Ceramics
are
More than Clay Alone

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About the Author

Paul H.W. Bormans was born in 1945 in Hengelo, Netherlands. After his education in chemistry at the University of Nijmegen, Netherlands, he became a teacher at a school for laboratory personel. His extensive interest in natural sciences resulted in a number of books about mineralogy and the environment. In the years 1980–1985 he worked on the integration of natural sciences in his school. He started to teach ceramics at the department material technology of his school. The basis of his teaching materials is the scope of this book.

The Dutch manuscript was translated in English by his colleague F. Achten.

Preface

In this preface I would like to reflect on the aspects which played a part in creating this book.

In 1964 I embarked on my chemistry studies. Apparently the subjects ‘inorganic chemistry’ and ‘crystallography’ had most appeal for me during my education, because some years later I became interested in geology and mineralogy as a hobby. The earlier mentioned specialities stood me in good stead here (or were they the cause of my interest ?) and my hobby developed into a large collection of silicate minerals.

After graduating I started to teach at a laboratory school where I have been employed ever since. At the beginning of the eighties Dutch trade and industry were of the opinion that materials science ought to be introduced into laboratory education. Since ceramics are mainly based on inorganic compounds and silicates play a major role here, I gladly volunteered to teach this subject. I enthusiastically threw myself into ceramics and have since written a lot of instructional material from a multidisciplinary approach. This means that ceramics can only be studied successfully by students with an interest in natural sciences, varying from the geology of the formation of raw materials to the use of ceramics implants in man and animals, with an extensive range of applications and specialities in between.

My spheres of interest and my disposition to teach natural sciences as a whole comprising of related subjects were my main inspirations for writing this book. An interest in ceramics and a readiness to gain more knowledge of other specialities are important prerequisites in order to successfully utilize it.

Finally, I would like to take this opportunity to thank all the companies and people who contributed either in the form of literature, photographs or texts. Special thanks go to my colleague Sis Achten for translating my Dutch text into the English language.

Paul Bormans

Susteren, The Netherlands

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1

Introduction

On reading the title of this book, you may have thought: ‘Yet another book on ceramics? So much has already been written about that subject’. Or perhaps: ‘ What can this book possibly add to existing literature?’ The answer to the latter question can partly be found in the approach the author has chosen, which is tightly linked to the book’s target groups. This book has been written for interested lay persons, for educational purposes at a senior secondary level and for ceramicists

What does an interested lay person know about ceramics? Ask any ten people what ceramics are, and nine out of ten will only be able to supply you with a few examples like crockery, vases and sculptures.

Ceramic market in Maaseik, Belgium (photograph by H. Raadschelders, Sittard, Netherlands)

Only few people know that bricks, floor tiles, washbasins and toilet bowls are also ceramic objects. You need to have come across many more aspects of ceramics to know that they are now also used in synthetic hip joints, femur heads, jaw parts, spark plugs, the production of aluminium, ball bearings, abrasives, superconductors, laboratory equipment, car engines, electronics, nuclear reactors, cutting equipment, insulation material, space travel and many more applications. And what did the German television station WDR broadcast on 18 June 1997?: ‘In a few days the speed record on skates will be broken behind a Ferrari’. The skates were equipped with ceramic ball bearings. On 18 November of the same year a Dutch newspaper published a photograph of the German Jurgen Kohler on inline skates behind a Porsche. He had qualified for the Guiness Book of Records because he had broken the world record by having himself dragged along a distance of 1900 metres with a speed of 288 km/hour. Could this have been the same person as the one on 18 June?

It is very understandable that people know so little about ceramics. Ever since time immemorial, clay has been an important ceramic raw material. Not until approximately 1850 were other (synthetic) raw materials introduced in ceramics. The objects which are made of the latter often have specific properties which clearly differ from those of the clay ceramics and which meet the requirements of the sophisticated high-tech world of the nineties. So ceramics involve much more than simply clay ceramics and are, in my view, well worth writing a book about.

Which approach has been applied in writing this book? As the author I was well aware of the fact that the book needed to be innovative. I teach ceramics and chemistry at an institute for senior secondary vocational training. At this school students are trained to be laboratory technicians, so I had in mind a book in which all aspects of ceramics would be discussed at precisely this level. In this way my book would be aimed at both interested lay persons and students of secondary vocational schools. In addition, there has been a trend to teach natural sciences cross-curricularly for some years now and this has created a void in which this book on ceramics fits nicely.

The set-up of this book is comparable to a spider’s web. Ceramics are materials which can very well be described as the centre of the web. The threads of the web are the sciences which study ceramics: geology, archeology, chemistry, physics, even medical and many other sciences. The material is excellently suited for use in technical, cross-curricular education. Consequently many curricular subjects will be dealt with in order to understand ceramics and all of its applications. In my lessons I constantly try to crystallize these educational principles. Unfortunately examination requirements have to be considered, but now and then liberties can be taken. Lessons only become interesting for students when teachers do not limit themselves to textbooks, but illustrate the relationships with other subjects and facts. Natural sciences fade into one another and should be taught in exactly such a way.

I have attempted to create ceramics from the atom, the smallest building block of matter. Atoms are linked to bigger building blocks. How does that link lead to the formation of plastics in the one case, and ceramics in the other? And in which ways do these material groups differ from metals and other materials?

The book is aimed at ceramics in the year 2000 and the subject is introduced via two routes, i.e. the period of approximately 25,000 BC until about 1850 AD in which clay and related natural raw materials prevailed, and the period from 1850 until 2000 with clay and other, mainly synthetic raw materials. Despite the length of the period in which only clay was used, this book will pay relatively little attention to it. The reason for this is the fact that the number of application of ceramic materials increased considerably with the introduction of synthetic raw materials. Moreover, natural sciences have boomed enormously after World War II and consequently so did the education in ceramics. The main part of this book is therefore devoted to ceramics after 1945. Because one of the applications of this book is in the field of education, the text is occasionally illustrated with simple experiments.

2

History and Future of Ceramics

2.1 INTRODUCTION

Before starting to write this book, and especially this chapter, I visited the Rijksdienst voor het Oudheidkundig Bodemonderzoek (Dutch Department for Archaeological Soil Research). My main questions were: how do I briefly describe the history of ceramics in the period of about 25,000 BC until AD 2,000 and which subjects should definitely be included ? I shall never forget one particular remark made by an employee of the above-mentioned department: “ Do not copy other books, make sure that your book will be new, it should be part of you.” I have never encountered my approach to the subject at hand, i.e. the discussion of the entire scope of ceramics covering a period of 27,000 years in one book, so it is new. However, he did not answer my questions. We discussed his work - dating and analysing earthenware and the clay in the vicinity of the site. When the earthenware still contains straw the ^{14}C-method is applied to date the item. In addition, the baking temperature is determined and data on the composition is collected, with the help of some microscope techniques. When I inquired whether there had been any spectacular changes in the field of ceramics in the past centuries, he replied that these changes may appear simple in hindsight, but at the time they were spectacular. Some examples are the transition from earthenware to stoneware, the discovery of porcelain and the development of faience pottery. I can fully support his view, after all who is nowadays impressed by the take off and flight of a spaceshuttle? The purpose of this chapter on the history of ceramics is to give the reader some information on approximately 27,000 years of ceramics, without, however, writing a chapter on the history of art. The use of ceramics is set alongside the use of other materials and the acquiring of knowledge. Next, we end up in the period of technical ceramics and pay attention to education. Finally, the chapter will end with a view to the future.

2.2 THE BEGINNING

More than 10,000 years ago, the first developments in the field of metallurgy were made in the Near East. Until that time man had used tools made of wood, bone and stone and with these materials he was able to meet all his requirements for devices and tools. An example from that period is the knife made of obsidian, a shiny black, brown or grey magmatically formed rock. The material is very finely crystallized owing to rapid cooling and is therefore often called volcanic glass. By beating it with another rock, you can break off extremely sharp pieces, a property shared with the flint that was mined in the south of The Netherlands in prehistoric times (fig.2.1).

Fig. 2.1 Flint miningtool from prehistoric flintmine in Rijckholt, the Netherlands. (by: NITG-TNO, Heerlen, Netherlands).

Because man did not feel that he lacked anything, the arrival of metals was almost unnoticed. S. Smith, a well-known metallurgist, writes: “Making jewellery from copper and iron most certainly preceeded the use of these metals in arms, just like baked figurines of clay preceeded the useful pot....”. “The first indications for something new always appear to be an aesthetic experience”. The same applies to ceramics. Other experts, however, think that the use of clay started as a kind of end phase in the successive techniques of weaving mats, making baskets and covering the inside of the latter with a thin layer of clay or pitch in order to make them suitable for storing or transporting corn and such, but also for liquids.

In literature, the oldest ceramic objects are said to be anywhere between 26,000 and 15,000 years old. They date from the Stone Age, or more precise from the period which is called the Upper Paleolithic Period (figure 2.2)

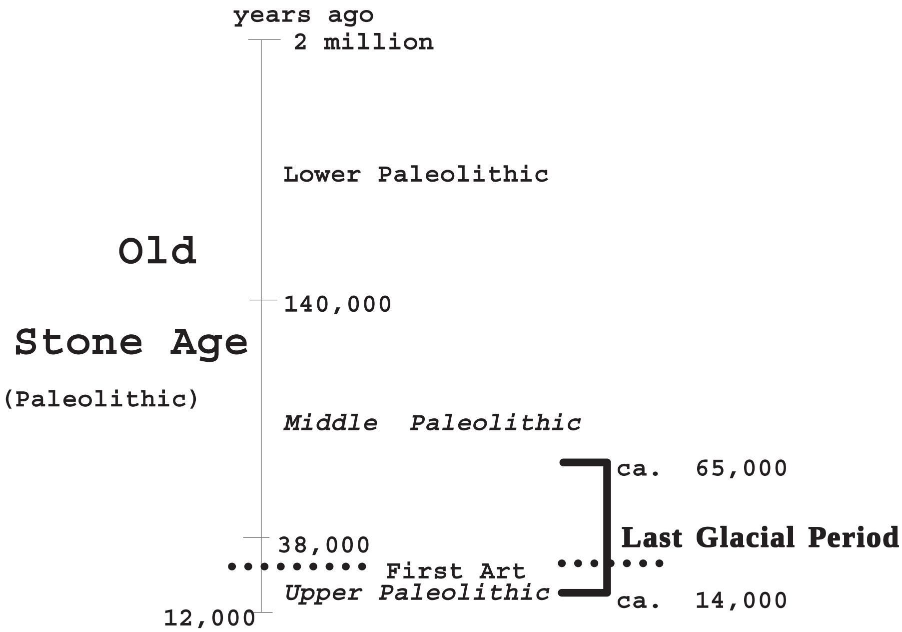


Fig. 2.2 The first art is made in the last Glacial Period.

In that time there was a corridor between the ice layers in the north and the Alps in the south of Europe. It consisted of relatively warm tundra area which extended from former Czechoslovakia to the Ukraine and Siberia. It that area, or to be more precise in Dolni Vestonice (in the Czech Republic) archeologists found three huts not far from each other and next to a small river. These huts were found to be from around 27,000 BC. The place where they were found is situated in low-lying countryside and on limestone covered with loess. The framework of the walls and roofs was made of bones and tusks from mammoths (fig.2.3)

The smallest of the three huts had been equipped with a fireplace in its centre. It appeared to be an oven in the shape of a beehive. It was an oast oven and one of the first for baking clay ever to be found. The Cro-Magnon man had learnt to control fire well. This can be inferred from a series of shallow grooves which had been made in the bottom of the fireplace. Their function was to improve the air supply and in this way higher temperatures could be reached. All around the oven thousands of little clay balls were found, as were fragments of the heads of bears and foxes, but also of the statue,

Fig. 2.3.

now known as the Venus of DolniVestonice.

This is a baked statue representing a woman. It is thougth to be a fertility symbol or a representation of femininity. About 15 important sites have been identified where such statues can be found, but the most well-known one is in Dolni Vestonice. Here an approximately 27,000 year old finger or toe print was also found on a piece of clay which had been hardened to ceramics by the fire. The Venus is about 11 cm high and was found in 1924 by Karel Absolon. An amusing anecdote: in 1980 the editor of the East Texas Newspaper in the USA refused to print a picture of the statue because he considered it unsuitable for a family newspaper.

And now another important question is: “Should these Venus sculptures be classed as ceramic materials?” Initial analyses proved that they were made of silicon-containing ash and mammoth bone and possibly also mammoth fat, but no aluminium oxide or potassium oxide - which are always present in clay - were found. A later analysis of the Venus of Vestonice led to the concusion that a mixture of mammoth fat and bone, mixed with bone ash and local loess had been used; but still no traces of potassium nor of aluminium. In the eighties the Venus was examined using more sophisticated equipment and the result was: no bone or other organic components and no stone fragments. In the period 1955–1965 some researchers concluded that the animal statues of Dolni Vestonice were made of clay, and they called this “terra cotta” which means “burned soil”. Present studies indicate that the loess of Dolni Vestonice was used as raw material for the animal figurines.

The material was found not to contain any apatite or hydroyapatite, which indicates that no bone was used.

Obviously all these facts do not contribute to an unambiguous answer. Why were the raw materials used for the Venus different from those used for the animal figurines? Nowadays it is possible to determine the composition of the Venus minutely, but whether or not this has already been done is not important. What is much more important is the fact that the definition of ceramics is changing again. The current defintion of ceramics is broad enough to include the combination of animal and geological materials. Let me give you two examples. A friend of mine, Paul Rayer of a firm called Arcilla Research in Epen, The Netherlands, who is a ceramicist, has developed an interest in so-called cold-hardening ceramics over the years. Working purely empirically, he has produced all kinds of materials from a mixture of simple geological materials like sand and pumice and argicultural waste products like straw. He is especially interested in developing countries and therefore his aim is to produce materials from cheap ingredients and with as little power consumption as possible. His binding agent is a closely guarded secret. He simply allows his mixture to dry and the result is a hard and extremely tough material which often has properties of ceramic materials. This is described more elaborately in chapter 12.

In April 1997 I visited Euromat '97, a symposium and exhibition on the latest developments in the field of materials science. During one of the poster presentations, a Japanese scientist presented a new product which he called "wood ceramics" . These examples serve to illustrate that there are grey areas between the different groups of materials. So obviously an unambiguous definition is no longer possible.

I would like to end this paragraph *The Beginning* by pointing out that the oldest piece of earthenware is estimated to be about 12,000 years old. It is a potshed which was found in a cave in the south of Japan. Unfortunately this piece, together with other samples found in its vicinity, did not reveal anything about the shape of the original object.

2.3 MATERIALS THROUGHOUT THE CENTURIES

The materials man used for thousands of years and is still using now can be divided into five groups: metals, polymers, composites, ceramics and natural materials. As you can see in figure 2.4 the share of the different materials in the total use often varies considerably from time to time.

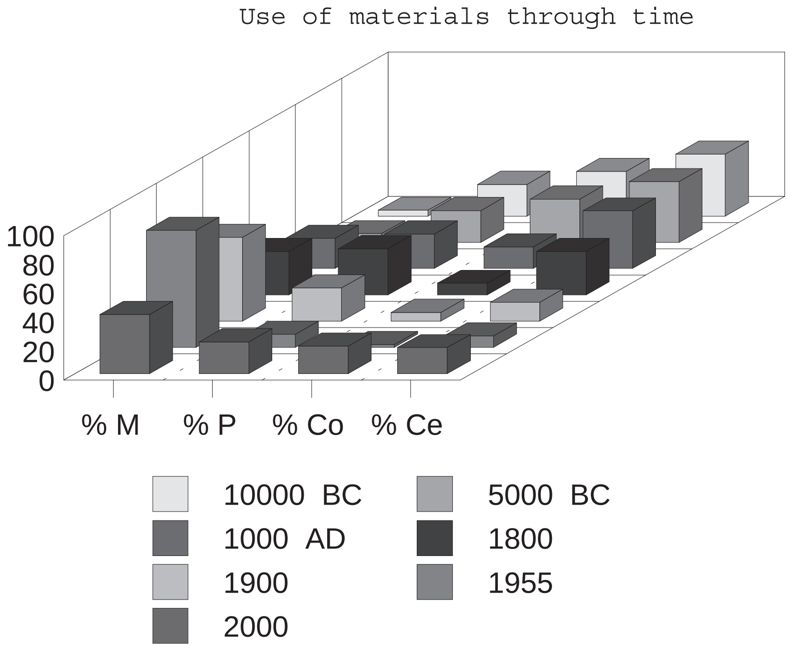


Fig. 2.4 Use of materials through time (M – metals, P – polymers, Co – composites, Ce – ceramics).

The data for this graph comes from the original graph made by professor M.F. Ashby. It is clear that all material groups have always been present in nature and have been used and worked by man from an early date. But how do you determine that ceramics used to be quite important in 5000 BC and metals did not? I wrote to professor Ashby from Cambridge University and asked him how he constucted his graph whereupon I received the following reply:

"Making a diagram like this requires, as you can imagine, a good deal of interpolation. Data for the Stone Age, Bronze Age, etc. can be inferred from the findings of archaeologists. The Encyclopaedia Britannica is helpful here, and so too is Tylecoate (1976) A history of Metallurgy, The Metals Society, London, U.K.

Data for 1960–1980 is relatively straightforward. I tried two different approaches. One was to look at U.K. trade statistics, assuming the U.K. to be more or less typical of the Western World, and I checked this against some U.S. data. The other is to examine the number of lecture - hours devoted to each subject area in major universities, since that gives some idea of the importance attached to them in an intellectual sense rather than an economic one. The two approaches don't give exactly the same results, but they are broadly similar.

Data for post-2000 is of course an extrapolation. Various organisations attempt this, notably, the National research Council of the U.S. It's instructive in this regard, to look at the way in which the amount of metal in a family car has shrunk, and the amount of polymer, elastomer and glass has increased. All of these point to trends a little like those shown in the diagram, but it would be imprudent to attach any major significance to the absolute values of the numbers.

In around 10000 BC the relative distribution in the use of materials was:

metals	approximately	4%
polymers		22
composites		31
ceramics		43

However, it should be noted that natural materials form no separate group in Ashby's graph and that glass and cement are listed under ceramics. During Euromat '97 I got hold of the book "Materials Research in the Czech Republic" in which I found a graph on the material use from 10000 BC till 2020 AD. This graph was quite similar to professor Ashby's, but deviated strongly in some percentages. For example: for around 10000 BC this graph lists the following percentages:

metal	approximately	6%	
polymers		42	!!
composites		12	!!
ceramics		42	

Among other reasons, these differences are due to the fact that Ashby considers wood to be a composite material and the Czech book defines it as a polymer. So it is a matter of interpretations. According to Ashby's graph, the period of approximately 1955 should be seen as a period of growth for the metals and, at the same time, as an all-time low for the other material groups:

metals	approximately	81%
polymers		9
composites		2
ceramics		8

For the period from 1955 until the year 2000 the graph illustrates the expectation that the metal share will decrease in favour of the other material groups, the largest relative increase being expected for the composites. And as a matter of fact Euromat ‘97, the earlier mentioned symposium, already demonstrated that the fierce development of composites has started. In my opinion this points to a clear tendency to use more vegetable materials. In order not to put too much strain on the environment, we will have to find materials which can be grown easily and fast. Within this framework the so-called Agromaterialenplein (Agromaterial Platform) was present at Euromat for the first time. This is a joint initiative of several firms whose goal it is to give publicity to the possibilities and applications of materials made of recycled (natural) raw materials. These will have to compete with synthetic and environmentally unfriendly materials.

The developments in the field of materials science are subject to a number of propelling forces. In wartime and at the time of the cold war, research was mainly aimed at (possible) war events. Now, in the period after the cold war, four propelling forces remain, i.e. the requirements of the consumer, the pressures of science, the solution of worldwide problems and so-called megaprojects. Consumers demand increasingly lighter, stronger, cheaper and more durable materials for a durable and cheap product. Because the industry funds fundamental research, a flow of new ideas is preserved. These do not have any immediate economic effects, but might have so in the long run. A good example of this is the history of superconducting materials, more on this in the chapter on electroceramics.

Energy requirements are a world-wide problem. The bottleneck is the low efficiency in energy transfer, e.g. in cells for energy storage. New materials play a crucial role in trying to find solutions for these problems.

Finally the so-called megaprojects, i.e. projects with almost inconceivably large budgets. Some examples are the space-shuttle, the preparations for a space station and the trip to Mars. These projects make high demands on the creativity of the researchers because of the materials in question, which will have to be able to perform under extreme circumstances.

2.4 A BRIEF HISTORY

The history of ceramics can be described in several ways, i.e. from a cultural or from a technical point of view. The developments of both branches of ceramics are characterized by a number of events and discoveries that some people calls highlights, e.g. the potter's wheel for design, the use of fire for baking, the use of glazing to seal earthenware, transparent pottery, modern moulding techniques like extrusion and the compressing of powders and the continuous oven. But what can be considered to be a "ceramic highlight"? No doubt different experts will give different answers. I found an article with 12 milestones from the history of ceramics on the Internet. I subsequently placed these 12 milestones in the historical survey below, each in its own individual framework. Then I emailed the author to ask him why he had selected these facts. The answer was that it was a random choice throughout history; it was not based on anything. A number of them are somehow related to glass and that points to the writer being American, since the American definition of ceramics includes glass. In September 1998 the American Ceramic Society was writing a book on ceramic highlights of the past 100 years. I am curious to know what their choice is based on.

The natural sciences have always felt the need to classify. I thought about my approach to tackling this chapter for a long time. How could I write a chapter on the history of art based on technical developments ? I consulted many people, none of whom could solve my problem. Until I read the following extract from the book "Ceramics for the Archeologist" by Anna O. Shepard: "Since I entered the ceramic field by way of archeology and have never forgotten the sense of hopelessness I experienced on opening a book on optical crystallography for the first time, I can understand the archeologist's attitude towards the physics and chemistry of pottery." This text aptly describes how I felt when I had to tackle the problem in the opposite direction because ceramics in archeology, together with related subjects, should certainly be incorporated in this book. I can motivate this with the help of a summary of analytical properties on which archeological ceramics are tested (table 2.1).

In order to find some guidelines for the organization of this chapter I visited the Hetjens Museum/Deutsches Keramikmuseum in Düsseldorf, Germany. In this museum you can see numerous items which together cover 8000 years of ceramics and I hoped I would find my classification there. The exhibition included 2 wall charts: a classification based on the kind of ceramic and a classification based on the development in different areas.

Table 2.1 Analytical properties for archeological ceramics

colour
hardness
texture
porosity
petrographic microscopy
stereomicroscopy
X-ray diffraction
analysis of the clay of the site
baking (firing) techniques
imitating found pottery
analysis of glazing
kind of decoration

Historical ceramics

earthenware	glazed earthenware	faience	stoneware (vitrified pottery)	stoneware (German: Steinzeug)	porcelain

The differences between these forms of ceramics can best be described by means of the shard type. For example, stoneware and faience have porous, white shards whereas Steinzeug has a dense and coloured shard.

The classification based on area was as follows. The bold print is the classification of the Hetjens Museum to which I have added information from other literature sources.

The Old World	Prehistory (near East, Europe)
	Greece
	Rome
Africa	earthenware, glazed earthenware, faience
Near East	earthenware, glazed earthenware, faience
	Islamic countries: Mesopotamia, Iran, Afghanistan, Egypt, Syria and Turkey
Far East	earthenware, glazed earthenware, Steinzeug, porcelain

	Several dynasties: e.g. the Ming dynasty
Europe	earthenware, glazed earthenware, Steinzeug, faience, porcelain
America	(Los Angeles - Lima) earthenware, glazed earthenware

By linking both classifications it ought to be posssible to describe the technical developments in classical ceramics (clay ceramics) for each specific area. In this chapter I have confined myself to a brief description of the history of cultural and technical ceramics.

