, or as oxide compounds with a net charge of 1+ or 2+. Strong acid cation resins would remove the transuranics, along with the common metals such as calcium and magnesium. Cation resins would have a higher selectivity for transuranics than for the common ions; however, the concentrations of the transuranics would be so much lower that the amount of groundwater that can be treated before regeneration of the resin is required will mostly be driven by the concentration of Ca and Mg in the water. Complexing resins such as Diphonix and iminodiacetic would have a higher selectivity, so could generally treat more water before the resin was spent. The spent resins would typically be disposed of as solid radioactive waste, rather than regenerating the resins, which would generate a high-concentration liquid stream for treatment and disposal.

The transuranics will precipitate at high pH, but the initial concentrations may be too low to achieve good removal. Adding coagulants such as aluminum or iron salts should reduce the final concentrations. The sludge will contain large amounts of calcium and magnesium and any added coagulant solids in addition to the radionuclides.

RO will remove transuranics from water, along with all of the other ions. Precipitation could then be used to treat the retentate. The lower volume and higher contaminant concentration would improve the efficiency of the precipitation process, compared to treating the original groundwater; however, these savings would need to offset the cost of the RO treatment.

10.5.8 Tritium

Tritium is a radioactive isotope of hydrogen (half-life = 12.3 years), containing two neutrons and one proton in the nucleus. Extremely low concentrations occur naturally, produced from the interaction of cosmic rays with nitrogen gas in the atmosphere. Tritium is produced in nuclear reactors by neutron activation of the hydrogen in the reactor cooling water or from neutron bombardment of lithium-6 or boron isotopes. Tritium can be produced as a gas, but is normally found as tritiated water, where one of the hydrogen atoms in water is replaced with a tritium atom (US EPA, 2014).

Several methods have been developed to recover tritium from high-concentration sources for commercial or governmental use. Until recently there have been no practical methods for removing low concentrations of tritiated water from groundwater. The only options were to somehow retain the water until the tritium had decayed sufficiently for discharge, or to provide sufficient dilution water. Any tritium gas that was dissolved in water could be removed by air stripping, but the tritium is almost always present as tritiated water.

Adsorbents that have some selectivity for tritiated water over normal water have been tested at small scale. Loading aluminum (Al^{3+}) salts on a cation exchange resin and then drying the resin produced an adsorbent with a greater affinity for tritiated water over normal water (Jeppson, Furlong, Collins, & Stockinger, 2000). Tritium reduction of up to 97% was achieved with four columns in series. The loaded tritiated water could be removed by drying the adsorbent. The water that was removed from the adsorbent, which would be enriched in tritiated water, would need to be solidified for disposal.

10.5.9 Uranium

Uranium occurs naturally in rock and soil and is widespread, but the concentration varies considerably. Uranium chemistry is complex, with many possible oxidation states and various complexes that can form, depending on the other ions in the water. The most common soluble form that is found in groundwater is the uranyl ion (UO_2^{2+}) complexed with carbonate. There are several different possible uranium–carbonate complexes that form; depending on the pH of the water, the complex could be the neutral UO_2CO_3 (maximum concentration at a pH of 6), or the negatively charged complexes $UO_2(CO_3)_2^{2-}$ (maximum concentration at a pH of 7) or $UO_2(CO_3)_3^{4-}$ (maximum concentration above a pH of 9). If the pH is below 4, the uncomplexed uranyl ion (UO_2^{2+}) predominates. At a pH of 8, the hydroxide complex $(UO_2)_3(OH)_5^+$ is present, along with both $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. Under strong reducing conditions, the uranyl ion can be converted to insoluble UO_2 (Cothem & Rebers, 1990). Which ion predominates can strongly affect the results of treatment processes to remove the uranium.

A survey of various treatment technologies for removing uranium from groundwater by Odell (2010, pp. 165–170) shows that anion exchange typically removes 90–100%, lime softening removes 85–99%, and RO removes 90–99% of the dissolved uranium. These removal efficiencies are for the relatively low concentrations found in drinking water aquifers.

Strong base anion exchange resins are the most common means of removing uranium from groundwater, and also from leaching solutions generated by *in situ* uranium mining. Dowex 21K anion-exchange resin, which is marketed specifically for recovery of uranium, achieved a cumulative loading capacity of almost 50 mg U/g resin in a field column test using near-neutral–pH (6.5) groundwater. In an acidic ($pH=5$), high-nitrate–concentration groundwater, metal-chelating resins, such as Diphonix and iminodiacetic, removed more uranium than anion-exchange resins (Phillips, Gu, & Parmele, 2008). The anion resins are readily regenerated, but the high concentration regenerant stream would need to be treated for disposal. The chelating resins are usually more difficult to regenerate. Any of the spent resins can be disposed of as solid radioactive waste, rather than being regenerated.

Activated alumina was effective in removing uranium from a near neutral ($pH=7.6$) groundwater containing 0.2 mg/L U, with >99.9% removal in a laboratory-scale test (Laul, Rupert, Harris, & Duran, 1995).

Precipitation is an effective treatment method for removing uranium from water, particularly if a coagulant such as aluminum or iron is added. Uranium can be precipitated at any pH above about 4, but using a pH of 10 or above will provide much more reliable treatment. The common cations such as calcium and magnesium, but not sodium, will also be precipitated, producing a uranium-containing sludge for disposal.

Zero-valent iron (iron filings) can chemically reduce uranyl ions to insoluble uranium dioxide (UO_2). The ferrous and ferric hydroxide reaction products from the zero-valent iron can also adsorb uranyl ions (Farrell, Bostick, Jarabek, & Fiedor, 1999). Zero-valent iron has been tested for *in situ* treatment of uranium-contaminated groundwater. The iron filings are placed in a trench, and subsurface barriers are used to direct the flow of groundwater through the iron filings. The iron is inexpensive and has a large capacity for retaining uranium, but the kinetics are slow.

Bacterial growth can be stimulated *in situ* by adding an organic carbon source, which depletes the oxygen in the groundwater and creates chemically reducing conditions that precipitate soluble uranium (Watson et al., 2013).

RO will remove U from water, along with all of the other ions. Precipitation could then be used to treat the retentate. The lower volume and higher contaminant concentration would improve the efficiency of the precipitation process, compared to treating the original groundwater; however, these savings would need to offset the cost of the RO treatment.

10.6 Future trends

The treatment processes that are commonly used to remove radionuclides from groundwater, such as ion exchange and precipitation, are well developed, and any future improvements are likely to be incremental. Some highly selective ion exchange materials have been developed in recent years, which can achieve difficult separations, such as almost quantitatively removing cesium ions from a solution that initially contains 5 M sodium and 0.001 M cesium. The high cost of these specialty sorbents normally limits their use to situations in which no other options are available. *In situ* treatment technologies have seen major advances, and deployment of these systems is likely to increase in the future.

10.7 Sources of further information and advice

The US Environmental Protection Agency has a series of Websites on various treatment options for removing radionuclides from drinking water, which describes the applicability of each option for a list of naturally occurring radionuclides. (http://cfpub.epa.gov/safewater/radionuclides/radionuclides.cfm?action=Rad_Treatment)

There are a variety of reference books that describe treatment processes for contaminated water, usually applied to common contaminants rather than radionuclides, but most of the information is directly applicable to radionuclides also. Examples are listed in the References (Belfort, 1984; Eckenfelder, 1989, p. 366–376; Nyer, 1985, p. 47–54; Odell, 2010, p. 165–170; Perrich, 1981). The manufacturer or supplier of treatment equipment and materials can usually provide detailed information about previous applications that are relevant to specific treatment needs.

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