Although this book covers most aspects of ceramics, most attention is paid to the period from approximately 1850 until now. This period is characterized by a rapid growth of industrial ceramics and a flourishing period for the type of ceramics which hardly used clay as a raw material, the co-called technical ceramics. The number of applications of ceramic materials in the period from 1850 until 2000 is much larger than in the entire ceramic history before 1850 (figure 2.5)

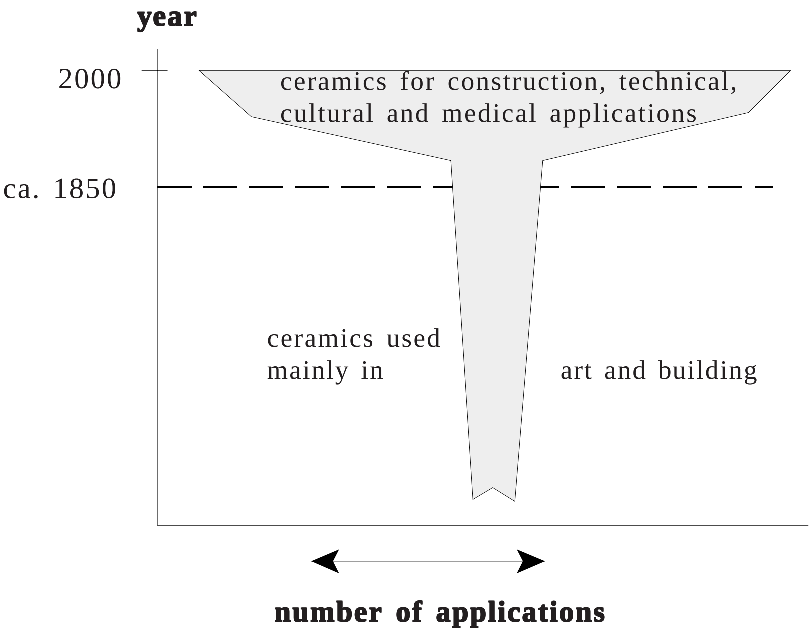


Fig. 2.5 Increase in the number of applications of ceramic materials after appr. 1850.

Cultural History of Ceramics

The cultural history of ceramics mainly deals with making pottery, the oldest craft on which continuous knowledge is available. Of course this knowledge has increased over the years, but in numerous places in the world pots are still being made in a way which hardly differs from the methods which were applied thousands of years ago. This is also true for the production of non-cultural ceramics, like for example bricks.

Obviously religion is also a part of a culture and many ceramic objects were used in religious ceremonies. The idea of an "afterlife" was common in many religions. Clay vessels containing food for the long journey to this afterlife were placed in the dead person's grave, as were implements and utensils.

Vessels containing internal organs of the pharaoh

In Palestine in about 3500 BC the bones of the dead were put in urns which were shaped like houses. The idea to decorate pottery almost certainly came from early forms of art. In Anatolia, for example, painted pottery was found in places where basket-making and weaving had been practised since long before and where the art of wall-painting was also known.

Studying cultural ceramics first of all requires a thorough knowledge of history. Should you limit this study to a particular area, then you will inevitably find that surrounding fields have to be included. Outside influences, from trade and war, have always affected art and religion and consequently also ceramic activities. Of course all the dates of the development described here are approximate.

26000 BC	The discovery that a mixture of mammoth fat and mammoth bone, to which bone ash and loess have been added, has plastic properties. The mixture could be moulded into certain shapes and dried in the sun. The material was brittle and heatproof. **The beginning of ceramics** ? From 1995 until 1998 a research at the department of chemistry of the University of Bristol which was called “New criteria for the identification of animal fats from prehistoric pottery”.
10000 BC	*Japan* First crockery, found in the Fukui caves.
6000 BC	Ceramic fires are applied for the first time in Ancient Greece. Development of the Greek pottery “Pithoi” which was used to store food and drink, for funerals and as an art form.
4000 BC	*Egypt* Terra cotta
4000 BC	Discovery of glass in ancient Egypt. Initially it was used to manufacture jewelery. The best-known example is the burial mask of pharaoh Tutankhamen.
4400–4000 BC	Limburg, The Netherlands Bandceramic culture

The oldest pottery to be found in The Netherlands dates from around 4000 BC and is called “band ceramics’’. The name is derived from the decorations which were impressed into the clay when it was still soft. Old cultures are often given names which have been derived from objects characteristic of that period of time.

2000 BC	A recipe for a copper / lead glaze from about this period is found on a clay tablet in North Iraq.
1700–1400 BC	In 1946 a beautiful blue / green glaze from about this period is dug up in Atchana in North Syria. This discovery is considered to confirm the invention of this technique in Northen Iraq.

900 BC–AD100 *Greece* decorated vases

210–209 BC In March 1974 farmers drilling a well discovered the “Chinese Terra Cotta Army” near the tomb of a Chinese emperor some 30 km east of the city of Xi’an. The army consists of more than 7000 life-size terra cotta soldiers and horses which were buried together with the emperor in 210–209 BC.

50 BC–AD 50	`The start of the production of lenses, mirrors and windows in Rome.These techniques are spread by the Roman conquests.
AD 600	The first porcelain is made in China by heating a mixture of clay, feldspar and quartz. It was mainly used as crockery.
AD 900–1500	*Persia* (Iran) glazed and painted earthenware wall tiles

In 751 the Perian Abbasids defeated the Chinese. Chinese prisoners introduced fine ceramics in Mesopotamia. This pottery flourished in the 9th and 10th century.

The Fatimid dynasty was founded in Tunisia and occupied Egypt from 969 until 1171. This was the origin of the so-called Fatimid pottery in Egypt.

AD 1300–1600	*Italy*	Majolica
AD 1400–1700	*China*	Porcelain from the Ming dynasty
Middle Ages	*Germany*	Cologne stoneware
14th & 15th century	*Spain*	Golden Age of the Spanish ceramics which started in Malaga in the mid-13th century. Products were even exported to Egypt.
1564	*The Netherlands*	The first records of the foundation of a stoneware factury in Middelburg. Later Delft (1586), Haarlem (1573) and Rotteram (1612) followed.
1759	*Great Britain*	Wedgwood

History of Technical Ceramics

7000 BC	*Jericho*	Clay tiles
3500 BC	*Mesopotamia*	The ***potter'wheel*** for modelling *The use of the potter's wheel can be derived from the structure of the manufactured pottery.*
3200 BC	*Syria*	Sewer pipes made of fired clay
1500 BC	*Egypt*	Fired clay moulds are found in a bronze foundry.
750 BC	*Etruria*	Roof tiles made of fired clay
25 BC	*Italy*	Vitruvius describes the different clay types used for making bricks.
50 BC–AD 50	In ancient *Rome* glass is being produced for the first time; it is used for lenses, windows, etc.	
AD 600	Start of the development of porcelain in *China*; later used as insulation material in electrical applications.	
1020	*Germany*	First German floor tiles
1550	*Italy*	Cipriano Picolpasso writes a instruction method for the "Toepfer", the potter
1794	*Germany*	The Prussian government first draws attention to the dangers of lead glaze
1808	*France*	Production of a porcelain false tooth
1809	*England*	Introduction of a mechanical press for the production of ceramic buttons.
1840	*Denmark*	A patent for a tunnel oven is applied for.

1855	*The Netherlands*	Schlickeysen develops the clay mill and screw for the transport of plastic material.
1859	*France*	Discovery of silicon carbide.
1861	*Italy*	Porcelain filter for drinking water purification
1874	*Germany*	Aron, Seger and Kramer introduce clay analysis
1886	*Germany*	Seger introduces his Segel cone for temperature measurements.
1887	*Germany*	Refractory stone in blast furnaces
1900	*Germany*	Rosenthal sets up the manufacture of electroporcelain
1929	*Germany*	Drying installations for plates.
1949	*Germany*	Oxide-ceramic cutting tools (chisels).
1954	*Germany*	Discovery of piezoceramics.
1965	*USA*	Ceramic tiles to cover space craft
1969	*USA*	First applications of joint prostheses made of aluminium oxide.
1980	*Japan*	Heatproof turbine rotors made of silicon nitride and silicon carbide.
1987	*Switzerland*	discovery of superconducting ceramics.

2.5 HISTORY OF TECHNICAL CERAMICS IN THE NETHERLANDS

At the beginning of the 1980s trade and industry complained about the inferior knowledge in the field of technical ceramics, i.e. ceramics made from mainly synthetic ingredients. A research programme was set up. With a budget of 30 million Dutch guilders the Dutch Energy Centre in Petten and the universities of Delft and Eindhoven started their fundamental research. The programme ended some time ago. A committee which studied the final results concluded that “the short-term commercial effects are not expected to be significant”. In 1987 the same Energy Centre set up the NKA, Nederlands Keramisch Atelier (Dutch Ceramic Workshop), where much know-how in the field of technical ceramics is concentrated. The NKA has applied itself to energy-related products, which is pre-eminently the field of the Energy Centre. Among other things these activities have led to the development of a ceramic burner for central-heating boilers, fuel cells and membranes for the separation of gases.

Globally about 15 thousand million guilders were spent on technical ceramics in 1992. The electronics industry accounts for 75% of this; in Europe this industry is dominated by Philips. This firm has a research laboratory in Roermond, The Netherlands where they work on iron oxides in magnetic heads for VCRs and other appliances. 20% is allotted to mechanical construction like engine components and tap washers. The remaining 5% is spent on bioceramics, i.e. the ceramics of which implants are made. Negative and positive reports take turns. On 10 September 1994 a renowned Dutch newspaper, De Volkskrant, published an article under the title: “Technical ceramics are impeding their own progress”, in which it is said that people were very enthusiastic about the use of sophisticated technical ceramics about ten years ago, that is around 1984. In Japan there was talk of ceramic car engines which would lead to a fuel consumption reduction of dozens of percentages, heat-resistant tiles were needed for the spaceshuttle, etc. However, by the time the first ceramic engines were ready to be tested, the designers of conventional engines had already succeeded in making the latter more economical.

The initial enthusiasm for technical ceramics has plummeted. Yet you will come across many applications in this book. An inconsistency perhaps? Ashby’s graph illustrates the increasing expectations for ceramics, and especially for technical ceramics, in the decades to come.

2.6 TEACHING CERAMICS

The origins of the instruction in ceramics lies in Germany where Herman August Seger, originally a chemist, set up research and training at the University of Berlin in 1870. Thanks to Edward Orton jr. ceramics became the subject of academic studies at the Ohio State University in the USA in 1894. Eighteen American universtities offered courses in ceramics as early as 1949.

The number of course programmes is directly proportional to the demand made by trade and industry. Many factors have been of influence on this instruction, among others the Gibbs phase rule (see the chapter on Phase rule), X-ray diffraction to clarify the structure of solids and the development of synthetic barium titanate and other ceramic materials whose properties could be influenced by controlling composition and process conditions. As early as 1900 it became clear that the study of ceramics required much knowledge of other subjects, as appears from the Ohio State University's course programme of that year.

The Ohio State University, USA,
1900 course programme Ceramics

Plane geometry - geometry, analysis, algebra, projective geometry, descriptive geometry
Inorganic chemistry, quantitative analysis
Free drawing
Writing reports
French or German
Physics (electricity, magnetism, light, sound, mechanics)
Ceramics, ceramic laboratory
Mining, mineralogy, geology
Glazes, cement
Photography
Presentations

Mathematics is an indispensable adjunct to any technical study. Drawing is related to the designing of ceramic objects. In developing technical ceramic products we often look to nature and that is why knowledge of mining, mineralogy and geology is important. When studying chemistry you learn about the synthesis, chemical properties and analysis of subtances. Since technical ceramic products are also found in physics, this subject is also essential. Glazes are used to cover ceramics. Perhaps the item “cement” is surprising in the list above because this material is usually not associated with ceramics. However, when you look at the paragraph in which the definition of ceramics is discussed, it will be clear that there are many definitions in circulation.

How did the developments in the USA continue?

In 1925 493 university graduates were already employed in the ceramic industry. By then the American Ceramic Society had been founded and it consisted of 7 departments: art, enamel, glass, fireproof materials, whiteware, terra cotta and heavy clay. Unfortunately World War II caused a decrease in the number of students of ceramics. In order to postpone the conscription of ceramic engineers an attempt was made to have ceramic studies and ceramic engineering pronounced essential for the war, to no avail however. The fact that there was no good definition of ceramics was partly to blame for this failure.

After the war the number of enrolments increased rapidly. In 1960 the transistor, space travel and the cold war with its demand for new materials exercised a clear influence on the studies. This even resulted in a new discipline: “materials science”. It was clear at that time that materials should not be taught individually. Should this be considered as a first indication towards combining materials? Did they already realise that composites would become increasingly important?

Let us concentrate a little longer on ceramics. Here micro-analysis only slowly won ground and the application of solid state physics lagged behind. Very slowly the relationship between the properties of a material and its microstructure was being discovered. Metallurgy had already been characterized by a theoretical approach for some time and consequently metals were about 15 times as important as ceramic materials in 1960 (see Ashby’s graph). This was of course influenced by the fact that metals have relatively simple structures which, in their turn, simplify theoretical comtemplations. Ceramic structures are very often complex and are characterized by multiphase systems. However, at present ceramic materials are approached much differently than for instance in 1900.

An ideal foundation course programme in ceramics now looks like this:

Current ideal ceramics course programme

Foundation subjects: chemistry, mathematics, languages, report-writing, etc.
Electronics *(75% of the ceramics sales in 1992)*
Statistics and strength of materials *(among other things*

dependent on the microstructure)
Thermodynamics and phase equilibria
Thermal and mass transport of processes
Firing processes *(theoretical approach of the firing process)*
Defect – chemistry and transport *(properties at an atomic base)*
Kinetics
Dielectrics, optics and magnetism *(properties of certain ceramic materials)*

2.7 A VIEW TO THE FUTURE

The future will mainly bring developments in the field of technical ceramics. On The Internet I came across a report with the title: "Fundamental Research Needs in Ceramics" which listed the following subjects for working groups in a 1997-workshop and so is trendsetting for the future:

- structural and electromechanical ceramics
- electrical and chemical ceramics
- glass and optical materials
- processing
- integrating ceramics with other materials
- education

What new developments the future holds nobody knows for certain. In electronics people will try to miniaturise electric equipment even further. Non-functional, ceramic packaging will be converted into functional components. For this new ceramic materials are necessary, as are ways to process them. High-temperature superconductors will lead to magnetic levitation craft, cheap electricity and improved MRI (magnetic resonance imaging).

The car industry, which already uses ceramics, expects better sensors for movement, composition of exhaust fumes, electrical and thermal changes. In addition developments in that branch of industry must focus on light-weight engine components which are not only strong but must also be able to withstand high temperatures. In the energy sector, fuel cells and energy transport via optical fibres are the centre of attention. And finally, the medical world will make more use of ceramics in diagnostic instruments and the possibilities of bone replacement will be expanded, as will the use of capsules to gradually release drugs for chemotherapy.

3

Chemistry

3.1 INTRODUCTION

All matter is built up of dozens of kinds of particles, the so-called *elementary building blocks*. These building blocks together form larger particles, which we call *atoms*. Most atoms tend to bind to other atoms to form even larger particles which can consist of two atoms, but also of several thousands and some atoms do not bind to other atoms at all.

Particles consisting of one or more atoms are called substances and have chemical and physical properties. For instance, a characteristic of the metal sodium is that it reacts very quickly with water in which process hydrogen gas – among other things – is formed. The hydrogen gas was not present before the reaction took place and afterwards there is no trace of sodium. This is an example of a chemical reaction and, consequently, it is a chemical property of sodium that new substances with other properties are formed from water and sodium. The boiling point of water is 100 °C and that of natural gas –162 °C; the difference is 262 °C. But particles of water and natural gas are almost equally heavy. From this it appears that the evaporation of water costs much more energy than the evaporation of natural gas. The reason for this is that water molecules are more tightly bound than natural gas molecules. During evaporation, the nature of the particles does not change. This is a physical process and the boiling point is a physical property.

From the previous we can conclude that

> Most of the chemical and physical properties of substances are determined by their structure.

In order to get to know this structure, we have to penetrate the substance quite deeply and then we will find the three most important building blocks of matter, *the elementary particles*:

PROTON **NEUTRON**

ELECTRON

You might imagine these particles as minute spheres, with minute masses and the smallest possible charges: the elementary charges. In Table 3.1 the masses and charges are listed. Knowledge of the dimensions is not required to understand the rest of this story.

Two things are remarkable in this table. First, it is important to bear in mind that the mass of an electron is negligible compared with the mass of a proton and a neutron. Furthermore, a neutron appears not to have any charge, whereas a proton and an electron do.

Now that the main building blocks have been introduced, we can start arranging certain numbers of protons, neutrons and electrons in a specific way with regard to each other and thus "build" atoms. Six rules have to be met during this arranging.

Table 3.1 The three most important elementary particles

particle	mass (kg)	charge	symbol
proton	1.67265×10^{-27}	+	p^+
neutron	1.67495×10^{-27}	0	n
electron	9.1095×10^{-31}	–	e^-

3.2 THE STRUCTURE OF AN ATOM

An atom is built up of protons, electrons and neutrons according to the six rules mentioned below:

1. An atom is not charged, in other words it is "electrically neutral". This means that the number of protons p^+ is equal to the number of electrons e^-.

2. It is not possible to establish the number of neutrons in an atom with the help of simple rules. Their number is always bigger than or equal to the number of protons, with the exception of the hydrogen atom which has one proton and most of its atoms no neutrons.

3. Protons and neutrons are situated in the centre of the atom and

together form the *nucleus* of the atom.

4. The electrons circulate around the nucleus in specific orbits. These orbits are also called shells and can be compared to the orbits in which satellites travel around the Earth. When more electron orbits are present in one atom, these differ in diameter.

5. The maximum number of electrons in a shell depends on the diameter. The bigger the diameter, the larger the maximum number of electrons will be. The shells are designated with the letter K, L, M, etc. The K-shell has the smallest diameter. In that order the shells are also denoted with $n = 1$, $n = 2$, etc. The maximum number of electrons per shell can then be calculated using the formula $2 \times n^2$.

6. The maximum number of electrons in the outermost shell – which is the shell with the largest diameter – is usually 8 for the 20 smallest atoms. When the atom only contains one shell, the maximum number is 2.

To illustrate these "rules for the structure of atoms", the electron distributions over the shells of the 20 smallest atoms are given here. These distributions are called the *electron configurations*.

Table 3.2 Electron configurations of the twenty smallest atoms

atom kind	symbol	electron distribution over the shells K	L	M	N
hydrogen	H	1			
helium	He	2			
lithium	Li	2	1		
beryllium	Be	2	2		
boron	B	2	3		
carbon	C	2	4		
nitrogen	N	2	5		
oxygen	O	2	6		
fluorine	F	2	7		
neon	Ne	2	8		
sodium	Na	2	8	1	
magnesium	Mg	2	8	2	
aluminium	Al	2	8	3	
silicon	Si	2	8	4	
phosphorus	P	2	8	5	
sulphur	S	2	8	6	
chlorine	Cl	2	8	7	
argon	Ar	2	8	8	
potassium	K	2	8	8	1
calcium	Ca	2	8	8	2

Most of the more than 100 kinds of atoms which are known up until now are present in nature as simple atoms. Examples are most metals and the noble gases such as neon and argon.

Reactive atoms, like for instance those of sodium and chlorine, are not present in nature. They react with each other or with other reactive atoms and form compounds which are a lot less reactive and consequently can be found in nature. Sodium and chlorine, for example, react to form the well-known sodium chloride, also called table salt. This compound is abundantly found in many places in nature.

The kinds of atoms which are not present in nature as simple atoms have found allies with which to form larger units. Examples of these are sulphur which consists of shells of eight sulphur atoms and diamond which is in fact an accumulation of interlinked carbon atoms.

Whether a simple atom or a larger unit, all atom kinds are called *elements*. Each element is represented by means of a symbol consisting of a capital or a capital and a lower-case letter.

The hydrogen atom with the symbol H is the smallest atom. It contains one proton and one electron in the K-shell. The model of the atom in Fig. 3.1 which meets all 6 requirements for building an atom is called ***the Bohr atomic model*** after Niels Henrik David Bohr, the Danish physicist who lived from 1885 until 1962.

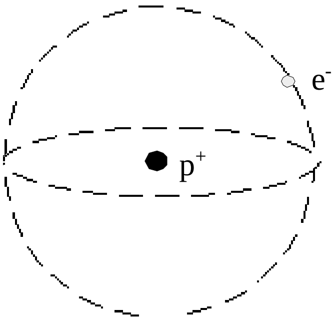


Fig. 3.1 The Bohr atomic model of a hydrogen atom.

Two other kinds of hydrogen atoms exist. Figure 3.2 is a simplified representation of the 3 kinds of H atoms in cross-section.

These three kind of hydrogen atoms differ in the number of neutrons in their nuclei. This phenomenon occurs with all atom kinds. Atoms of the same kind but with different numbers of neutrons in their nuclei are called *isotopes*.

We have already seen that protons and neutrons are much heavier

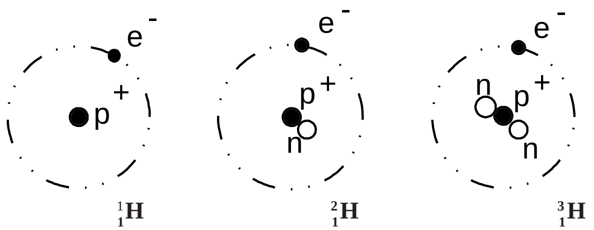


Fig.3.2 Three kinds of hydrogen atoms.

than electrons and that the atomic mass is consequently mainly determined by the mass of the protons and neutrons. From Table 3.1 we can conclude that the mass of a proton is more or less equal to the mass of a neutron. It is customary to place two numbers to the left of the atomic symbol

$^{A}_{Z}X$

A: mass number = number of protons + neutrons

X: atomic symbol

Z: atomic number = number of protons

The element symbol, the mass number and the atomic number together represent the atom kind or the nuclide. An example:

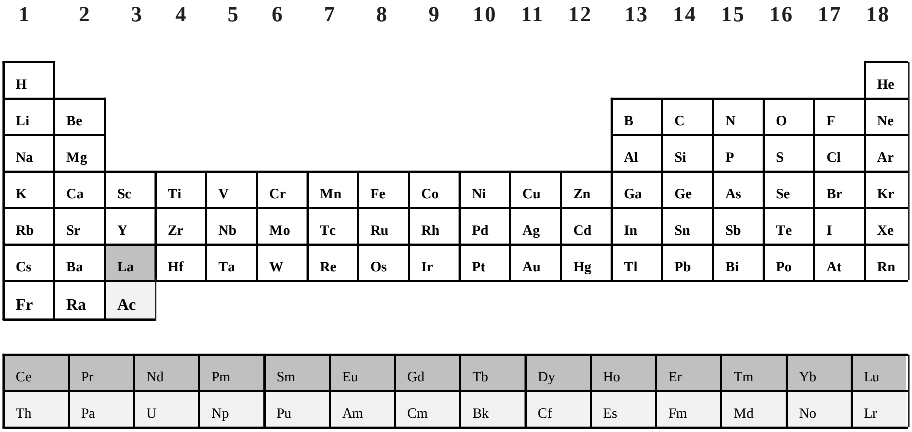
$^{12}_{6}C$ →mass number: 12 (protons + neutrons) [6 protons + 6 neutrons]
→ atomic number: 6 protons

3.3 THE PERIODIC TABLE OF ELEMENTS

At this moment more than 100 kinds of atoms are known. The exact number is open to debate because the atoms with an atomic number of 85 or higher are no longer stable, i.e. these atoms are radioactive. When an atom is radioactive it emits certain kinds of radiation which can for example contain protons, electrons and neutrons. Every kind of atom represent a kind of element, all of which can be arranged in a table according to the increasing atomic numbers and the similarities in properties. This table is called the periodic table of elements, abbreviated PT. Similarities in properties are mainly caused by the same number of atoms in the outermost shell.

The similarity in properties among the elements is mainly determined by the number of valence electrons in the valence shell.

The very schematic and simplified table in Fig. 3.3 is a first introduction to the PT.



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

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

Fig. 3.3 The periodic table of elements.

The horizontal rows in the PT are called *periods* and are numbered 1 up to and including 7 from top to bottom. The classification in periods is mainly based on similarities in the number of electron shells. An example: all elements in the second period have two shells. The vertical columns are called *groups*. Classification into groups is mainly based on the number of electrons in the valence shell. An example: all elements in group 2 have 2 electrons in their valence shells.

The rows of shaded elements should be placed immediately behind the elements which are shaded in a similar way. Both rows have been placed outside the PT because they contain extremely rare or radio-active elements which are only seldom used as a result.

3.4 CHEMICAL BOND

3.4.1 Electronegativity

In order to form larger units atoms can bind with similar or different atoms in several ways. The chemist says: “the atoms form larger particles”. How atoms are bound to each other is mainly determined by the atom structure of the binding atoms. When a bond is formed the valence electrons of the binding atoms will realise the bond.The nature of that bond is mainly determined by the force with which the binding atoms attract each other’s valence electrons. As an example we shall compare the attraction to electrons of respectively a lithium (Li) and a fluorine (F) atom. Both atoms can be found in the same period of the PT, lithium at the extreme left and fluorine almost at the extreme right.

Both atoms have two shells. A fluorine atom however has a larger nuclear charge (9 protons) than a lithium atom (3 protons). That is why the nucleus of F attracts the negatively charged electron more powerfully than the Li nucleus does (Fig. 3.4). Therefore a F-atom is smaller than a Li-atom.

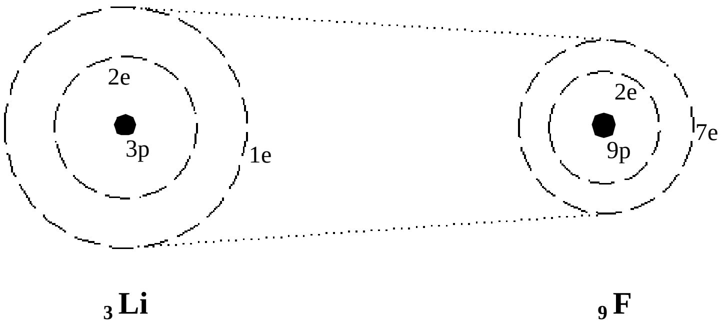


Fig. 3.4 Bohr model of a lithium and a fluorine atom.

Electrons of different atoms are also attracted more powerfully by an F atom than by an Li atom. As a result, an F atom will take up electrons in its valence shell more easily than a Li atom. By doing this the atom will obtain more electrons than protons, and so it will be negatively charged. We no longer call this an atom, but a (negatively) charged) ion. To express the difference, one says: *a fluorine atom has a larger electronegativity (EN) than a lithium atom.*

As a general rule the EN in a period of the PT increases from left to right. The reader should determine for him/herself why the EN in a group of the PT decreases from top to bottom.

In Table 3.3 the EN-values of a number of elements are listed to illustrate the previous theory about the changing EN within the PT. Irregularities within a group or period are due to the fact that some other factors also influence the EN-value.

3.4.2 *Kinds of bonds*

The nature of the bond between two atoms is mainly determined by the difference in electronegativity between both atoms. As of now this difference will be denoted as EN. When a bond is formed between two atoms, they both endeavour to obtain completely filled valence

Table 3.3 EN-values of some elements

Period no.	Group number 1	2	13	14	15	16	17	18
1	H 2.2							
2	Li 0.97	Be 1.47	B 2.01	C 2.50	N 3.07	O 3.50	F 4.10	Ne --
3	Na 1.01	Mg 1.23	Al 1.47	Si 1.74	P 2.06	S 2.44	Cl 2.83	Ar --
4	K 0.91	Ca 1.04						

shells after forming this bond. The use of the word "endeavour" implies that there are exceptions to this rule. After bonding there can be question of a so-called noble gas electron distribution or *noble gas configuration*. In the noble gas configuration an atom possesses a completely filled valence shell. When the K shell is the valence shell, it is completely filled with two electrons; in the case of the other shells, eight electrons are required. To illustrate this obtaining of the noble gas configuration when forming a bond, some examples are given in Fig. 3.5, 3.6 and 3.7.

The H atoms form a larger unit by means of a common electron pair, a pair which is situated in the valence shell of both atoms. A bond which is formed by means of one or more common electron pairs is called *a covalent bond*. A common electron pair is represented by a small line between the atom symbol in the *structural formula*.

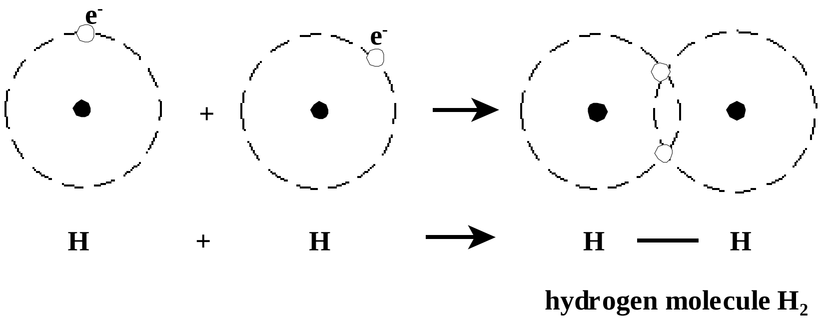


Fig. 3.5 The formation of a hydrogen molecule.

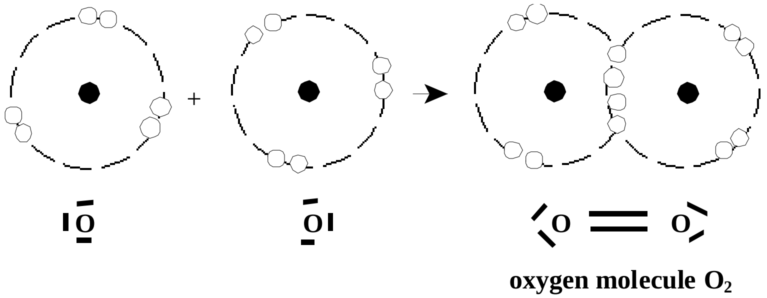


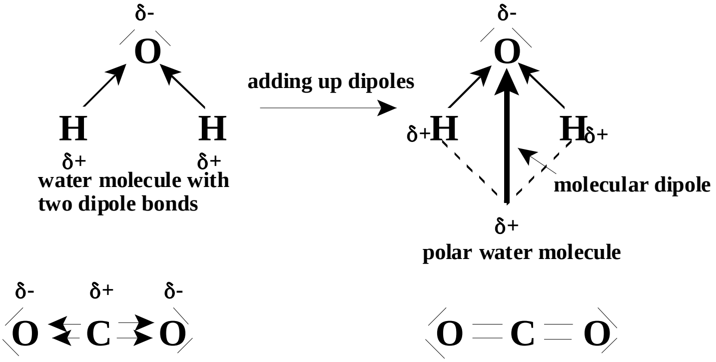
Fig. 3.6 The formation of an oxygen molecule out of two oxygen atoms.

Fig. 3.7 The formation of a carbon dioxide molecule.

An oxygen molecule is formed out of two oxygen atoms by means of two covalent bonds (Fig. 3.6). It should be pointed out here that only the nuclei and the valence shells (L shells) of the oxygen atoms have been drawn. Both atoms are bonded by means of both L shells and after the bond has been made these shells should contain eight electrons. This can only be realised when four electrons, two electrons of each atom, are commonly used. This results in a double bond. It is customary to reproduce all electrons in the valence shell in the structural formula. The electron pairs between the atoms are called *common* or *binding electron pairs*. All other electrons in the structural formula are called *free electron pairs*. One molecule of oxygen has two binding electron pairs and, for every oxygen atom, two free electron pairs.

Multiple, covalent bonds are also possible between different kinds of atoms. An example of this is the formation of a carbon dioxide molecule form one carbon atom and two oxygen atoms (Fig. 3.7).

We should now have a closer look at the difference between a covalent bond between two atoms with EN = 0 (so two similar atoms) and a covalent bond between two atoms with EN 1.7. In the first case the binding electrons are situated in the exact centre between the atomic nuclei and consequently are for 50% part of both atoms. This means that both atoms are neutral. In the second case the binding electron will have shifted in the direction of the atom with the largest EN-value.An example of this is the O–H bond in which the O atom has the largest EN-value. The binding electron pair might then belong for 60% to the O atom and for 40% to the H atom. *The O atom is in that case slightly negatively charged with regard to the H atom, but there is still no question of ions*. To indicate this situation the Greek letter delta δ is added to the atoms together with a minus or plus sign, so respectively δ– (pronounce delta minus) and δ+. The bond now has a minus and a plus pole and is consequently called a *dipole* or *dipole bond* (di = two) or a *polar covalent bond*. An arrow is placed above the bond, a so-called vector, which indicates the direction of the electron shift. In order to learn more about the properties of a molecule, all vectors of the bonds must be added up. When one vector remains, then the molecule in total has a dipole and there is question of a *polar molecule*. However, when no vector is left over, the molecule is *apolar*. Adding up vectors takes place by means of a parallelogram, in exactly the same way the forces are added up. This can be seen in Fig. 3.8.



A carbon dioxide molecule does have dipole bonds, but is an apolar molecule (the vectors cancel out)

Fig. 3.8 A polar water molecule and an apolar carbon dioxide molecule.

The *ionic or electrovalent bond* is a third kind of linkage. When EN between the binding atoms exceeds the value of 1.7, there is hardly question of common electron pairs. In that case the valence electrons of the atom with the smallest EN-value are almost entirely transferred to the other atom with the largest EN-value. One atom loses one or more electrons and becomes a positively charged ion, whereas the other gains one or more electrons and becomes a negatively charged ion. The character of the bond is now predominantly ionic. In literature there is constantly question of a twofold character of the bond. The nature of the bond is described in the form of a percentage of covalent and a percentage of ionic character. An example of an ionic bond is sodium fluoride, whose formation has been represented in Fig. 3.9. In this figure the first reaction illustrates the formation of two sodium ions from two sodium atoms. In the second reaction the fluorine ions or fluoride ions are formed. In the fifth reaction the formation of sodium fluoride from sodium and fluorine is represented in the form of an equation.

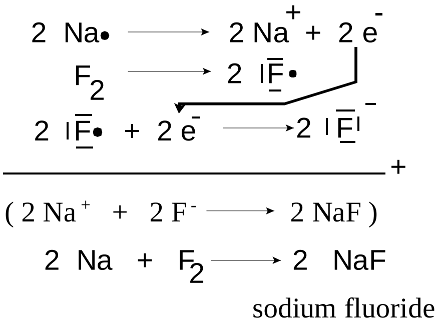


Fig. 3.9 The formation of sodium fluoride.

In the example above the resulting attractive force between the oppositely charged ions and not the electron transfer nor the formation of positive and negative ions take care of the formation of the bond.

The kinds of linkages discussed here were all brought about by means of one or more common electron pairs or by means of electron transfer from one atom to another. However, there are also bonds which are formed differently, e.g. the so-called metallic bonds.

The *metallic bond* occurs in the crystals of metals. In metals the positively charged metal ions are packed according to a certain pattern. This is called the crystal lattice. The electrons which have escaped from each individual atom are not exposed to strong attractive forces from the remaining positively charged ion and consequently are free to move through the crystal. Together they form a wandering cloud of electrons which is responsible for the conduction of mainly current and to a lesser extent heat by metals. The interaction between the negatively charged electron cloud and the positively charged metal ions results in a binding force that holds the metallic crystal together. Figure 3.10 is a simplified representation of the crystal lattice of copper.

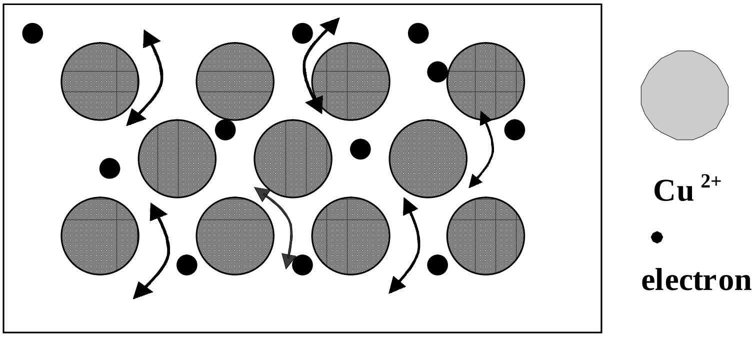


Fig. 3.10 Simplified representation of the crystal lattice of copper.

3.5 PHYSICAL PROPERTIES OF SUBSTANCES

In this paragraph only two physical properties are discussed: viz. the boiling point and solubility. These properties are affected by the attractive forces which the particles of the pure substance or in a mixture exert on each other. Particles attract when they are charged, so when they are ions, when they possess a dipole or when they are able to form hydrogen bridges.

In general substances which consist of positive as well as negative ions have high boiling points because a lot of energy is required to loosen the particles from the crystal lattice. These substances mostly dissolve well in a solvent whose molecules possess a dipole. These dipoles surround the ions, due to which the latter are no longer able to unit to form a crystal. This surrounding by molecules of the solvent is called solvation, or, in the case of water, *hydration*. In Fig. 3.11 you can see what happens to the ions when sodium chloride (NaCl) is dissolved in water.

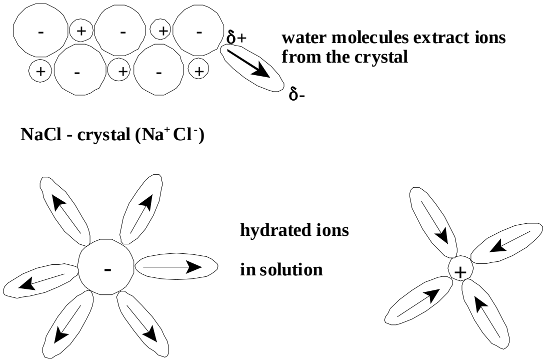


Fig. 3.11 Dissolving sodium chloride in water.

The degree in which substances are soluble in water varies from very well (hundreds of grammes per litre) like in the case of sodium chloride, to extremely bad (about ten milligrammes per litre) like for instance calcium carbonate (just think of marl).

When a substance consists of molecules and a hydrogen atom is linked to a strongly electronegative atom (O,N,F or Cl) in these molecules, the molecules attract each other by means of so-called *hydrogen bridges* or *H-bridges*. Figure 3.12 represents the way in which a grid of H-bridges keeps the water molecules together.

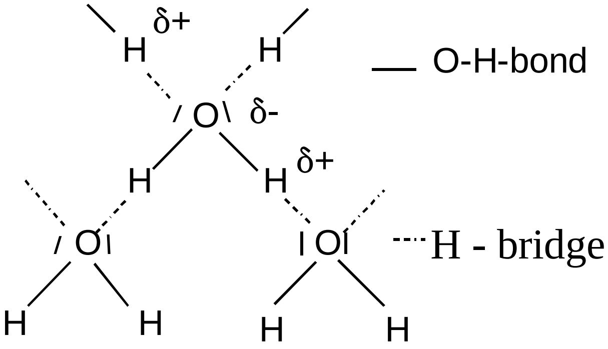


Fig. 3.12 Hydrogen bridges between water molecules.

Owing to these H-bridges water has the relatively high boiling point of 100 °C. In comparison: methane (CH_4) has a similar particle mass as water, but is unable to form H-bridges. That is why methane is a gas with a boiling point of –164 °C. Substances which can form H-bridges generally dissolve well in solvents which can do the same and their molecules mostly possess dipoles.

When particles possess *dipoles*, they attract. The attraction between the – end of one molecule and the + end of another results in the formation of a network. This attraction is third in strength, after the ion attraction and the H-bridge formation. In general, the boiling points of these substances are consequently lower than those of substances with nearly equal particle masses with ion bonds or H-bridge formations.

3.6 ELEMENTS AND COMPOUNDS

In chemistry, an element is simple substance which cannot be resolved by chemical means into chemically different components. The particles of an element can comprise one atom, molecules consisting of two atoms of the same kind, larger units of more than two atoms of the same kind or ions with moving electron clouds. Some examples of *elements* are

particles consisting of one atom	noble gases	*e.g.* neon Ne
particles consisting of two atoms	oxygen O_2	
particles consisting of more atoms	sulphur S_8	

The element carbon occurs in nature in two so-called *allotropic forms,* different crystal structures with the same chemical formula. In Fig. 3.13 the crystal structure of diamond and graphite have been represented. In *diamond* the C atoms are closely packed and each C atom is linked with four other C atoms. Thus a tight network of atoms is formed which, together with the binding strength, is responsible for the extreme hardness of diamond. *Graphite* has a layered structure and the space between the layers is relatively large.

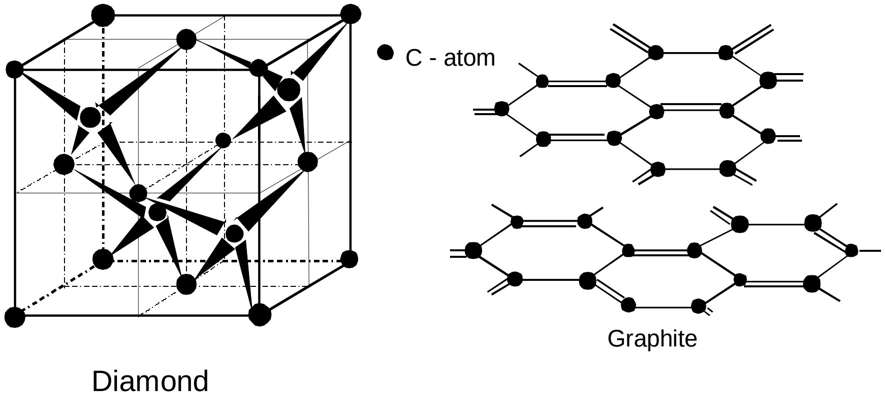


Fig. 3.13 Crystal structures of diamond and graphite.

Graphite has a layered structure and consequently is a very soft material, in spite of the fact that the bonds within one layer are extremely strong. When you rub graphite between your fingers, they become black. You displace and remove the layers of the crystal lattice one at a time by rubbing it.

Finally, it should be pointed out that most elements are metals. As we have seen earlier, they are built up of positively charged metal ions and an electron cloud.

Compounds

Compounds are substances whose particles consist of more kinds of atoms and / or ions and which can be subdivided into three groups.

The first group is formed by the compounds with exclusively covalent bonds. Examples of this group are water, sulphur dioxide and carbon monoxide. The *nomenclature* or systematic naming of these compounds is quite simple, as appears from the following examples:

SO_2	monosulphur dioxide or sulphur dioxide
N_2O_3	dinitrogen trioxide
Si_3N_4	trisilicon tetranitride

The atom on the left (with the lowest EN-value) is denoted by means of the English name, the one on the right by means of the Latin one. In addition, the number of each atom is indicated by the prefixes mono (one), di (two), tri (three), tetra (four), etc. The prefix “mono” is often omitted.

The second group of compounds is formed by the compounds with *exclusively ionic bonds*. These compounds include metals (left in the formula and with the lowest EN-value) and the chemical formulas are simple, for example:

NaCl	BaO	AlF_3
sodium chloride	barium oxide	aluminium fluoride

Quite often the charge of both ions can be deduced from the atomic number of the atom in question. NaCl, for example, is formed from $_{11}Na$ with the electron configuration K2 L8 M1 and $_{17}Cl$ with K2 L8 M7. The sodium atom will lose one electron and thus become Na^+, the chlorine atom will gain one and thus become Cl^-. The compound is electrically neutral and a particle consists of one sodium ion and one chlorine ion.

A number of metals (especially those of group 3 up to and including 12 of the PT) can form more kinds of positive ions. In that case the kind of ion must be mentioned in the name by placing a Roman number behind the name of the metal:

CuCl	copper(I) chloride	contains Cu^+ and Cl^-
$CuCl_2$	copper(II) chloride	contains Cu^{2+} and Cl^-
$FeBr_3$	iron(III) bromide	contains Fe^{3+} and Br^-

The third group is formed by the compounds which possess both ionic and covalent bonds and their negative ions consist of several

Table 3.4 Names and formulas of some negatively charged ions

Name	Formula	Name	Formula
carbonate	CO_3^{2-}	phosphate	PO_4^{3-}
chromate	CrO_4^{2-}	sulphate	SO_4^{2-}
nitrate	NO^-_3	silicate	SiO_3^{2-}
hydroxide	OH^-	dichromate	$Cr_2O_7^{2-}$

kinds of atoms. One example is potassium nitrate KNO_3, built up of potassium ions K^+ and nitrate ions NO_3^-. There is an ionic bond between the potassium and nitrate ions and a covalent bond between the nitrogen and oxygen in the nitrate ion. The positively charged ion is usually a metal ion. Some formulas and names of negatively charged ions are mentioned in Table 3.4.

Some examples of salts:

$Cu(NO_3)_2$	copper(II) nitrate
$Na_2Cr_2O_7$	sodium dichromate
$CaCO_3$	calcium carbonate
$NaOH$	sodium hydroxide

3.7 CHEMICAL CALCULATIONS IN PURE SUBSTANCES AND IN MIXTURES

3.7.1 The concept 'mole'

We already know that all atoms possess isotopes. For hydrogen these are:

$$^1_1H \qquad ^2_1H \qquad ^3_1H$$

The top number in the symbols is the mass number and the bottom number is the atomic number. The atomic mass of the element hydrogen is the weighed average of the mass numbers of the three isotopes; according to several tables:

Atomic mass H = 1.0079

Which unit should be placed behind that number? kg, g, mg, ...? None of these is correct. In daily life we are used to adapting the mass unit to the mass of the 'object'. No-one would say: "I would like to have 5×10^9 mg of sand", but they would say: "I would like 5 tonnes of sand". At the butcher's you would not ask for "0.2 kg of liver pate, but you would want to have "200 grammes of liver pate". It has been determined that 6×10^{20} H-atoms weigh about 1 mg and that means that even the unit mg would be much too high for atomic masses. Therefore, a new unit has been introduced for the atomic mass:

the unified atomic mass unit u:

$$1\ u = 1.6605402 \times 10^{-27}\ kg$$

We have already seen that a chemist who weighs 1 mg of hydrogen atoms in the shape of hydrogen molecules actually weighs 3×10^{20} molecules. Because the number of weighed particles is extremely large even when weighing minute amounts of a substance, we needed a new unit to represent the number of particles. This new unit will now be introduced with the help of two calculations:

– atomic mass of boron B = 10.81 *u*

i.e., 1 atom of boron B has a mass of: $10.81 \times 1.6605402 \times 10^{-27}$ kg = 17.95×10^{-27} kg.

Suppose we were to weigh 10.81 g of boron. How many B atoms would this mass contain?

answer: $$\frac{10.81 \times 10^{-3}\,(kg)}{17.95 \times 10^{-27}\,(kg)} = 6.022 \times 10^{23}\ \text{atoms}$$

– atomic mass of platinum Pt = 195.09 u

i.e., 1 atom of platinum Pt has a mass of $195.09 \times 1.6605402 \times 10^{-27} = 3.239547 \times 10^{-25}$ kg.

Consequently, the number of Pt atoms in 195.09 g of platinum is

$$\frac{195.09 \times 10^{-3}}{3.239547 \times 10^{-25}} = 6.022 \times 10^{23}$$

The following may be concluded from these calculation examples:

*** When you weigh as many grammes of a substance as the particle mass amounts to, then this amount will always contain the same amount of particles, viz.

6.022045×10^{23} particles

That the calculations do not always produce this number is caused by the fact that rounded values are used for the atomic masses. This amount of particles is called

Avogadro's number N_A

$$N_A = 6.022045 \times 10^{23} = 1 \text{ mole of particles}$$

In this connection we say: the molar mass M is the mass of one mole of particles with the unit 'grammes per mole', abbreviated g/mole. So for instance: the molar mass of platinum is

195.09 g/mole, abbreviated M(Pt) = 195.09 g/mole.

3.7.2 Density

The density (also called specific gravity) of a substance is calculated by means of the formula:

$$\rho = \frac{m}{v} \text{ kg/m}^3 \quad (\rho = \text{Greek letter rho})$$

The unit is represented according to the international system of units (SI system). It is however often deviated from. In chemistry the units g / l and g / ml are often used. All substances, whether solid, liquid or gaseous and pure or impure have a certain density. The numerical value of this density indicates how much mass classifies under a certain volume and is dependent on the temperature. When a certain mass is heated, the substance will expand whereas the mass remains the same, the volume increases and consequently the density decreases. The density of a substance can be minute, e.g. 0.000082 g / ml for hydrogen, but also large, e.g. 24.1 g / ml for platinum.

3.7.3 *Mass fraction, volume fraction, mole fraction* (mass percentage, volume percentage, mole percentage)

Analysing pure substances and mixtures is common practice in the natural sciences. In a pure substance the content of an element can for instance be determined and in a mixture the amount of one of the components. These contents can be represented in several ways, the most used ones of which will now be discussed briefly.

The *mass fraction w(A)* of a substance A in a mixture or of an element A in a compound is calculated using the formula

$$\text{mass fraction } w\,(A) = \frac{\text{mass of the substance A (element A)}}{\text{mass of the mixture (compound)}}$$

The mass fraction does not have a unit because the masses in the fraction have the same units.

An example: *a mixture has a mass of 25.0 grammes and contains 5.0 grammes of water and 20.0 grammes of sugar. This means: w(water) = 5.0/25.0 = 0.20 and w (sugar) 20.0/25.0 = 0.80.*

Note: *the sum of the mass fractions and also the sum of the volume fractions and mole fractions still to be discussed = 1.00*

Another way to indicate the content of water is:

mass percentage water: %(m/m) = w × 100% = 0.20 × 100% = 20%

For the *volume fraction* (A) and the *volume percentage* analogous formulas hold. It is however not possible to calculate the volume fraction of an element in a compound.

$$\text{volume fraction } \Phi\,(\text{A}) = \frac{\text{volume of substance A}}{\text{volume of mixture}}$$

volume percentage % (v/v)A = $\Phi \times 100\%$

In phase diagrams, a subject which will be dealt with later in this book, the *mole fraction x* is a common indication to represent the composition and can be applied to both pure substances and mixtures.

$$\text{molar fraction } x\text{ (A)} = \frac{\text{number of mole A}}{\text{number of mole A + mole B + ...}}$$

In this formula A, B, ... are the elements in a pure substance or the components in a mixture

$$\text{mole \% (A)} = x\text{ (A)} \times 100\%$$

A calculation example: A mixture contains 30 g A (molar mass = 90 g/mole) and 60 g B (molar mass 120 g/mole). Then:

the number of mole A = 30/90 = 0.33
the number of mole B = 60/120 = 0.50

$$x\ (A) = \frac{0.33}{0.33 + 0.50} = 0.40 \qquad x\ (B) = \frac{0.50}{0.33 + 0.50} = 0.60$$

3.7.4 Mass concentration

In the case of solutions, the strength of the solution is usually not represented as a mass fraction, but as a mass concentration. Suppose a substance A has been dissolved in a solvent and the volume of the solution is V. The mass concentration is then represented by means of the formula:

$$\text{mass concentration } \rho\text{ (A)} = \frac{m(A)}{V}\ \text{g/l}$$

Instead of the unit g/l, the following units are also used: mg/l, mg/ml, g/m^3, etc.

A calculation example: when 1.80 g KCl is dissolved in water and the total volume is then 250 ml, then ρ (KCl) = 7.20 g/l, 7200 mg/l, 7.2kg/m^3, etc.

3.7.5 Analytical concentration

The analytical concentration is a measure for the concentration of solutions. Chemists use it a lot to indicate how much mole substance has been dissolved in a certain volume.

$$\text{analytical concentration } c(\text{A}) = \frac{\text{mole solute A}}{\text{volume of the solution}} \text{ mole/l}$$

When 12.0 g HCl with a molar mass of 36.5 g/mole is dissolved in water and the volume is then 1 litre, the c(HCl) is 0. 329 mole/l.

3.8 CHEMICAL EQUATIONS

In a chemical reaction starting materials or reagents react under specific circumstances and thus produce reaction products. Such a reaction is represented by means of an equation. It is common to indicate the state of aggregation of the substances: solid (s), liquid (l) or gaseous (g).

Suppose liquid A reacts with solid B at a temperature of 250 ^{o}C and solid C and gaseous D are formed in the process. This reaction would be represented with the following equation:

$$A_{(l)} + B_{(s)} \xrightarrow{250°C} C_{(s)} + D_{(g)}$$

A concrete example is the reaction of solid sodium with water which results in a solution of sodium hydroxide and hydrogen gas:

$$Na_{(s)} + H_2O_{(l)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)} + H_{2(g)}$$

The sodium hydroxide dissolved completely (aq = aqua, English: water) and separated into ions. The equation is not yet complete, however. That is only the case when there are equal numbers of atoms of the same kind both to the left and the right of the arrow. In addition, the charges on both sides of the arrow have to be equal. In other words: “an equation must meet the law of conservation of mass and charge”. This can only be achieved by placing as small as possible whole numbers in front of the substances, the so-called coefficients.

$$2\ Na_{(s)} + 2\ H_2O_{(l)} \rightarrow 2\ Na^+_{(aq)} + 2\ OH^-_{(aq)} + H_{2\ (g)}$$

It should be noted that the addition “aq” is usually omitted. When a substance is noted in ions, this means that it has dissolved in water.

An equation should be “read” as particles which react in a specified ratio and in which process particles are formed in a specific ratio. In the reaction above sodium atoms react with water molecules in the ratio 1:1, thus forming sodium ions, hydroxide ions and hydrogen molecules in the ratio 2 : 2 : 1. Consequently the particle ratio is:

Na		H_2O		Na^+		OH^-		H_2
2	:	2	:	2	:	2	:	1

Every number in this ratio can be multiplied with Avogadro’s number without this affecting the ratio. Thus a mole ratio is made and this can easily be converted to a mass ratio by multiplying each number of the ratio by the molar mass in question.

	Na	:	H_2O	:	Na^+	:	OH^-	:	H_2
molar ratio	2	:	2	:	2	:	2	:	1
molar mass (g/mole)	22.99		18.016		22.99		17.008		2.016
mass ratio (g)	45.98		36.032		45.98		34.016		2.016

Checking the law of conservation of mass:
mass to the left of the arrow: – 82.012 g –
mass to the right of the arrow: – 82.012 g –

Checking the law of conservation of charge:
charge to the left of the arrow: – 0 –
charge to the right of the arrow: 2 (+) + 2 (–) = 0

3.9 ACIDS AND BASES

Acids and bases belong to the so-called *electrolytes*, substances which conduct electric current when they are melted or dissolved in water. For this to be possible, ions have to present.

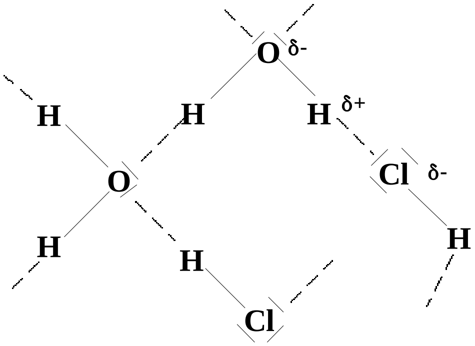


Fig. 3.14 H-bridge formation when HCl gas is introduced in water.

Acids

Any substance which, once dissolved in water, releases one or more *protons* (= H^+ ions) to the water molecules is called an acid. Let us have a closer look at how the gas hydrogen chloride (HCl) dissolves in water (Fig. 3.14). For the HCl molecules to penetrate the water molecules, they have to destroy the H– bridges between those water molecules. HCl dissolves very easily in water since it is capable of forming new bridges. After the H atoms of the HCl molecules have actually formed these new bridges with water molecules, competition arises: the O atom of the water wants to bind to the H atom, but for that the H–Cl bonds needs to be broken. In this case the H-bridge to the O turns out to be stronger than the H–Cl bond. The H atom moves in the form of H^+ to the water molecule.

$$HCl_{(g)} + H_2O \rightarrow H_3O^+ + Cl^-$$

The thus formed H_3O^+ is called a *hydronium ion* and is characteristic for acid solutions in water. When the H-bridge with a water molecule is much stronger than the bond of the H atom, then the proton is very easily transferred to the water molecule and there is question of an *extremely strong acid.* When the bond is much stronger, we speak of an *extremely weak acid*. In between these extremities the strength of an acid can consequently vary from extremely strong to extremely weak, which depends on the ratio between the strength of the bridge and the strength of the bond. Only six extremely strong acids exist, among which are dihydrogen sulphate H_2SO_4 (the solution of which is called sulphuric acid) and hydrogen nitrate HNO_3 (solution: nitric acid). An example of a weak acid is hydrogen cyanide, of which only some of the molecules release a proton in water:

$$HCN_{(g)} + H_2O \rightleftarrows CN^- + H_3O^+$$

The double arrow in the equation indicates that there is the question of a reaction from right to left and from left to right. This is characteristic of a weak acid and means that there are also HCN molecules present! Consequently not all HCN molecules will have released a proton.

Solutions of certain salts in water can also react as an acid. To illustrate this, let us have a look at what happens when sodium hydrogen sulphate is dissolved in water:

the particles separate into ions:

$$NaHSO_4 \rightarrow Na^+ + HSO_4^-$$

the hydrogen sulphate ion releases a proton:

$$HSO_4^- + H_2O \rightarrow SO_4^{2-} + H_3O^+$$

Bases

There are also substances which, once dissolved, accept a proton from a water molecule to bind it to a particle of their own. In this way the so-called *hydroxide ions* OH^- are formed which are characteristic for an alkaline solution. Three kinds of compounds are capable of this: a) *certain salts*, e.g. sodium cyanide (NaCN), b) *hydroxides*, e.g. sodium hydroxide (NaOH) and c) *molecular bases*, e.g. ammonia (NH_3).

When NaCN is dissolved, the ions are first hydrated and the cyanide ion subsequently reacts with water. Hydroxides already contain hydroxide ions and these are released when the crystals dissolve. Molecular bases as a whole take up particles one or more protons.

$$CN^- + H_2O \rightleftarrows HCN + OH^-$$

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

Acidity of a solution in water

In pure water the water molecules are continuously colliding and simultaneously transferring protons. As the temperature rises, so will the frequency and intensity of the collisions between the water molecules. As a result more protons will be transferred. However, the number of hydronium ions per litre of water is not that high:

$$H_2O \;+\; H_2O \;\rightleftarrows\; H_3O^+ + \;OH^-$$

at 24°C the concentration of the H_3O^+ ions will be 1.00×10^{-7} mole/l, in formula: $[H_3O^+] = 1.00 \times 10^{-7}$ mole/l.

In acid solutions the concentration of hydronium ions is higher and in basic solution it is lower than the above value. Contrary to expectations the acidity of a solution in water is not expressed in mole H_3O^+/l, but as pH with the formula:

$$pH \;=\; -\log\,[H_3O^+]$$

There are two reasons for this: a) numbers with many decimals and powers of 10 can now be represented more simply, b) with the help of the pH the entire range of acidities can be graphically represented.

To illustrate this, some examples:

a) Suppose $[H_3O^+] = 5.458 \times 10^{-4}$ mole/l

Expressed as pH the acidity is: $pH = -\log(5.458 \times 10^{-4}) = 3.26$

b) Expressed in $[H_3O^+]$ the acidity of a solution can vary from appr. 1 to appr. 10^{-14} mole/l. Numbers in this range cannot be plotted on one axis in a graph.

Expressed in pH the acidity of this solution varies from appr. 0 to appr. 14 and these numbers can easily be represented on the axis of a graph.

The reader can now calculate for him/herself that the pH of pure water at 24 °C is 7.00. We can relate all solutions to pure water at 24 °C and refer to

a solution with	$pH < 7.00$	as	an acid solution
a solution with	$pH = 7.00$	as	a neutral solution
a solution with	$pH > 7.00$	as	an alkaline solution.

To measure the pH of a solution, we can avail ourselves of accurate and less accurate methods. A pH-meter measures a pH to two decimal places. The result can be read from a digital display. You

Table 3.5 Some acid-base indicators

name indicator	pH of 'acid' range and colour	pH of transition range and colour	pH of 'alkaline' range and colour
methyl orange	< 3.1 red	3.1–4.4 orange	> 4.4 yellow
bromothymol blue	< 6.0 yellow	6.0 – 7.6 green	> 7.6 blue

can also use an acid-base indicator. In general such indicators are complex, organic molecules with different colours in different pH areas. They are used in a solution, three drops of which are added to the solution whose pH you want to measure. Most of them are characterized by three colours and three corresponding pH areas (Table 3.5). The terms acid and alkaline are placed between inverted commas because they have a different meaning here than an acid solution with a $pH < 7$ or an alkaline one with a $pH > 7$.

With one indicator the pH can only be determined very roughly. For instance, when a solution turns red after methyl orange has been added, the pH is < 3.1. By combining a number of indicators it is possible to determine the pH more accurately. When a solution with methyl orange is yellow and also yellow with bromothymol blue, then the following holds: $4.4 < pH < 6.0$.

3.10 ELECTROLYTES

Also in this paragraph we mean water when we speak of a ‘solvent’. Earlier in this chapter we learnt that water molecules are linked to each other by means of H-bridges and that there are two kinds of substances which generally dissolve well in water, i.e. a) substances which are built up of ions and b) substances which can form H-bridges with water molecules.

In this paragraph we will have a closer look at electrolytes, which are substances which conduct electric current once they have been dissolved in water (or melted). To do this, ions are needed. We distinguish two kinds of electrolytes:

a) with ionogenic building blocks: the *salts*, among which the *metal oxides* and the *hydroxides*, e.g. LiF, Na_2O and KOH. Whey they are dissolved in water, they first separate into ions and subsequently none, one or both ions react with water.

b) electrolytes which form ions after reacting with water: *molecular acids* (e.g. HCl) and *molecular bases* (e.g. NH_3).

Acids and bases generally dissolve well in water. In general, the solubility of acids increases as the temperature rises. In a simplified model you might state that the firmness of the salt crystals and the ease with which the ions are hydrated determine the solubility. After all, the water molecules must first ‘ease away’ the ions from the crystals and that requires energy. Subsequently the loose ions are hydrated and that releases energy. The energy balance determines the solubility which varies from some milligrammes to several hundreds of grammes per litre.

Some equations of the reaction with water of a few ionogenic electrolytes are given below; the reactions of molecular acids and bases were discussed in the previous paragraph.

– salts

$$NaF(s) \xrightarrow{H_2O} Na^+ + F^-$$

$$F^- + H_2O \rightleftarrows HF + OH^- \qquad \text{solution is alkaline}$$

$$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+ + Cl^-$$

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+ \qquad \text{solution is acid}$$

– metal oxides

$$K_2O(s) \xrightarrow{H_2O} 2K^+ + O^{2-}$$

$$O^{2-} + H_2O \rightarrow OH^- + OH^- \qquad \text{solution is alkaline}$$

– hydroxides

$$NaOH(s) \xrightarrow{H_2O} Na^+ + OH^-$$

$$OH^- + H_2O \rightarrow H_2O + OH^- \qquad \text{solution is alkaline}$$

To end this paragraph, some information on the oxides. As mentioned earlier, metal oxides react in an alkaline way and for that reason are called alkaline oxides. In ceramics, for instance, we come across them as components in glazes and fire proof materials. Oxides of non-metals are not built up of ions and immediately react with water to form acid solutions. When for example N_2O_5 gas is led through water, hydrogen nitrate is formed, or in case of an excess of water, a solution of it, called nitric acid. An then there is the small number of oxides which can have both acid and alkaline functions, the so-called amphoteric oxides. In relation to glazes these oxides are also called neutral oxides, a name which can cause some confusion as the concept ‘neutral’ is mostly used to denote a solution with a pH = 7.00. An example of an amphoteric oxide is aluminium oxide, which reacts as a base with nitric acid and as an acid with the base sodium hydroxide.

$$Al_2O_{3(s)} + 6\ H_3O^+ + 6\ NO_3^- \rightarrow\ 2\ Al^{3+} + 6\ NO_3^- + 9\ H_2O$$

$$Al_2O_{3(s)} + 6\ Na^+ + 6\ OH^- \ \rightarrow\ 6\ Na^+ + 2\ AlO_3^{3-} + 3\ H_2O$$

When we mix a solid alkaline and a solid acid oxide at a sufficiently high temperature, the following reaction occurs and that is a ceramic example:

$$K_2O_{(s)} + SiO_{2\ (s)} \rightarrow K_2SiO_{3\ (s)}$$

3.11 ORGANIC CHEMISTRY

3.11.1 Introduction

Organic chemistry is a branch of chemistry which is involved in the structure and properties of organic compounds. These compounds mainly consist of carbon and hydrogen atoms, next to mostly oxygen, nitrogen, sulphur and halogen atoms. The name ‘organic chemistry’ dates from the beginning of this science when scientists limited themselves to the study of substances of animal and plant origin.

Organic chemistry obtains its raw materials from petroleum or natural gas. Petroleum is a mixture of many substances. After it has been extracted out of the earth this mixture is separated by means of distillation into a number of mixtures. In this process the mixture is heated and the components evaporate one by one, starting with the substance with the lowest boiling point. The vapours are cooled down and collected in the form of liquids. Before and after the distillation the petroleum is often subjected to different processes, such as cracking. During this cracking, substances are heated without oxygen to about 400 – 500 °C with or without a catalyst. Long chains are broken down and small side chains disappear. Thus new products are formed. A well-known cracking product is ethene, of which e.g. the plastic polyethene and ethanol (‘alcohol’) are made.

3.11.2 Organic compounds

The simplist organic compounds are branched or unbranched chains of C atoms to which H atoms have become attached and in which each C atom is bound to four other atoms. This ‘family’ is called alkanes and the names of the unbranched compounds serve as a basis for the nomenclature of other organic chain compounds.

Alkanes

The general molecular formula of the alkanes is C_nH_{2n+2}. In this formula the *n* is a whole and positive number and, as can be derived from the formula, the number of H atoms is two more than double the number of C atoms. In Table 3.6 the formulae and names of the first ten unbranched alkanes are given.

Every branched or unbranched alkane chain is built as a zigzag chain. When a chain contains three or more C atoms a part of the molecule can turn freely around a single bond in relation to the rest of the molecule. In a spontaneous process the molecule converts from one three-dimensional structure to another. According to a chemists: “the molecule changes from one *conformation* into another”. Figure 3.15 is a representation of an alkane chain and two conformations of the same molecule.

Alcohols

Alcohols are compounds which contain one or more OH groups, the so-called *hydroxyl* groups, bound to different carbon atoms. However, this definition has one limitation: no O atom with a double bond may be bound to the C atom with the OH group. In Fig. 3.16 the structural formulae of two alcohols have been drawn. Note that the

Table 3.6 Names and formulas of the first ten unbranched alkanes

name	formula	name	formula
methane	CH_4	hexane	C_6H_{14}
ethane	C_2H_6	heptane	C_7H_{16}
propane	C_3H_8	octane	C_8H_{18}
butane	C_4H_{10}	nonane	C_9H_{20}
pentane	C_5H_{12}	decane	$C_{10}H_{22}$

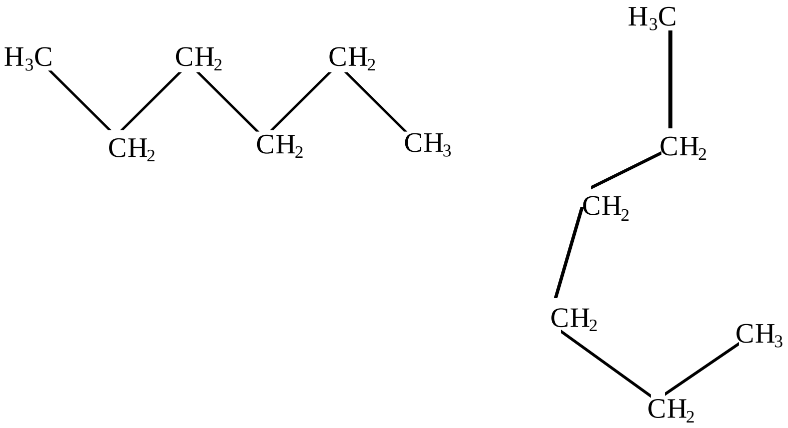
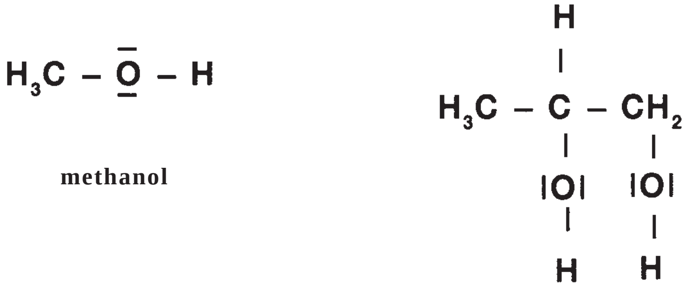


Fig. 3.15 Two conformations of the hexane molecule.



methanol

1,2 – propaniedol

Fig. 3.16 Two alcohol molecules.

names have been derived from the alkanes and that holds for all chainlike, organic molecules.

In accordance with the number of OH groups, we speak of monovalent, bivalent, etc. alcohols. Alcohols with one OH group derive their names from the corresponding alkane to which the ending -ol has been added. With two OH groups the ending is -diol, etc.

Like water, alcohols can form H-bridges and they are also polar solvents due to the fact that they possess one or more OH groups. The carbon chain in an alcohol is apolar. This means that the polarity of an alcoholmolecule is determined by the contribution of the polar groups (OH groups) and the apolar carbon chains. Alcohol molecules can contain extremely many C atoms and OH groups and we then refer to them as polyalcohols (poly = many). An example of this is polyvinyl alcohol which has many uses in ceramics, e.g. in the making of glazing mixtures (Fig. 3.17).

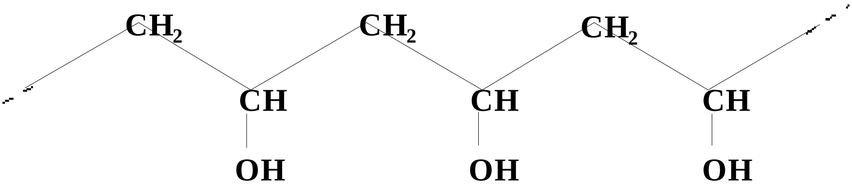
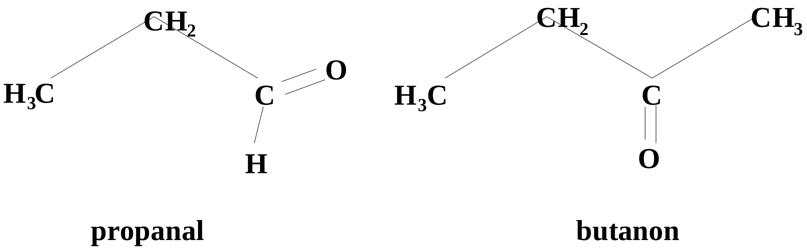


Fig. 3.17 Polyvinyl alcohol (PVA).



propanal **butanon**

Fig. 3.18 An alkanal and an alkanon.

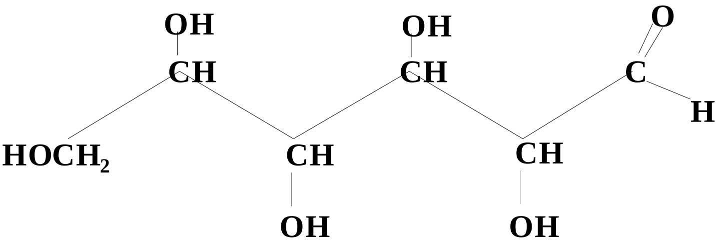


Fig. 3.19 A saccharide molecule.

Alkanals (or : aldehydes) and Alkanons (or : ketones)

Alkanals and alkanons are compounds which are characterized by a double bound between an O atom and a C atom. In addition, only H and /or C atoms may be bound to that C atom (Fig. 3.18).

In an alkanal the oxygen atom is bound to a terminal C atom. In a alkanon one the C atom which is linked to the oxygen atom is also bound to two other C atoms.

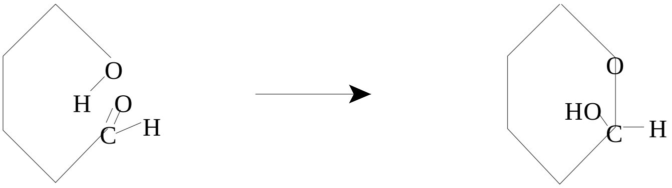
Well-known molecules with an alkane or alkanon group are the *saccharides*, with the even better known examples glucose and fructose. A saccharide contains 5 or 6 C atoms, an alkane or alkanon group and an OH group at the remaining C atoms (Fig. 3.19).

Most saccharide molecules are ring-shaped. This ring finds its origin in a chain structure as shown in Fig. 3.19 because an OH group reacts with the alkanal or the alkanon group to form a five or six ring. Figure 3.20 represents the basic reaction and an example of a ring structure.

Saccharide molecules can be interlinked while producing a water molecule. In this way polysaccharides are formed. Well-known examples are cellulose and starch. In Fig. 3.21 you can see a small piece of a polysaccharide chain.

In a polysaccharide two rings are attached to each other because two OH groups produce one water molecule. A single oxygen atom remains which can act as a bridge molecule between the two rings. The groups attached to the rings are of course OH and CH_2OH groups.

reaction of the ring closure in a saccharide



example of a cyclic saccharide molecule

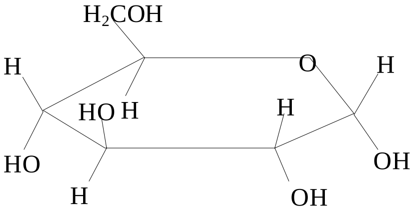


Fig. 3.20 Ring closing reaction in a saccharide molecule and an example of a cyclic saccharide molecule.

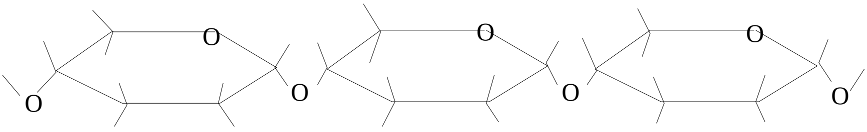


Fig. 3.21 Small piece of a polysaccharide chain.

As we already saw in Fig. 3.20 a polysaccharide is a polar molecule and is consequently also used as a binding agent.

A CH_2OH group can be converted to an acid COOH group. By reacting with e.g. NaOH, the acid group becomes a sodium salt COONa. The sodium salts of some polysaccharides are commercially available. A well-known example is sodium alginate, the salt of alginic acid which is extracted from seaweed. Biologists use this substance to immobilize enzymes. The applied technology resembles the one used to make ceramic micrograins for all kinds of applications. This makes it a simple, but very illustrative experiment (see paragraph 11.7).

Amino-acids

Amino-acids are organic compounds containing both an acid group, the so-called carboxyl group –COOH, and an alkaline group, the amino group $–NH_2$. The rest of the molecule consists of a carbon chain with mainly H atoms and some other groups which need not be specified further and possibly one or more additional carboxyl and/or amino groups (Fig. 3.22).

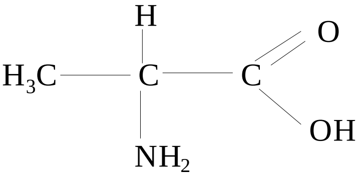


Fig. 3.22 Structural formula of a simple amino-acid.

In water the carboxyl group can give up a proton and thus become $–COO^-$, an alkaline group, and the amino group can take up a proton and thus become $NH_3{}^+$, an acid group. When the pH of the solution is changed, the COO^- group can take up an H^+ molecule (in an acid environment) or the $NH_3{}^+$ can give up an H^+ (in an alkaline environment). The charge of the molecule can consequently be influenced by means of the pH. By means of a reaction between the amino group and the carboxyl group amino-acids can be interlinked to form a polyamide, also called a protein. In this reaction a water molecule is produced and between two amino-acids a so-called amide bond is formed. Figure 3.23 shows the simplified structure of a polyamide with some additional amino groups. The carbon chain is represented as a zigzag line. If the pH is sufficiently low, the amino

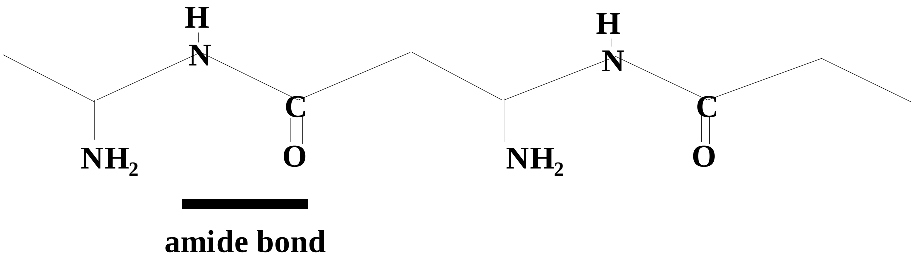


Fig. 3.23 Simple representation of a polyamide chain (both NH_2 groups do not belong to the basic structure).

groups take up a proton and the polyamide chain is positively charged. When this compound is used as a binding agent, the ceramic particles are “wrapped up” by the polymer molecules and in this way they obtain a positive surface charge (see the chapter on Colloid chemistry).

4

Crystallography

4.1 INTRODUCTION

The crystals of solids are built up of ions of non-metals, ions of metals, atoms, molecules or a combination of all these particles. These possibilities result in four different crystal lattices, i.e. the ionic lattice (e.g. sodium chloride, NaCl), the atomic lattice (e.g. diamond, C), the molecular lattice (e.g. iodine, I_2) and the metallic lattice (e.g. copper, Cu). The forces which hold the building blocks of a lattice together differ for each lattice and vary from the extremely strong coulombic forces in an ionic lattice to the very weak Van der Waals forces between the molecules in a molecular lattice.

4.2 CRYSTAL STRUCTURE

Close-packed structures

The structure of a crystal lattice is similar to packing billiard balls in a box. By forming a lattice the particles will be arranged in such a way as to leave as little as possible space empty, or, in other words, the available space is filled as effectively as possible. The structure in one layer is shown in figure 4.1.

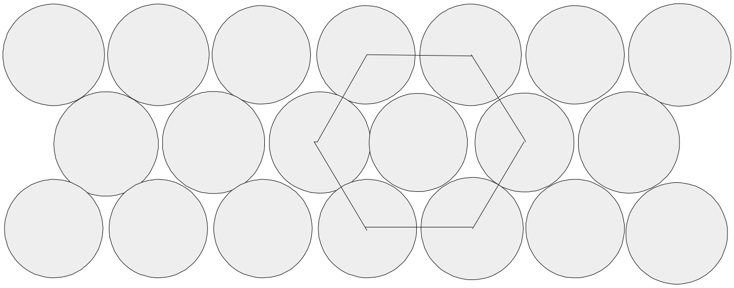


Fig. 4.1 Close-packed structure of spheres in a layer.

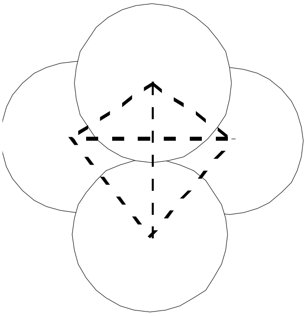
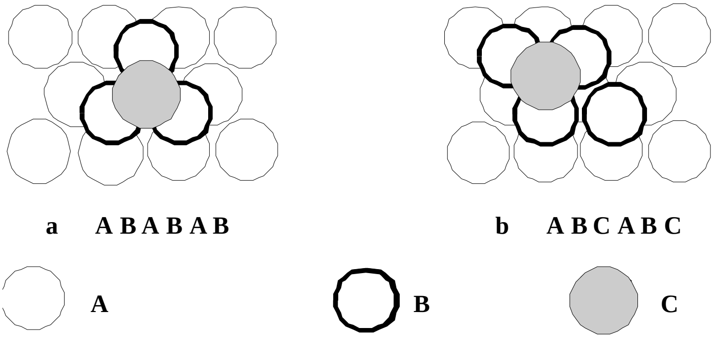


Fig. 4.2 Pyramid-formation by spheres in a close-packed structure.

As you can see, a very regular pattern arises when the centres of the spheres are linked. In figure 4.1 six centres are linked and together they form a regular hexagon. It is however also possible to link three centres to form an equilateral triangle or four which will result in a parallelogram.

So how is the second layer stacked onto the first one? It will be evident that a sphere in the second layer will be placed in the cavity between three spheres in the first layer. The centres of the four spheres thus form the angles of a trilateral pyramid (figure 4.2).

The third layer of spheres can now be placed on top of the second in two ways.These three layers are called A, B and C, the spheres of a layer with the same letter are placed vertically above each other. By placing the third layer vertically above the first and the fourth above the second, a packing A B A B A .... arises, a so-called *hexagonal close-packed structure*, abbreviated hcp. A second possibility is a packing of the type A B C A B C ..., a so-called cubic close-packed structure, abbreviated ccp. Both types of packing are shown in figure 4.3.



a **ABABAB** **b** **ABCABC**

Fig. 4.3 Hexagonal (a) and cubic (b) close-packed structures of spheres.

The crystal structures of many compounds can be described in a simplified way as an hcp or a ccp with part of the cavities filled with other particles.

Cavities in close-packed structures

When a sphere lies on top of three other spheres in a close-packed structure, there is a cavity between those spheres, the so-called tetrahedral cavity (figure 4.2). Those same close-packed structures also contain octahedral cavities formed by six spheres, as shown in figure 4.4.

Figure 4.4 represents two layers of spheres in a close-packed structure. The three spheres with a little dot in their centres form the bottom layer (A layer), the three crossed ones the top layer (B layer). Together the six centres of the spheres form the vertices of an octahedron with an octahedral cavity between the spheres.

Many crystal lattices can be described by filling the tetrahedral and /or octahedral cavities in close-packed structures with other particles. In many cases the particle will be too big to fill a certain cavity. In those cases the particles of the close-packed structure will shift a little and in this way the perfect close-packed structure is lost. Small particles sooner fit in a tetrahedral cavity and larger ones in an octahedral one. Thus we speak of a tetrahedral and an octahedral coordination of a particle in the cavity and the number of nearest neighbours is called the coordination number.

Suppose we would call the radius of the positive ion in an ionic lattice r^+, that of the negative ion r^- and the positive ion occupies cavities between the negative ions. Then the positive ion would fit in a certain cavity when one of the following ratios between the rays

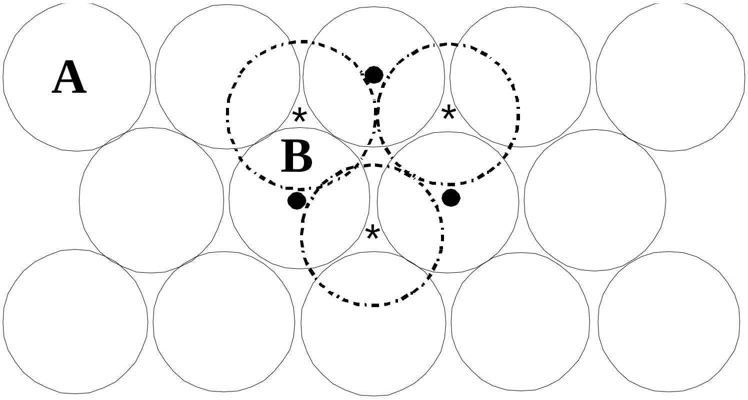


Fig. 4.4 An octahedral cavity in a close-packed structure.

of the negative and positive ions is met:

tetrahedral coordination $$\frac{r^+}{r^-} = 0.225 - 0.414$$

octahedral coordination $$\frac{r^+}{r^-} = 0.414 - 0.732$$

In order to be able to describe the “ideal crystal structure”, it is important to bear in mind that there are two tetrahedral cavities and one octahedral one present for every sphere in a close-packed structure. With the help of Table 4.1 and the rules for octahedral and tetrahedral coordination the description of the following crystal structures are now easily understood when we bear in mind that in an ionic crystal lattice the larger negative ions form the close-packed structure and that the octahedral and tetrahedral cavities are filled with positive ions.

Table 4.1 Some ion radii

ion	radius (nm)	ion	radius (nm)	ion	radius (nm)
Ba^{2+}	0.153	Hg^{2+}	0.110	Br^-	0.196
Ca^{2+}	0.099	Mn^{2+}	0.080	Cl^-	0.181
Cd^{2+}	0.097	Na^+	0.097	F^-	0.133
Ce^{4+}	0.092	Pb^{2+}	0.120	I^-	0.220
Cu^+	0.096	Zn^{2+}	0.074	O^{2-}	0.132
Cu^{2+}	0.072	Zr^{4+}	0.079	S^{2-}	0.184
Al^{3+}	0.051				

NaCl structure

This structure can be described as a cubic close-packed structure of chloride ions. For every chloride ion there is one octahedral cavity which is occupied by a sodium ion. However, you might also describe the structure as a cubic close-packed structure of sodium ions with chloride ions in the octahedral cavities. The following compounds have similar structures: Li_2O, MgO, CaO, AgF and NH_4Cl.

Zinc blend (ZnS) structure

This structure can be described as a cubic close-packed structure of sulphide ions. For every sulphide ion there are two tetrahedral cavities, one of which is occupied by a zinc ion. Other compounds with this structure are for example: CuCl, BeS and CdS.

Fluorite (CaF_2) structure

The crystal structure of fluorite is characterized by a cubic close-packed structure of calcium ions with fluoride ions in all tetrahedral holes. Other compounds with this structure include the fluorides of Ba, Pb(II) and Hg (II) and the oxides of Ce(IV) and Zr(IV).

Point lattices, elementary cells and crystal classes

When drawing a crystal structure we could also draw the centres of the spheres instead of the spheres themselves. This has been done in figure 4.5 for a close-packed structure of spheres in one layer. The spot where two lines intersect is the centre of a sphere and in this way a diamond-shaped pattern is formed. Figure 4.5 is an exact fit of figure 4.1. In this close-packed structure of spheres in one layers the centres of the spheres can also be linked to form other geometrical figures, e.g. a triangle and a hexagon, both of which can be seen in figure 4.5.

By linking the centres of the spheres in a three-dimensional packing you can create a three-dimensional pattern of centres, a so-called space lattice. Such a lattice consists of many elementary cells. An elementary cell is the smallest possible spatial unit in the crystal lattice which is repeated in three directions (according to the mathematical *x*-, *y*- and *z*-axes) in the lattice. Figure 4.6 shows a space lattice and an elementary cell.

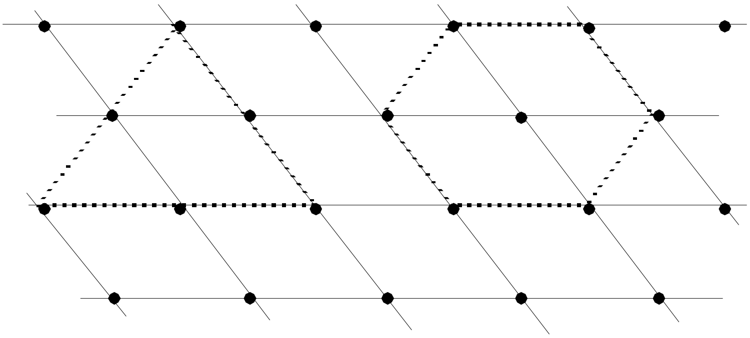


Fig. 4.5 Mathematical figures in a layer of closely packed spheres.

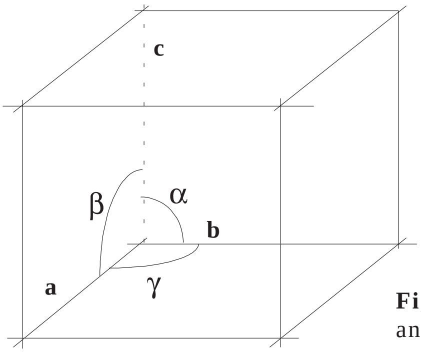


Fig. 4.6 A three-dimensional point lattice and an elementary cell from the lattice.

It is important to realise that we are still talking about one kind of building block or, in other words, elements. This means that all distances between the centres of the spheres are equal. To describe the compounds several space lattices must be combined. Nevertheless the above figure of an elementary cell is a simple aid to describe the 7 crystal classes. These classes are described by means of the lengths a, b and c and the angles α, β and γ in the elementary cell. Figure 4.7 illustrates the cubic and hexagonal crystal classes.

4.3 DEFECTS IN CRYSTALLINE MATERIALS

Many things can go wrong when crystals are formed out of a solution or a smelt. As a result the crystals will not have a perfect shape, but will have defects. These can affect the material properties to a large extent. It is often easier to regulate the crystallization proc-

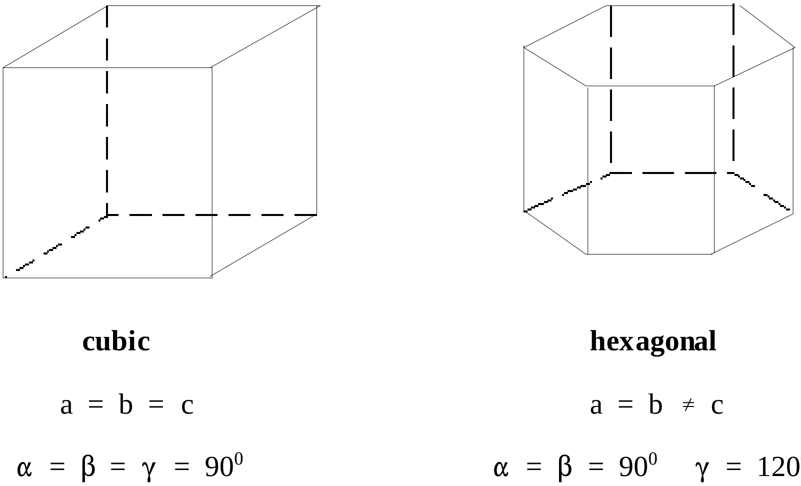


Fig. 4.7 The cubic and hexagonal crystal classes.

ess in a laboratory than it is in nature, but even there imperfections occur in most crystal structures. On the other hand, certain defects are built in on purpose to obtain certain improvements or changes in properties (see for example paragraph 11.4 on semi-conductors.).

In literature the defects in crystalline materials are called 0-dimensional or point defects, 1-dimensional, also called line defects or dislocations and 2-dimensional or packing defects. In this book we will confine ourselves to a brief description of some of the many kinds of defects.

Point defects

One of the causes of point defects is a temperature increase which results in an increased thermal movement of the atoms which can subsequently lead to the atoms escaping from their place in the lattice. Other causes are the effects of radiation and inbuilt, foreign atoms. In an atomic lattice a vacancy can occur due to the movement of an atom, an absence of an atom or molecule from a point which it would normally occupy in a crystal. In addition to this vacancy an atomic will form elsewhere. This combination of an atomic pair and a vacancy is called the *Frenkel defect*. In ionic crystals an anion and a cation have to leave the lattice simultaneously due to the charge balance. As a result a vacancy pair remains and this is called the Schottky defect. Both defects can be seen in figure 4.8.

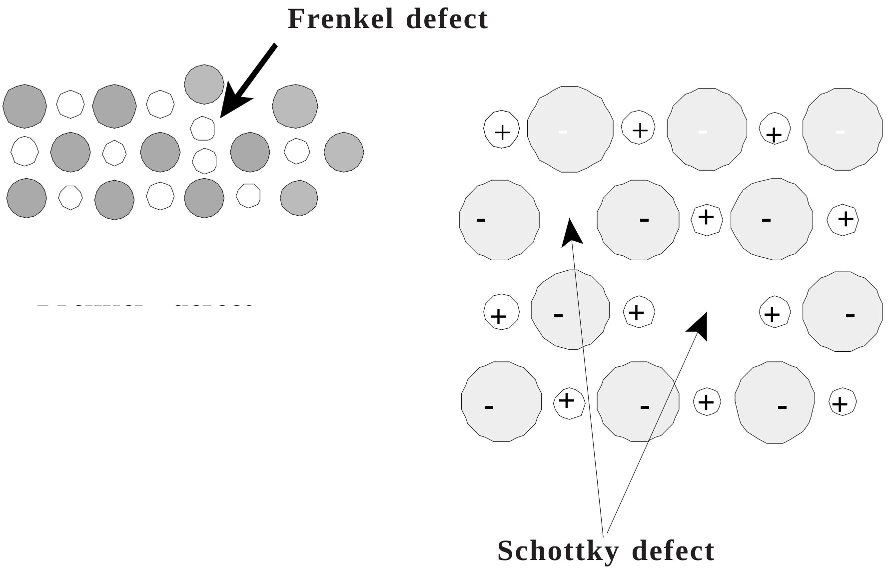
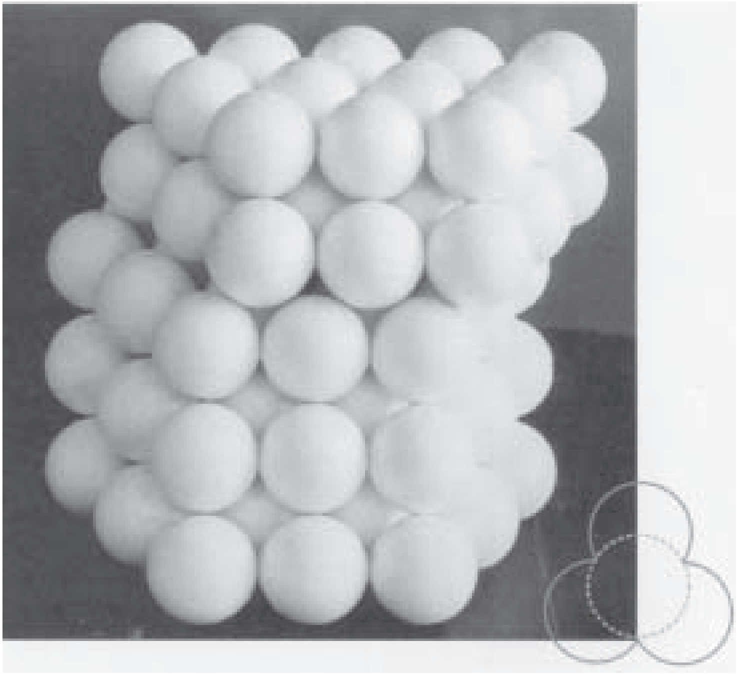


Fig. 4.8 Point defects.



Imperfection in a crystal lattice (Natuur & Techniek, Amsterdam)

Dislocations

In addition to the above-mentioned atomic or point defects, crystal may also have extensive “line” defects or dislocations. These are of two principal kinds: screw dislocations and edge dislocations. Both kinds can be imagined as a perfect crystal which has partly been strained open. If the dislocation consists of a gradually increasing shift of alignment between planes, it is called a screw dislocation. An edge dislocation may be thought of as resulting from the addition of an extra plane in the upper half of the crystal. Because of the added atoms in the upper half, this portion is strained by compression; however, the lower half of the crystal is strained by tension as the fewer number of atoms tries to fill the same volume as that filled in the upper part.

Packing defects

Solids are usually polycrystalline, which means that they are built up of many small, individually ordered crystals. Crystal defects are caused by disarranged grain borders.

5

Colloid Chemistry

INTRODUCTION

A solution of table salt (NaCl) in water is called a *true solution*. The dissolved particles consist of single, hydrated ions and cannot be seen with the unaided eye. A *suspension* contains particles which you can often see with the naked eye and most certainly with the help of a microscope. Some examples of suspension are flour in water and muddy water. The particles of a suspension usually *sediment* (sink to the bottom) after a certain time and can easily be filtered off. In between the true solution and the suspension there is the colloidal dispersion, the particles of which are bigger than ions and molecules, yet too small to be detected by an optical microscope. The particle size in a colloidal dispersion lies between appr. 0.2 μ (micron) and appr. 0.5 μ (1 μ = 10^{-6} m).

According to the dictionary the word ‘colloidal’ means “gelatinous”, but as we shall see later in this chapter, this term does not apply to most colloidal systems.

Suspensions and colloidal dispersions differ from true solutions in that they are systems with more than one phase. This means that the substances present do not mix very well. The system is said to be *heterogeneous* and is characterized by interfaces between the phases, for instance between the water and a clay particle in muddy water. However, true solutions are one-phase systems and as a result *homogeneous*. In addition, they differ because in suspensions and dispersions the solid phase can be separated by means of filtration.

Suspension can be filtered through filtering paper, colloidal dispersions through an *ultra filter* and true solutions cannot be filtered. A simple version of an ultra filter may look like this: a membrane built in as the bottom of a suction funnel which, in its turn, is placed on a suction flask connected to a water jet pump.

Particles of true solutions cannot be made visible. Colloidal particles

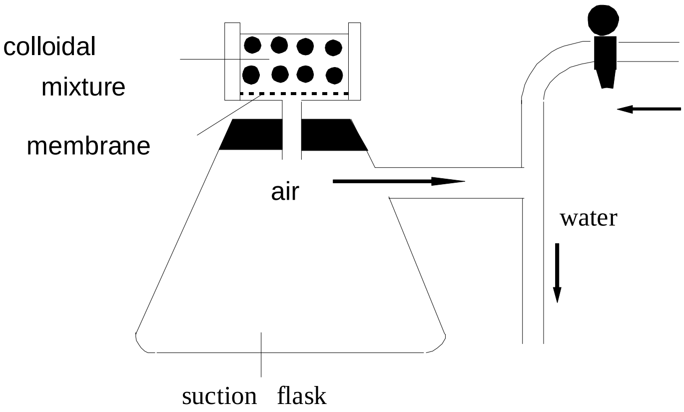


Fig.5.1 A simple ultra filter.

on the other hand can be detected with an *ultra* or *electron microscope*. For looking at particles in suspensions an ordinary light microscope is not sufficient. The ultra microscope is based on the principle that when you lead a beam of light through a colloidal system, the particles are visible as flashes of light. You might compare this to a beam of light in a room with a lot of cigarette smoke. This phenomenon is called the *Tyndall effect*.

The factors which contribute most to the behaviour of colloidal systems are the dimensions, the shape and the properties of the surfaces of the particles, but also the medium in which they are dispersed is of influence. The large to extremely large ratios between the surfaces and the volumes of the particles are of importance for all of these properties.

In a colloidal system the particles are dispersed in a medium; the dispersed particles form the *dispersed phase* and they are dispersed in a *dispersion medium*. Both the dispersed phase and the dispersion medium can be solid, liquid or gaseous, with the exception of the gas - gas combination. For a number of these colloidal system specific names are used (table 5.1). This table illustrates what was mentioned earlier, namely that the literal meaning of the word “colloidal” only applies to few colloidal systems.

The preparation of colloidal dispersions

In this paragraph the discussion of the preparation of colloidal dispersions will be limited to those in which a liquid is the dispersion medium and a solid is dispersed, consequently to sols. Sols can be divided into two groups: *lyophobic* (Greek for liquid hating) and *lyophilic*

Table 5.1 Kinds of colloidal systems (s = solid, l = liquid, g = gaseous)

dispersion medium	dispersed substance	examples
s	s	ruby glass (glass with Au)
s	l	a *gel* : e.g. gelatin
s	g	minerals with extremely fine gas enclosures
l	s	a *sol* : AgCl sol. S sol
l	l	an *emulsion* : milk, mayonnaise,
l	g	foam, whipped cream
g	s	smoke
g	l	fog, mist spray
g	g	not possible because gases are miscible in all proportions

(Greek for liquid loving) *sols*. When water forms the dispersion medium, we speak of *hydrophobic* and *hydrophilic sols*.The terms "lyophobic" and "lyophilic"are often used to indicate to which extent a surface is moistened. Lyophobic surfaces can be made lyophilic and vice versa. A clean glass surface for instance is hydrophylic, but can be made hydrophobic by rubbing it with wax. Oils drops in water are hydrophobic, but become hydrophilic after you add a protein or a detergent (figure 5.2).

A molecule of detergent is built up of a long, apolar carbon chain with the properties of an oil drop and an ionic sodium sulphonate group (SO_3Na) at the end of the chain. When the detergent is added to a heterogeneous oil–water mixture which is subsequently stirred, the carbon chains will attach themselves to the oil drops, the sodium ions will be separated and each drop will be surrounded by a number of negative ions. In this way the oil drop obtains a so-called negative charge coating and feels at home in the water.

An example of a lyophilic sol is the hydrophilic sol of starch and water. Rubber is hydrophobic, but benzophilic, which means that rubber is water resistant, but dissolves well in benzene. So apparently the

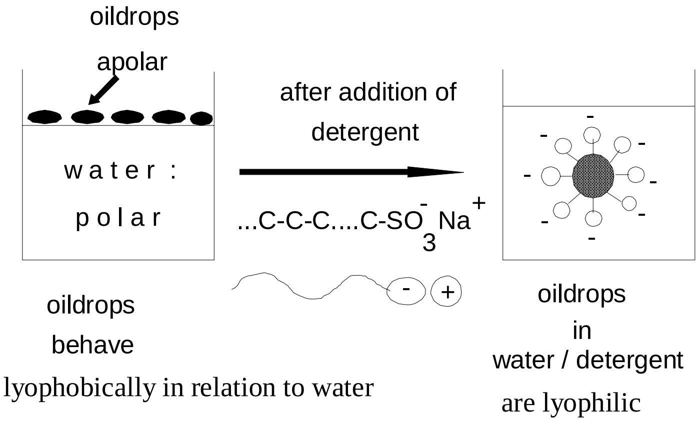


Fig. 5.2 Oil drops in water turn lyophilic after addition of a detergent.

lyophobic and lyophilic characters strongly depend on the kind of dispersing agent. And here the proverb *Like will be like* also applies, which means that when the structure of the dispersed substance is quite similar to that of the dispersion medium, there will be question of lyophilic behaviour.

The preparation of lyophilic sols is easy and most of the time a mixture of the dispersion medium and the substance to be dispersed need only be stirred. Gelatine, for example, disperses almost spontaneously in water. The hydroxides of iron, aluminium, chromium and zirconium as well as vanadium pentoxide and silicic acids all belong to the group of hydrophilic colloids.

More methods are available for the preparation of lyophobic sols; these can be divided into two groups: *dispersion methods* the starting point of which is the course material and *condensation methods* which use true solutions. Figure 5.3 is a schematic representation of both methods.

Reducing the course material in size in a colloid mill or by means of ultrasonic waves generally does not lead to a higher distribution ratio, i.e. to smaller particles. As it is smaller particles tend to form larger ones under the influence of mechanical forces and due to the attraction between the particles. These problems are solved to a large extent when a surface active substance and possibly a solvent are added during the reduction process.

An example: a sulphur sol can be made by grinding a mixture of sulphur and glucose, dispersing it in water and removing the dissolved glucose by means of dialysis.

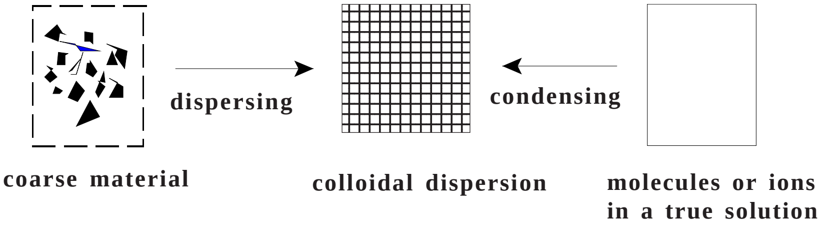


Fig. 5.3 Schematic representation of dispersing and condensating processes.

The glucose molecule is dipolar and surrounds the S particles (figure 5.4). The hydrophobic surface of the S particles is now changed in such a way by the glucose molecule that the glucose – sulphur particles become hydrophilic. In this way *coagulation* (= i.e. the increase in size of the particles) is prevented. In the case of dialysis a membrane is used through which the particles of the pure solution can pass but the colloidal particles cannot. When water is the solvent, a membrane separates the solution to be dialysed from pure water. In the case of the sulphur / glucose sol, the glucose molecules move in the direction of the pure water. If the pure water is not replaced, the transport of glucose molecules will stop once the concentration of glucose is the same on both sides of the membrane. A continuous supply of water ensures that the transport continues until all glucose molecules have disappeared from the sol (figure 5.5).

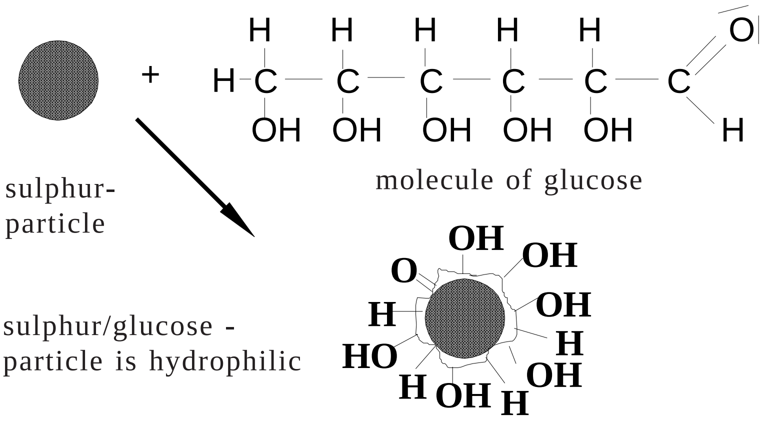


Fig. 5.4 A hydrophobic sulphur particle is made hydrophilic.

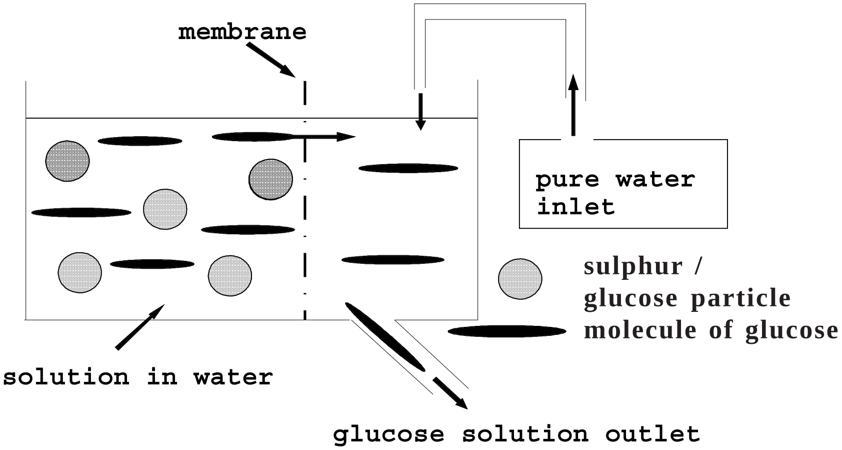


Fig. 5.5 Dialysis of a sulphur / glucose solution.

Lyophobic sols can also be made by means of condensation according to various techniques. Some sols are easily made and their syntheses are described below.

Some recipes

** A sulphur sol can be made by dissolving 2 grammes of sulphur in 100 ml of methanol while stirring and heating. When the maximum amount of sulphur has dissolved, the solution is filtrated. Next some millilitres of filtrate are added to 100 ml of distilled water while stirring vigorously.

** Silver halogenide sols are made by adding e.g. 50 ml of a solution of 0.01 mole/l KCl, KBr or KI solution to a little more of a 0.01 mole/l $AgNO_3$ solution, say 51 ml.

** By adding hydrochloric acid to a solution of sodium thiosulphate you can make a sulphur sol.

The charge of colloidal particles

When a solid is dispersed in water the particles usually receive a surface charge which is caused by the ionisation of the particles or by the fact that the dispersed particles absorb ions from the dispersion medium. Below you can find an example of both possibilities.

** In the paragraph on organic chemistry in chapter 3 a protein molecule was described as a polymer of amino acids which are linked by means of peptide bonds (not included in figure 5.6). The molecule can possess additional acid carboxyl (COOH) and alkaline amino (NH_2) groups. When dissolved in a polar environment like e.g. water

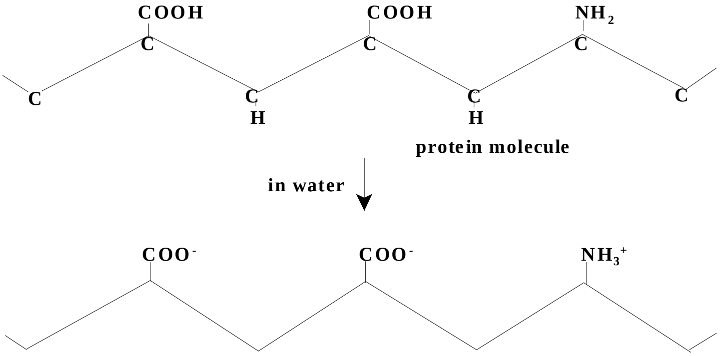


Fig. 5.6 A protein molecule obtains a surface charge in water.

the acid group will release a proton and an alkaline group will take up a proton. In this way the protein molecule obtains a surface charge (figure 5.6).

At the side groups of the carbon chain the molecule obtains some positive and negative charges and thus feels at home in the polar solvent water. The negative and positive ions on the chain are hydrated.

** A silver iodide sol can be positively as well as negatively charged, dependent on whether there is an excess of positive or negative silver iodide ions present (figure 5.7).

The stability of a sol, i.e. how resistant it is to flocculation (or

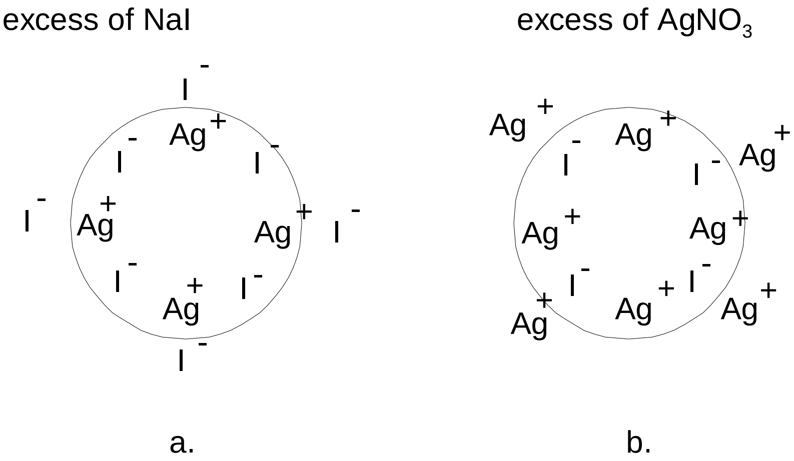


Fig. 5.7 Schematic representation of a negatively (a) and a positively (b) charged silver iodide sol.

precipitation) is determined by the electric repulsion among particles with like charges. When we have another look at figure 5.7a we can see that the iodide ions cause the surface charge of a particle. The sodium ion are the counter ions of the iodide ions and they are not bond to the particle, but orbit the charged particle.

The stability of colloidal dispersions

When dispersed particles in a lyophobic sol approach each other, two forces arise: *Coulomb forces* and *Van der Waals forces*. It is said that an interaction exists between the particles.

Coulomb forces are formed as a result of the fact that particles with like surface charges repel each other. The resulting energy is so-called “repulsive energy” which is by definition positive. Van der Waals forces attract. Particles are able to attract each other because they have mass. The forces are not large until the particles are very close to each other. The resulting energy is by definition negative.

Colloidal particles move at random through a suspension due to the fact that they possess kinetic energy (i.e. movement energy as a result of temperature) and because they collide with other particles. This movement is called *Brownian movement* (figure 5.8).

Owing to this Brownian movement particles diffuse throughout the dispersion medium, i.e. they move among the molecules of the dispersion medium. The particles can approach each other so closely that Coulomb and van der Waals forces arise. Consequently two kinds of forces act on particles which approach each other and thus also two kinds of energies, a repulsion E(R) energy as a result of the repelling Coulomb forces and an attraction E(A) energy caused by the attracting van der Waals forces. In figure 5.9 the E(R) and E(A) have been plotted as functions of the distance r between two particles. The total interaction energy of both particles is indicated by the curve E(T), which is obtained by added up the E(R) and E(A) curves.

The curve E(T) shows the energy threshold the particles have to overcome in order to be able to approach each other and thus form

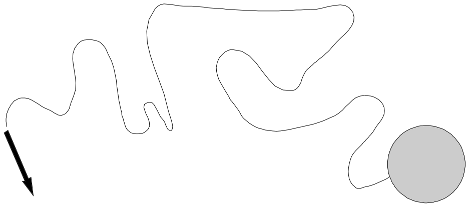


Fig. 5.8 Brownian movement of a particle in a suspension.

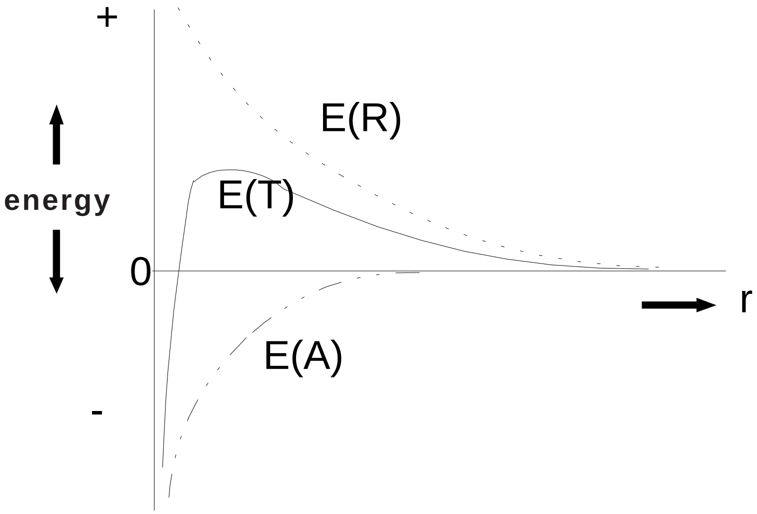


Fig. 5.9 Representation of the interaction energy E(T) between two colloidal particles [E(R) = repulsion energy E(A) = attraction energy E(T) = E(R) + E(A), *r* = distance between two particles].

larger particles. When these larger particles have attained a certain size *flocculation* can take place, as a result of which the particles sink to the bottom and the suspension becomes unstable. The higher the energy threshold, the more stable the suspension. The repulsion energy, and consequently the energy threshold, can be affected by adding an electrolyte to the suspension. This electrolyte mostly reduces the surface charges of the particles and the E(R) curve moves to the left. This results in a E(T) curve with a lower energy threshold.

The viscosity of colloidal dispersions

With the viscosity of a liquid we mean the resistance to flow of that particular liquid. This resistance is caused by internal friction and other interactions between the particles. Among other things, viscosity is dependent on temperature, the solid volume fraction and the properties of the particles. The viscosity of normal liquids, solutions and lyophobic colloids which are not too concentrated and contain symmetrical particles is measured by allowing a certain volume to flow through a capillary and measuring the time required by the liquid to flow through it. In figure 5.10 you can see the instrument which is used for this measurement: the Ostwald viscometer.

The meter is filled with liquid to just above the calibration marks B and C. Then the liquid is sucked up into the left tube of the ap-

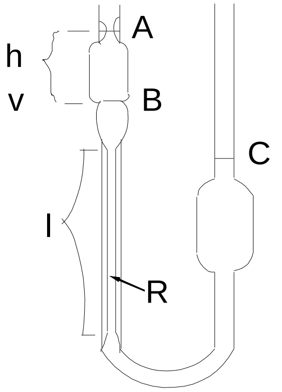


Fig. 5.10 Ostwald viscometer.

paratus to a level just above A; the other level should be at the bottom of the right bulb. Subsequently the liquid is allowed to freely flow down the left tube. The time the liquid takes to cover the distance A–B is recorded and is a measure for the viscosity of the liquid.

When the liquid, solution or lyophobic colloidal suspension contains asymmetric particles or when it is too concentrated, other methods must be applied to measure the viscosity. This is for instance the case with clay suspensions. In the past the viscosity of clay suspensions was measured by means of a bucket with a hole in it. The bucket was filled with clay suspension and after the stopper had been removed from the hole, the time required by the volume to drain was measured as a function of e.g. the volume and composition. Later mechanical methods were applied. One of them is based on the principle that a metal cylinder or disc, suspended from a torsion thread, is exposed to a certain resistance when you rotate it in the solution or suspension. Before the measurement the cylinder or disc is turned 360° anti-clockwise and then released. After having revolved over a certain angle, the cylinder or disc will change its direction of rotation. The rotation angle is a measure for the viscosity.

In yet another method a rotation viscometer is used. In this case a metal cylinder is turned round in a suspension or solution with a certain number of revolutions per minute. The resistance to which the cylinder is exposed is then measured.

You can change the viscosity of a suspension by adding a suitable electrolyte. The nature and concentration of this electrolyte determine the surface charge of the particles and consequently the particle size and viscosity. When you plot the viscosity in a graph as a function

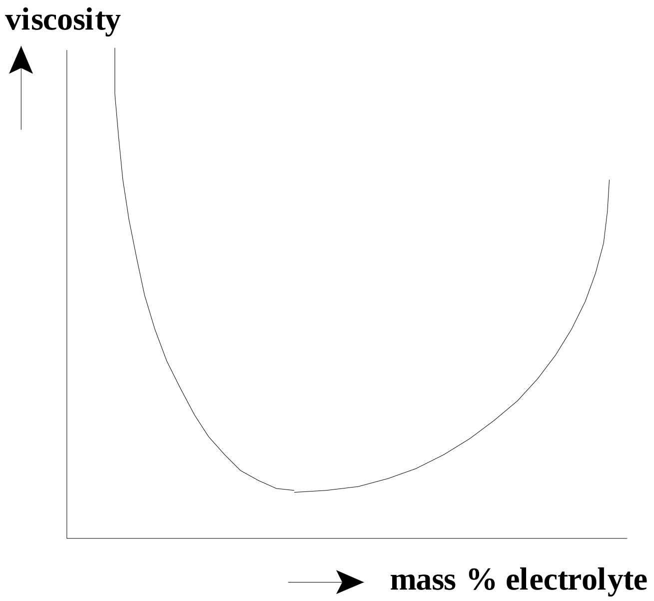


Fig. 5.11 A possible relationship between the viscosity of a colloidal suspension and the mass percentage of the electrolyte.

of the mass percentage of the electrolyte, all kinds of curves arise, for instance the one in figure 5.11.

For most applications a mass percentage of electrolyte which is situated close to the minimum of the curve is chosen.

6

Phase Rule

6.1 INTRODUCTION

In chapter 3 we saw that carbon is found in nature as diamond and graphite with the same chemical composition C, but with completely different crystal structures. Diamond and graphite are two different solid phases or *modifications* which can convert into each other under the influence of certain temperatures and and which can exist simultaneously.

Phase rule studies and describes the occurence of modifications and states of aggregation of pure substances or in mixtures in closed systems as well as the changes which occur in those systems when the pressure, temperature and composition of these substances in the system change. The behaviour of many pure substances and mixtures has thus been studied and recorded in diagrams. These diagrams constitute a vital aid for any scientist studying the development of materials, e.g. ceramics.

In phase rule the concept ‘*phase*’ has a wider meaning than “*state of aggregation*’, as appears from the following examples. A *homogeneous* system, e.g. an alcohol - water mixture, consists of one liquid phase and has one state of aggregation (figure 6.1). The circumstances described

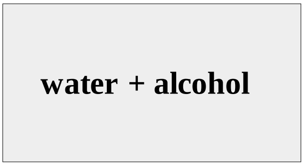


Fig. 6.1 The homogeneous system water – alcohol (no clear interface).

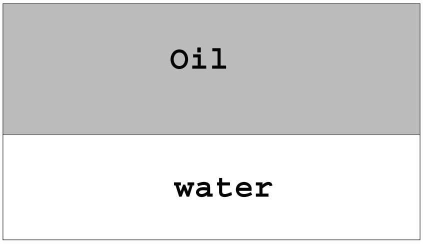


Fig. 6.2 The heterogeneous system oil – water (clear interface).

by temperature and composition are identical everywhere in the system. The *heterogeneous* system oil - water has two liquid phases and one state of aggregation (figure 6.2). There is a world of difference between the composition of a sample from the oil layer and one from the water layer.

As can be seen in figure 6.1 and 6. 2 a heterogeneous system exhibits interfaces or planes of separation whereas a homogeneous one does not. By increasing the temperature of the alcohol - water system, we can create a vapour phase next to the liquid phase (figure 6.3). Vapours are completely miscible which means that at most one vapour phase can occur in a system.

A system containing a solution of sodium chloride and sand exhibits one liquid and one solid phase (figure 6.4).

Another important concept in phase rule is "*component*". A component is a separate substance, i.e. a substance which cannot be formed out of one or more other substances in the system. For example: the system CO–CO_2–C consists of the solid phase carbon and the gaseous phases

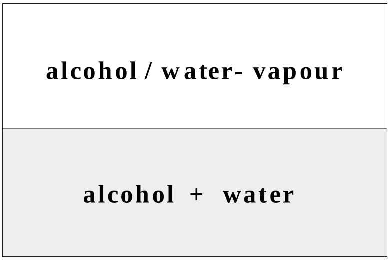


Fig. 6.3 A heterogeneous system with two phases.

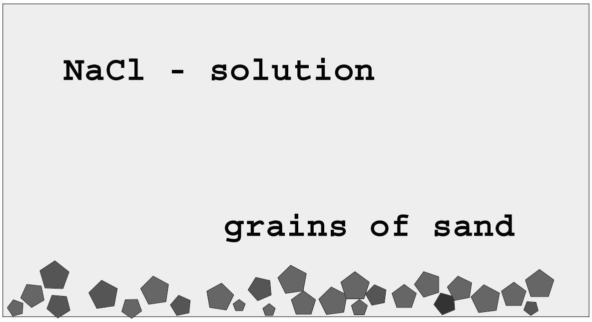


Fig. 6.4 The heterogeneous system NaCl solution – sand.

carbon monoxide and carbon dioxide. It only contains two components, since carbon monoxide can be made from the other two substances according to the reaction

$$2CO_{(g)} \rightleftarrows CO_{2(g)} + C_{(s)}$$

In phase rule systems are categorized according to the number of components: unary systems with only one component, binary systems with two components and (in this book) finally ternary systems with three components. The behaviour of the components in a system is determined by variables: pressure, temperature and composition.

6.2 THE GIBBS PHASE RULE

The Gibbs phase rule reveals the relationship between the number of freely chosen variables or degrees of freedom f, the number of components c and the number of phases p.

$$f = c + 2 - p \qquad \text{The Gibbs phase rule}$$

The number of degrees of freedom f equals the number of variables which has to be adjusted in order to define the system completely. This rule states that the factors mentioned here cannot be altered randomly without changes occuring in the system. Figure 6.5, the P, T diagram of water, serves to illustrate this. The change in pressure for H_2O is represented as a function of temperature.

In figure 6.5 three areas are indicated: S (solid), L (liquid) and G (gas, vapour) in which only ice, water and water vapour occur respectively. In the S-field the following rule holds: f =

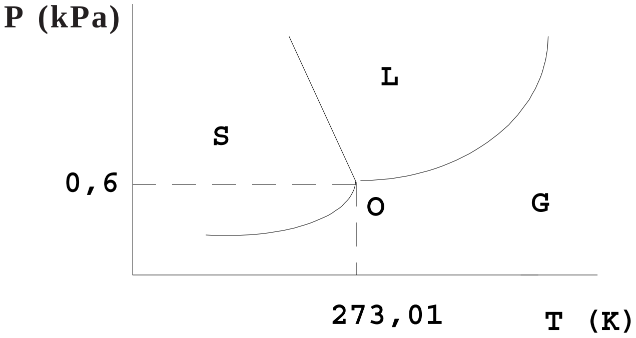


Fig. 6.5 *P*, *T* diagram of water.

1 + 2 – 1 = 2. This means that there are two degrees of freedom. We have to record both pressure and temperature in order to define a system, i.e. in order to be able to indicate a point (= system) in the graph. We are free to choose the pressure and temperature within certain values without changing anything in the system. No water nor water vapour will be formed.

Now let us have a closer look at the division between the L and the G area. With those combinations of pressure and temperature the system contains both water and water vapour, so one component and two phases: $f = 1 + 2 - 2 = 1$. Now there is only question of one degree of freedom. When we select a temperature and want to retain both water and water vapour, the system will determine the accompanying pressure. After all, the new combination of P and T must also be found on the line.

Finally, the point where the three lines meet, the so-called triple point: a system in which the S, L and G phase occur. In that case $f = 1 + 2 - 3 = 0$. We cannot choose any degree of freedom. The system determines at which unique combination of temperature and pressure the three phases can occur.

6.3 THE UNARY SYSTEM

In the previous paragraph the unary system H_2O was already introduced. It was represented in a P,T diagram in three phases. When studying ceramics it is especially important to have some knowledge of the different solid phases (modifications) in which a substance can occur. The S field in the P,T diagram of a substance with several modifications is split up in a number of subfields. Figure 6.6 is a representation of the P,T diagram of silicon dioxide (SiO_2) in which

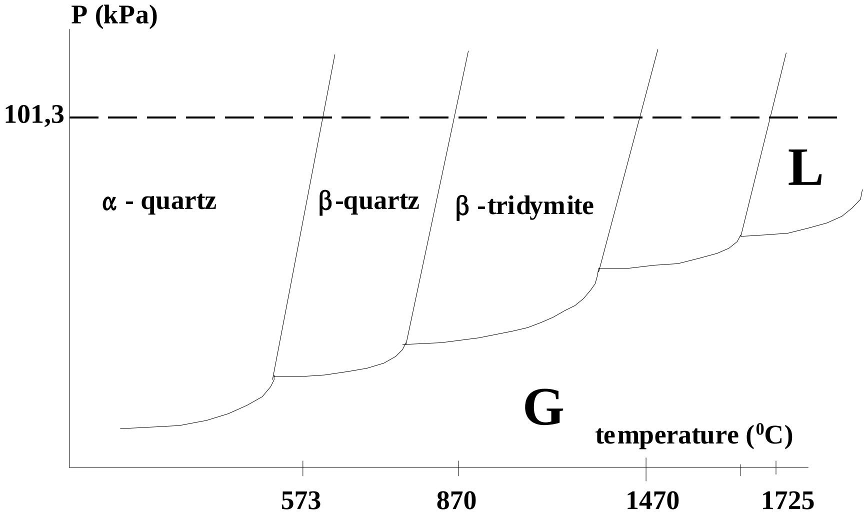


Fig.6.6 *P*,*T* – diagram of silicon dioxide with some of the possible modifications.

the pressure / temperature fields of some of the possible modifications have been drawn.

The main modifications of silicon dioxide are: α and β quartz, α and β cristobalite and α and β tridymite.

Conversions between the modifications quartz, tridymite and cristobalite progress only slowly because their crystal structures differ relatively much. The conversion between the α and the ß form of the same modification on the other hand takes place rather fast because the differences in structure are relatively small. All in all this means that transitions from one modification to another are only possible when they are slowly heated or cooled. This is the only way in which the building blocks are offered the possibility to regroup to form a new crystal structure. By heating or cooling quickly it is possible to skip certain modifications. As you can see in figure 6.6 the transition from α to ß quartz at standard pressure takes place at 573 ^{o}C.

6.4 THE BINARY SYSTEM

In a binary system the composition of the mixture can be varied and plotted on a horizontal line, usually as a mole fraction *x* or mass fraction *w*. At the ends of this line two vertical axes are drawn on which the temperature is represented most of the time. We shall now have a closer look at three kinds of binary systems.

The ideal binary system

The binary system which is easiest to describe is the so-called “ideal binary system”. As you can tell from the inverted commas, such a system does not really exist, but there are systems which come very close. In an ideal system the components in the S and L phase are completely miscible. In order to be so in the S phase, the substances need to be isomorphous, i.e. possess the same crystal structure. This is often accompanied by an analogous chemical structure. Some examples of these systems are silver (Ag) / gold (Au) and sodium nitrate ($NaNO_3$) / calcium carbonate ($CaCO_3$).

In figure 6.7 you can see the *T*, *x* diagram of the ideal binary system with the components A and B (the binary system A / B) for the L and S phases at one specific pressure.

The bottom line of the diagram is called the liquidus curve. This line represents a collection of the melting points of all mixtures and of the pure components A and B. The top line is called the solidus curve and is a collection of all the solidification points of all mixtures and the pure substances A and B. In the L field one liquid phase and in the S field one solid phase occur. In the L + S field a solid and a liquid phase are present. How should such a diagram be read? First of all it is important to realise that every point in the diagram represents a system which is characterized by a temperature, com-

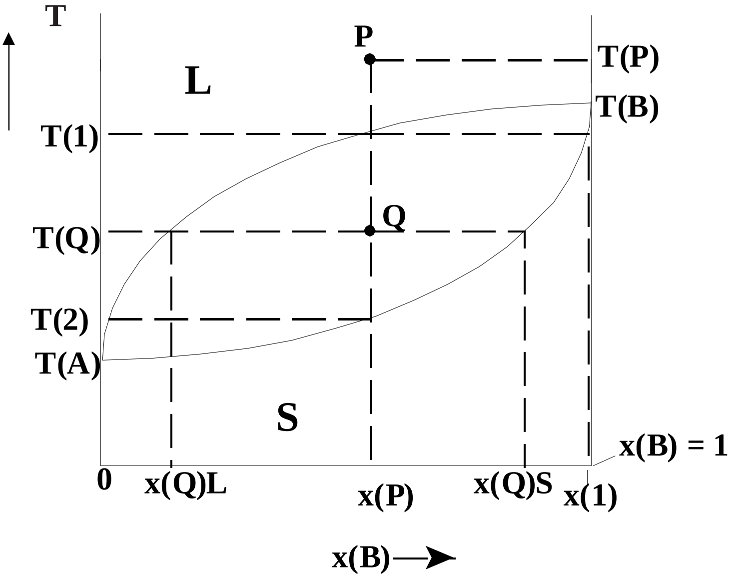


Fig. 6.7 The *T,x* diagram of the ideal A / B system for the L and the S phase.

position and one or two phases, and that includes the points on the curved lines and the vertical temperature axes. For instance: system P consists of an L phase with a temperature *T*(P) and a composition *x*(*P*). If this system P is cooled down (we descend along the vertical line), then the first crystal is formed at a temperature *T*(1) and it has a composition *x*1 (follow the horizontal and vertical dotted lines).

Between the temperatures *T*(1) and *T*(2) the system possesses an L and an S phase. The compostion of these two phases can be read from the diagram. For instance: system Q has a temperature *T*(Q), a solid phase with the composition *x*(Q)S and a liquid phase with composition *x*(Q)L. When the temperature of the system drops to *T*(2), the last drop of the L phase will disappear and further cooling will result in the presence of only one S phase. Now work out for yourself that heating an S mixture with composition *x*(P) and *T*(2) will result in the formation of the first L droplet with a composition close to value 0.

A binary system with an eutectic

Characteristic of a binary S / L system with an eutectic is the complete miscibility in the L phase, but not in the S phase. Figure 6.8 is the *T*,*x* diagram of such a system. The fact that it is not completely miscible

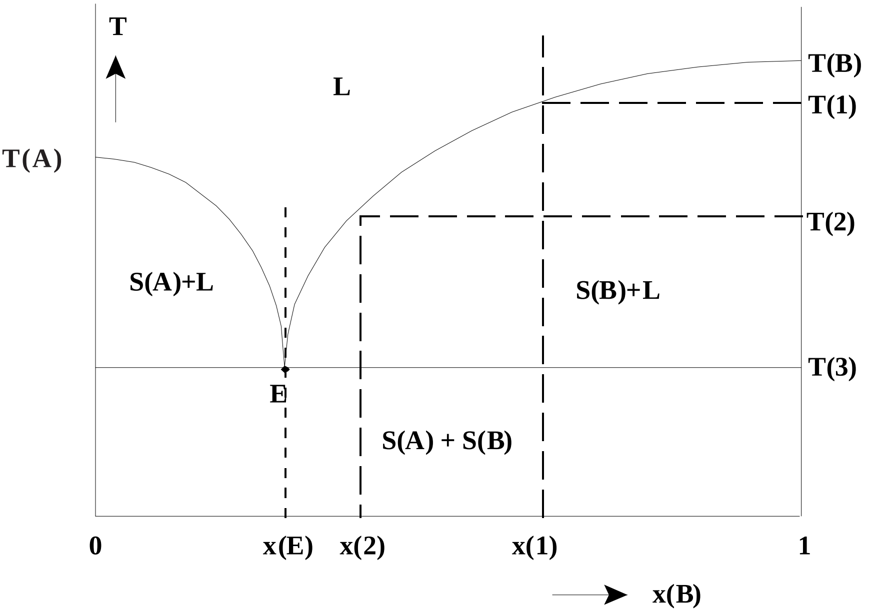


Fig. 6.8 *T*, *x* diagram of the binary S / L system A / B with an eutectic.

in the S phase is indicated by means of S(A) + S(B). When we look at such a mixture of solids through a microscope, we usually see two kinds of crystals. All mixtures of the solids A and B have the same starting melting point *T*(3). *T*(A) and *T*(B) are the melting points of the solids A and B respectively.

Point E is called the *eutectic point* or *eutectic*. In the field "S(A) + L" the system contains a homogeneous liquid mixture and crystals of the solid A.

When a mixture of the solids with composition *x*(1) is heated, it will start to melt at *T*(3) and the first droplet of liquid has the composition *x*(E). Between *T*(3) and *T*(1) the mixture will melt further and at *T*(3) everything will have melted. It is said that "the mixture has a melting range of *T*(3) to *T*(1)". Such a melting range is characteristic of most mixtures, whereas a pure substance always has a melting point. A eutectic mixture is however an exception to this rule. As you can see in figure 6.8 the eutectic mixture with the composition *x*(E) is the only mixture with a melting point T(3).

Let us return for one moment to the mixture *x*(1). As can be seen in figure 6.8 at temperature *T*(2) the mixture contains an L phase with the composition *x*(B) = *x*(2) and an S phase with the composition *x*(B) = 1 (the pure substance B).

Some examples of mixtures with eutectic behaviours are silicon/ aluminium and silicon dioxide / aluminium oxide.

A binary S / L system with a congruently melting compound

In a binary system the components A and B can form a compound under certain conditions. Some examples of this are the systems Al / Mg with the compound Al_3Mg_4 and Au / Sn with AuSn. Figure 6.9 is a representation of the *T*,*x* diagram of the binary S / L system A / B with the congruently melting compound AB_2 with composition *x*(B) = 2/3. Note that when this figure is hypothetically cut in two along the vertical axis above *x*(B) = 2/3, two diagrams of the type in figure 6.8 are formed.

The system P in diagram 6.9 has the composition *x*(B) = 1/2 and a solid phase with the composition *x*(B) = 2/3, the compound consequently. The liquid composition can be read by drawing a vertical line through P from the point where the horizontal dotted line and the curved line intersect. Finally, the pure substances A and B, the two eutectic mixtures and the compound all have individual melting points. The other mixtures have a melting range. The compound is congruently melting, i.e. when it melts a liquid with the same composition is formed.

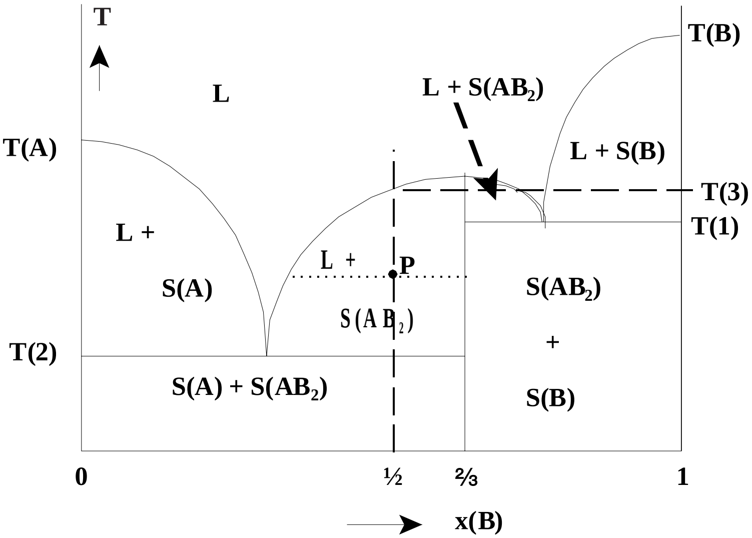


Fig. 6.9 *T*,*x* diagram of a binary system with a congruently melting compound.

6.5 THE TERNARY SYSTEM

Ternary systems contain three components. The composition of such a system cannot be represented on a line. For that reason an equilateral triangle is used. When the temperature is a variable, the composition triangle (figure 6.10) in a *T*,*x* diagram is the base on which three *T* axes are placed perpendicularly on the vertices of the triangle. In a system with the components A, B and C there are three mole fractions for which holds: $x(\mathrm{A}) + x(\mathrm{B}) + x(\mathrm{C}) = 1$.

Three kinds of systems can be represented in the composition triangle:

1. The vertices on the triangle represent the unary system with the pure components.

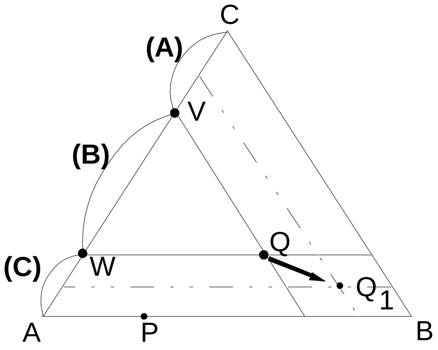


Fig. 6.10 The composition triangle of a ternary system.

2. Points on the sides of the triangle represent binary systems. For example: system P is a binary system with the components A and B and x(B) = 0.30.

3. The points in the triangle represent ternary systems.

How can we derive the composition in system Q from this triangle? In order to to so, two construction lines need to be drawn which are parallel to the sides of the triangle. In figure 6.10 the line AC is thus divided into three sections. Then:

x(A) = mole fraction of component A = length line (A) / length line AC

x(B) = mole fraction of component B = length line (B) / length line AC

x(C) = mole fraction of component C = length line (C) / length line AC

A calculation example:

AC = 10 cm (A) = CV = 3 cm (B) = VW = 5cm (C) = WA = 2cm

x (A) = 3/10 x (B) = 5 /10 x (C) = 2/10

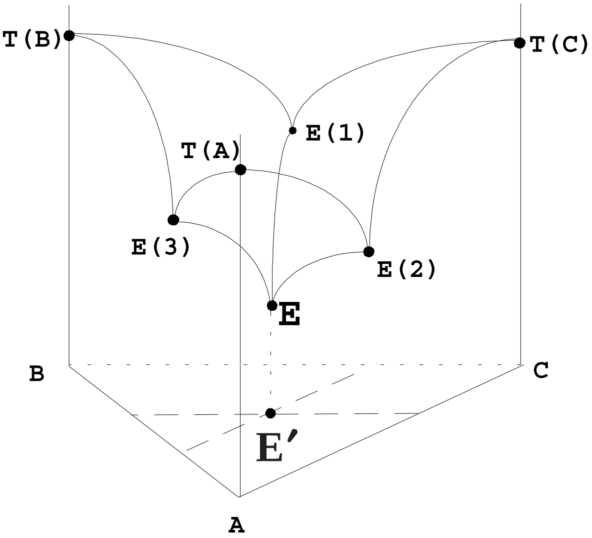


Fig. 6.11 Diagram of a ternary system with three binary eutectics and a ternary one.

So why is x(A) proportional to line (A) and x(B) to the middle part on line AC? This can be made clear by moving from system Q to system Q_1. We now approach vertex B and the system will consequently contain more B. This is confirmed by drawing two lines parallel to the the two sides of the triangle; as we can see x(B) has indeed increased in size. By moving point Q in the direction of vertex C you can increase the line (C) and consequently x(C).

Figure 6.11 is a T, x diagram of a ternary system. Suppose S / L systems are represented in this figure. Then T(A), T(B) and T(C) are the melting points of the pure substances. E(1), E(2) and E(3) on the other hand are the eutectics of the binary systems, represented in the sides of the prism. Somewhere in the prism there is a ternary eutectic E. The composition of E can be read in the base, the composition triangle, by drawing a vertical line downwards from E until point E' in the base. Subsequently, the composition can be read through E' on the side of the base. How this diagram should be read further is beyond the scope of this book.

7

Geology and Mineralogy

7.1 INTRODUCTION

Why are geology and mineralogy discussed in a book on ceramics? The main reason is the fact that nature shows us which materials might be suitable ceramic materials for various applications. Over the past millions of years nature has produced an enormous variety of rocks and minerals with numerous properties. Researching these products has taught us how nature shaped them and what their structure are like. Nowadays these production processes can be imitated in the laboratory, very often within a short period of time. In addition, most ceramic raw materials are obtained from nature and sometimes altered chemically or physically in the laboratory. This means that the ceramicist must have a good knowledge of these raw materials.

The previous paragraph might suggest that rocks are not built up of minerals. On the contrary! Rocks are usually built up of a collection of extremely fine grains of different minerals. For that reason you cannot see the crystal form of the composing minerals. That is only possible when thin sections are made for a special kind of microscopic research (polarisation microscopy). In geology and mineralogy we speak of minerals when there is question of a naturally occurring element or compound with a crystal form which can be seen in an untreated sample with either the naked eye or a microscope, although there are some exceptions. Consequently a mineral collector will mostly collect minerals and not rocks. This aesthetic argument plays an important role.

Most collectors limit themselves to the so-called micromount, pieces of mineral with dimen-sions of at most a few centimetres and they classify their collection as described in paragraph 7.3. Samples are identified by making use of their properties, most of which can easily be demonstrated. In addition, you can use information obtained with the help of stereo microscopy or of catalogues with photographs.

Table 7.1 Properties of minerals

crystal structure	cleavage
crystal shape	fracture
colour	hardness
translucence	magnetic behaviour
streak colour	radioactivity
lustre	solubility
flame colour	melt behaviour

Based on one or more of these properties (table 7.1) a specialized collection can be built up.

7.2 THE EARTH

Based on the kind of compounds which occur at certain depths in the earth, the globe can be subdivided into layers (figure 7.1). That certain compounds occur at certain depths is and was to a large extent determined by local temperatures and pressures.

The separations between the layers as indicated in figure 7.1 are not as clear as shown, but are gradual, which results in a gradual change in density and mineral composition. The thickness of the continental earth's crust or lithosphere (Greek: "lithos" = stone) varies between appr. 20 and appr. 60 km, with an average thickness of appr. 35 km. The elementary composition of the lithosphere is well-known,

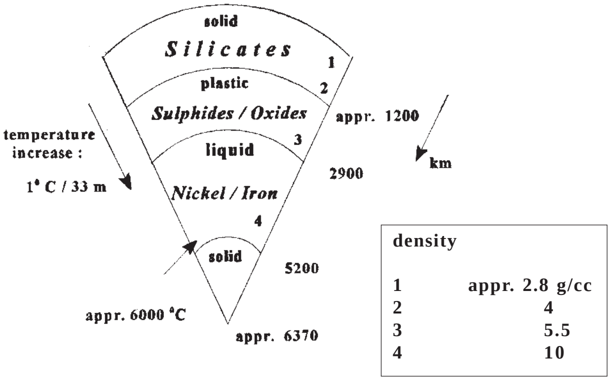


Fig. 7.1 Cross-section of the earth.

mainly thanks to many drilling operations, and is represented in table 7.2.

When we assume that the first minerals crystallized from a magma, a liquid rock mass, then the movement of the crystals in the magma will mainly be determined by their densities. Light minerals will rise to the surface, whereas heavy ones will sink. A number of densities of elements are listed in table 7.3 which will give you some idea of the occurrence of the various elements in the different earth layers. Please bear in mind that compounds are and were formed during the transport in magma and that this can lead to drastic changes in density.

Oxygen has an extremely low density and it is hardly surprising that the earth's crust consists for 47 mass % of oxygen. Figure 7.2 lists the most common elements on earth in the layer in which they are found in the highest mass percentages.

Another factor which determines the presence of minerals at certain depths is the tendency to combine with others or affinity of minerals and elements. Noble gases hardly react with other elements and will, because of their low densities, consequently end up in the atmosphere. Relatively light elements (alkaline and alkaline earth metals) with a strong affinity for oxygen are found in the silicate schaal. Heavy elements which are bound to sulphur or oxgen are situated in the sulphide /oxide scale, or even deeper in the nickel/iron scale.

Table 7.2 The most common elements in the continental crust (according to Brian Mason, 1966, Principles of Geochemistry, table 34). The mass % and volume % values have been rounded up or down

Element	Mass %	Volume %	Ion radius (nm)
oxygen	47	92	0.13
silicon	28	0.8	0.04
aluminium	8	0.8	0.06
iron	5	0.7	0.07
calcium	4	1.5	0.10
sodium	3	1.6	0.10
potassium	3	2.1	0.13
magnesium	2	0.6	0.08
titanium	1	0.2	0.06

Table 7.3 Densities of some elements

Element	Density (g/cm^3)
O	0.00143
Si	2.33
Al	2.70
Fe	7.87
Ca	1.55
Na	0.97
K	0.86
Mg	1.74
Ti	4.50

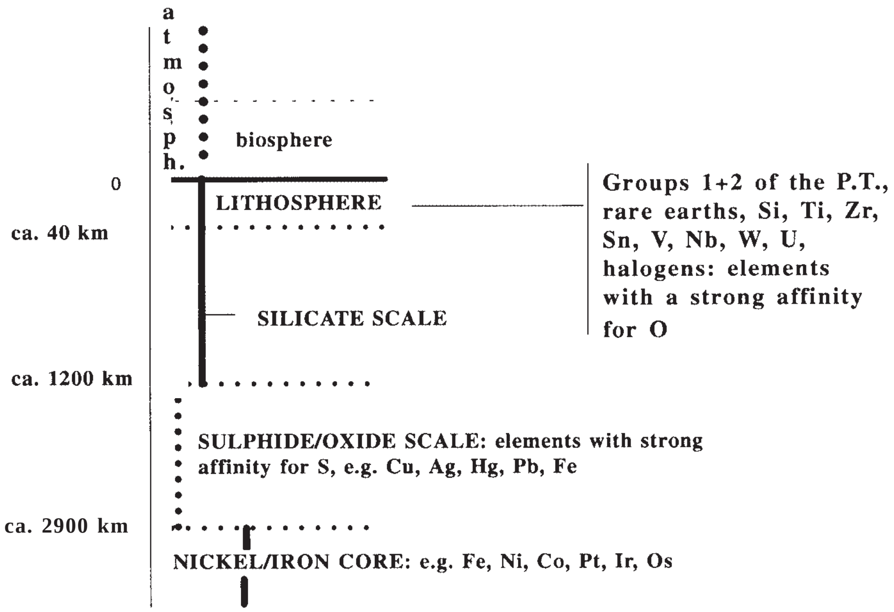


Fig. 7.2 The most common elements in the different earth layers.

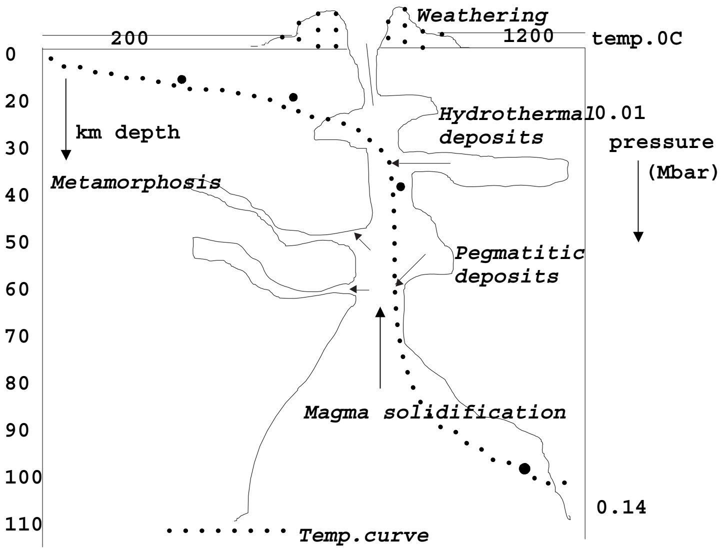


Fig. 7.3 Various kinds of mineral formation.

7.3 THE FORMATION OF MINERALS AND ROCKS

The natural formation of minerals, and consequently of rocks, takes place in a wide variety of ways, both in the earth and at the surface. In figure 7.3 some of these processes with the accompanying temperatures and pressures in the various layers are shown.

Let us assume that the minerals crystallize one at a time during the SOLIDIFICATION of the MAGMA, a molten mass which mainly consists of crystals and gases. In that case there will be question of crystals which float in a solution. Dependent on the difference in density of the crystal and that of the magma the crystal will rise or fall and deposit at a certain depth. Minerals crystallize very slowly and consequently the products (intrusive or plutonic rock) are completely crystalline and built up of relatively large crystals. During the crystallization of magma silicate solutions often arise which form the so-called pegmatites when they crystallize in the upper and outer regions of a magma chamber and in the cracks and open spaces of the adjacent rock. The composition of these pegmatites resembles that of the mother rock to which rare earth metals and minerals formed from volatile components have been added. For instance in granite pegmatite the main rock-forming minerals feldspar, quartz and mica occur, but also topaz, tourmaline, beryl, quartz, muskovite and zirkonium, often in large and beautiful crystals.

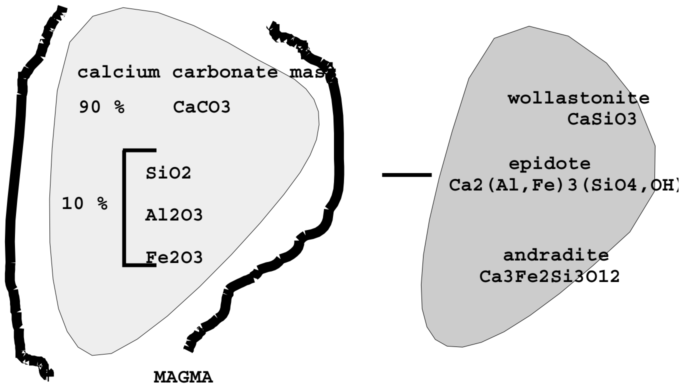


Fig. 7.4 An example of a metamorphic process.

The word METAMORPHOSIS is derived from the Greek and means "adopting a different form". In mineralogy the transitions in the minerals are studied which take place under the influence of pressure (dynamic metamorphosis), temperature (thermic metamorphosis), moisture, etc. Figure 7.4 is an example of a metamorphic process.

In the example above the ascending magma heats the carbonate mass together with the oxides of silicon, aluminium and iron(III). Owing to the high temperature different silicate minerals are formed, among which are andradite garnet, a semi-precious stone which was named after the Portuguese mineralogist J.B. d'Andrada.

A third way in which minerals can be formed is the HYDROTHERMAL DEPOSIT. The water-rich part of the magma contains volatile components like carbon dioxide (CO_2), hydrogen fluoride (HF), hydrogen chloride (HCl), hydrogen sulphide (H_2S), boron(III) oxide (B_2O_3) and heavy metals which combine with the above-mentioned substances. On its way to the surface this solution penetrates cracks of the adjacent rock. Then the solution cools and the minerals crystallize. The temperature and pressure at which this happens are specific for each mineral. Hydrothermal deposits are characterized by certain combinations of minerals, the so-called mineral parageneses, e.g hematite (Fe_2O_3), siderite ($FeCO_3$), barite ($BaSO_4$), fluorite (CaF_2) and calcite ($CaCO_3$) are mostly found together.

When "foreign" building blocks of roughly equal sizes are present during the crystallization process, these can be incorporated and in this way so-called mixed crystals are formed (fig.7.5)

Mineral formation as a result of weathering will be discussed in chapter 8, which deals with the formation of clay.

$Na[AlSi_3O_8]$ albite – $Ca[Al_2Si_2O_8]$ anorthite

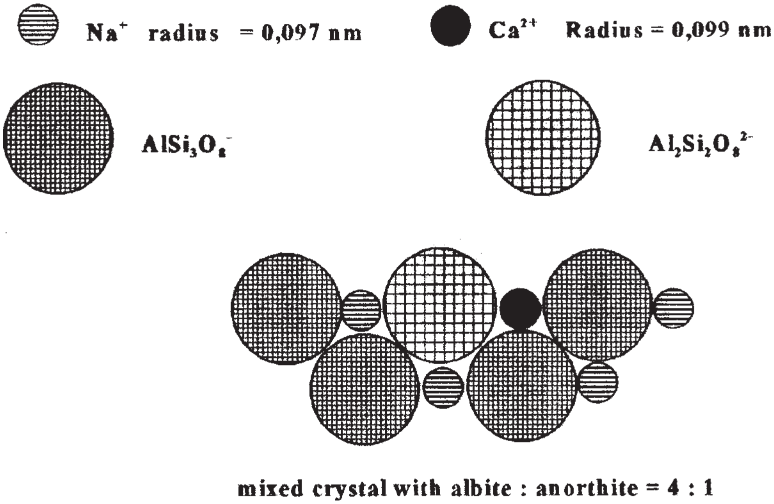


Fig. 7.5 An example of the formation of a mixed crystal.

When magma wells up to the surface under high pressure and through weak spots and openings it can be discharged and it that case we speak of volcanism. In this process the volatile components will escape from the magma into the atmosphere and sometimes sublimate near the ridge of the crater, as in the case of e.g. sulphur. The ejected magma cools down quickly and consequently there is hardly any possibility for large crystals to be formed. The arising so-called eruptive rock is characterized by porosity (many cavities), minute crystals and very often it also contains volcanic glass.

7.4 CLASSIFICATION OF MINERALS

Minerals are usually classified into 9 groups which each comprise a different type of compound with a specific structure and/or composition. In the classification below each of these groups is mentioned together with some representatives of that group and in some cases its specific structure is discussed in more detail. Important minerals as for as ceramics are concerned, are placed in a box.

I ELEMENTS

Members of this group are the naturally occurring, at ordinary temperatures solid or liquid elements and their homogenous mixtures (alloys). The group is subdivided into two groups:

Ia Metals	mercury, silver, platinum, gold, iron, lead, tin and zinc
Ib Non-metals	arsenic, sulphur, carbon in the form of diamond or graphite, antimony

II SULPHIDES and RELATED MINERALS

IIa	Sulphides	pyrites FeS_2, cinnaber HgS

Lead sulphides are used as raw materials for lead oxides (e.g. Pb_3O_4) which, in their turn, are components of glazes.

IIb	Selenides	bornhardtite Co_3Se_4 (rare)
IIc	Telllurides	tetradymite Bi_2Te_2S, empressite $Ag_{11}Te_8$ (rare)
IId	Arsenides	safflorite $CoAs_2$
IIe	Antimonides	dyscrasite Ag_3Sb

III HALIDES

IIIa Simple halides	halite NaCl, fluorite CaF_2, chlorargyrite AgCl
IIIb Double halides	ferrucite $NaBF_4$ or $NaF.BF_3$ (it is a mixed crystal)
IIIc Oxyhalides	mendipite $PbCl_2.2PbO$; the crystals are built up of Pb^{2+}, Cl^- and O^{2-} ions

IV OXIDES AND HYDROXIDES

IVa Simple and multiple oxides cuprite Cu_2O, ilmenite $FeO.TiO_2$, zincite ZnO, corundum Al_2O_3

Bauxite is a mixture of minerals and contains e.g. diaspore [α-AlOOH], gibbsite [γ-$Al(OH)_3$], iron hydroxides, clay minerals and quartz.

An important oxide in ceramics is silicon dioxide SiO_2 in the form of the minerals quartz and quartz sand (with aluminium oxide as a good second). Several crystal forms or modifications are known of this mineral (see the chapter on Phase Rule).

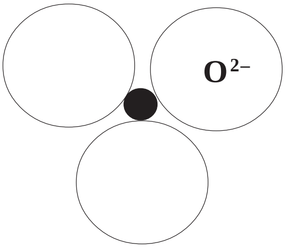
Chromite (Mg,Fe)(Cr,Al,Fe)$_2$O$_4$ with the main component FeO.Cr$_2$O$_3$ is used as a partial replacement of magnesite in magnesite (fireproof) stones.

IVb Hydroxides and oxides with OH-groups brucite: Mg(OH)$_2$, diaspore AlO(OH)

Synthetic quartz crystals (Natuur & Techniek, Amsterdam).

V COMPOUNDS WITH OXYGEN ATOMS IN A THREE CO-ORDINATED ARRANGEMENT

In these compounds the anion (negative ion) consists of a central particle, surrounded by three oxygen particles (figure 7.6). In order to cal-



● central particle in the anion of the minerals of group V

Fig. 7.6 Structure of the anion in the minerals of group V.

culate the charge we attribute a charge of 2^- to each oxygen particle and the charge of the central particle can then be calculated by means of the formula; e.g. in BO_3^{2-} the central particle is B^{3+}. We should note, however, that the bond between the B and the O particles is partially ionic and partially covalent.

Va Borates, containing BO_3^{3-} jeremejewite $AlBO_3$

Vb Carbonates are used, for example, in masses for fine ceramics and in glazes. Well-known examples are: **calcite** or calcspar $CaCO_3$ which is the main component of limestone, magnesite $MgCO_3$ and dolomite $CaMg[CO_3]_2$. In coarse ceramics lime is added to clay to obtain yellow-firing bricks.

During the firing process a carbonate is converted into CO_2 and the extremely reactive oxide which can bind with other substances to form the desired component. $BaCO_3$, witherite, is a raw material for glazes.

Vc	Nitrates, containing NO_3^-	sodium nitrate	$NaNO_3$
Vd	Iodates, containing IO_3^-	lauratite	$Ca(IO_3)_2$

VI COMPOUNDS OF SEVERAL ELEMENTS OF GROUPS 6 AND 16 OF THE PERIODIC TABLE WITH OXYGEN IN A FOUR CO-ORDINATED ARRANGEMENT

The negative ions consist of a central particle, surrounded by four oxygen particles in a pyramid formation (figure 7.7). The charge of the central particle can be calculated in the same way as in group V.

VIa	Sulphates	barite	$BaSO_4$

Gypsum $CaSO_4$ is used in the fine ceramic raw material mass.

VIb	Chromates	crocoite	$PbCrO_4$
VIc	Molybdates	tungstenite	$PbMoO_4$
VId	Tungstates	scheelite	$CaWO_4$

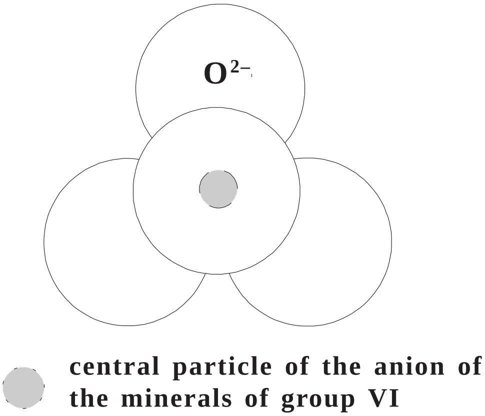


Fig. 7.7 Top view of the anion in the minerals of group VI.

VII COMPOUNDS OF SEVERAL ELEMENTS OF GROUPS 5 AND 15 OF THE PERIODIC TABLE

The structure of the anions is similar to that of group VI and the group is divided into three subgroups:

VIIa	Phosphates	vivianite	$Fe_3(PO_4)_2.8H_2O$
VIIb	Arsenates	scorodite	$FeAsO_4.2H_2O$
VIIc	Vanadates	vanadinite	$Pb_5(VO_4)_3Cl$

VIII SILICATES

The silicates are divided into five subgroups, which differ in the structures of their silicate anions. Each silicate anion consists of one or more SiO_4 tetrahedrons which are linked in various ways. This group of substances is discussed more elaborately than the other ones because these minerals are most abundant in the lithosphere and because the clay minerals in clay also belong to the silicates.

VIIIa *Silicates with isolated SiO_4 tetrahedrons*

In a SiO_4 tetrahedron the O atoms and the Si atom are mainly bonded covalently. The tetrahedron has a negative charge (4^-). In order to

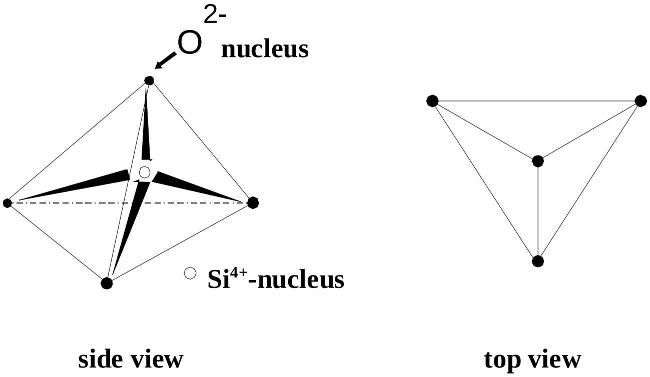


Fig. 7.8 Structure of the SiO_4 tetrahedron.

explain this charge the O particles need to have a negative charge (2^-) and the silicon particle a positive one (4^+). Figure 7.8 is a representation of a tetrahedron. In the top view the nucleus of the top O atom is situated in the middle of the triangle, with below it (and consequently not visible!) the Si atom.

Two examples of minerals with isolated silicate tetrahedrons are:

Zirconium $Zr[SiO_4]$ is the basic material of zirconium oxide ZrO_2 which is for instance used as a bioceramic in implants. In nature zirconium is mainly found in the form of sand.

Topaz $Al_2[SiO_4](F,OH)_2$

VIIIb *Silicates with isolated SiO_4 tetrahedral groups*

A possible anion structure is represented in figure 7.9 and for instance occurs in the minerals:

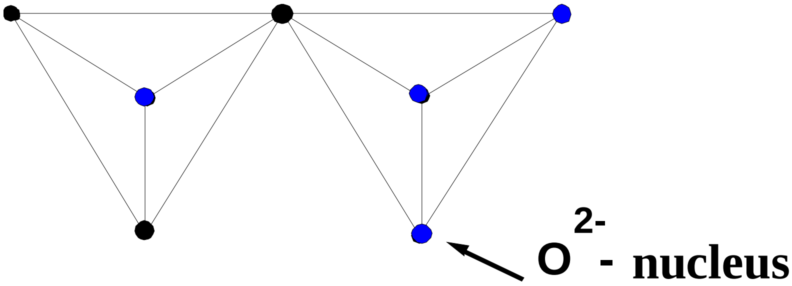


Fig. 7.9 Structure of the $Si_2O_7^{6-}$ anion.

hemimorphite	$Zn_4[Si_2O_7](OH)_2.H_2O$
zoisite	$Ca_2Al_3[Si_2O_7][SiO_4]$ (OH) (O)

VIIIc *Silicates with chains of silicate ions*

Again the anion can have many shapes, an example of which is a chain in which all tetrahedrons are aligned in a similar way (figure 7.10).

A chain as shown in figure 7.10 is found in the mineral diopsite $CaMg[Si_2O_6]$.

The unit which is repeated in the chain is indicated in between the dotted lines. Two whole and two half O particles, so in total three O particles and one Si particle, form the so-called repetitive unit. The formula of the unit is SiO_3^{2-}. In the structure of diopsite the unit consists of two units of SiO_3^{2-}, one Ca^{2+} and one Mg^{2+}.

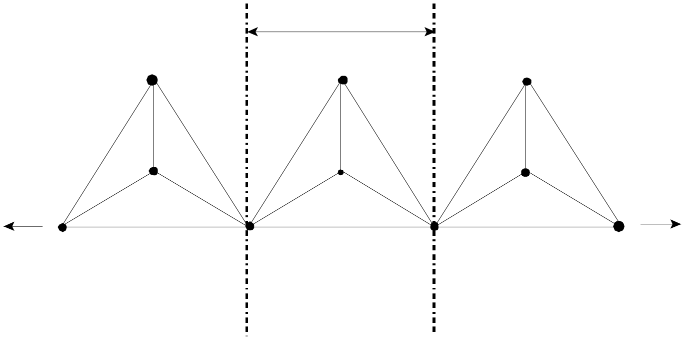


Fig. 7.10 Possible structure of a silicate chain.

VIIId *Silicates with layered anions (the so-called phyllosilicates)*

Figure 7.11 represents a way to link SiO_4 tetrahedrons in one layer. The repetitive unit in the structure of figure 7.11 is represented in between the dotted lines and has the formula $Si_4O_{10}^{4-}$. The anion described here for example occurs in the minerals:

talc	$Mg_3[Si_4O_{10}](OH)_2$	
biotite	$KMg_3[Si_3AlO_{10}](F,OH)_2$	
in clay minerals as	kaolinite	$Al_4[Si_4O_{10}/(OH)_8]$

The formula of biotite is remarkable because an Al^{3+} ion is in-

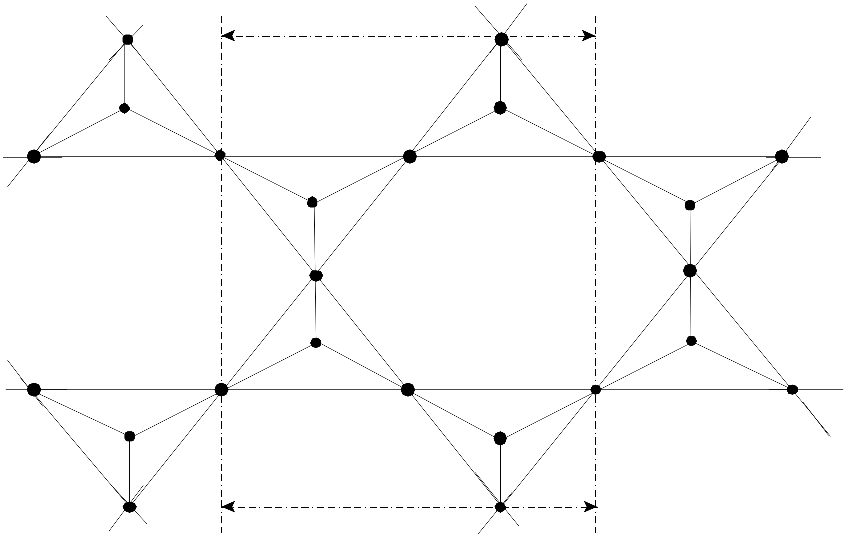


Fig. 7.11 Structure of the $Si_4O_{10}^{4-}$ ion.

corporated between brackets in the silicate ion instead of a Si^{4+} ion. Therefore, the charge of the anion is 5–. Per unit two F^-, two OH^- or one F^- and one OH^- are present amounting to a total charge of 2–. The total of negative charges is 7–, which is compensated by one K^+ and three Mg^{2+} ions.

VIIIe *Silicates with three-dimensional anions*

In figure 7.12, the SiO_4 tetrahedron is shown as the repetitive unit. However, each tetrahedron shares the four oxygen particles with neighbouring tetrahedrons. Consequently the formula of the unit is

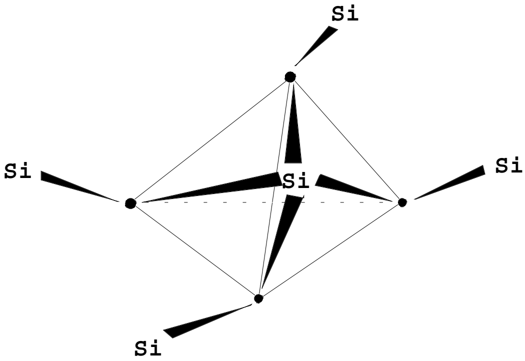


Fig. 7.12 Structure of the three-dimensional silicate anion.

SiO_2, but SiO_2 is a neutral molecule. How can there then be question of an anion? The answer to this question is simple. Figure 7.12 is not an accurate representation of the anion. A number of Si^{4+} particles has been replaced by an Al^{3+} particle, causing the anion to be constructed of SiO_2 and AlO_2^- units and the latter results in the negative charge of the anion.

The anions in figure 7.12 occur, for example, in the minerals albite $Na[AlSi_3O_8]$, celsian $Ba[Al_2Si_2O_8]$ and the group of the feldspars.

Minerals of the feldspar group are for example used in fine and coarse ceramics.

Feldspars are found in nature in the form of mixed crystals of the alkali feldspars orthoclase $K[AlSi_3O_8]$, albite $Na[AlSi_3O_8]$ and anorthite $Ca[Al_2Si_2O_8]$. Unlimited formation of mixed crystals of the alkali feldspars is only possible at high temperatures. During cooling demixing occurs. Potassium feldspar and calcium feldspar are not miscible.

IX ORGANIC COMPOUNDS

The mineral humboldtine $FeC_2O_4.2H_2O$, resins and coal are examples of members of this group.

8

Clay

8.1 INTRODUCTION

For most of us the first time we encountered clay was in our early childhood during our modelling classes; later quite a few of us come across it while we were digging in the garden. Every child makes use of plastic clay to make figures and shapes, which are then left to dry and perhaps even baked in a small oven. Digging in clay requires a lot of effort because the material is heavy and wet. The most important characteristic of clay is well known: it is able to retain a lot of water. And than there is a group ‘clay collectors’, a small group in the very wide spread hobby of collecting minerals.. Apparently clay is a fascinating material and from the fact that it is collected we can derive that there are many kinds of clay. My own modest collection comprises approximately 20 kinds of clay all of which were found in The Netherlands.

Which brings us to the question: “*What is clay?*”. According to the dictionary clay is a stiff sticky earth which can be distinguished into fat or heavy clay with less than 40 % (m/m) sand and light clay with 40–60 % (m/m) sand. In a more technical dictionary I found this description: “in soil science a water-containing plastic sediment containing a large proportion of inorganic particles with diameters < 2 µm”. It took a long time for scientists to agree on a good definition. We owe the following generally accepted definition to a joint committee of the AIPEA (Association Internationale pour l’Etude des Argiles / International Association for the Study of Clay) and the CMS (Clay Minerals Society):

The term “clay” refers to in nature present materials which mainly consist of fine granular minerals, which generally exhibit plastic behaviour at certain water contents and which harden after drying or baking. Although clay usually consists of phyllosilicates, it can also contain other materials which do

not affect its plastic and hardening behaviour. These so-called associated phases can contain minerals like quartz, calcite, dolomite, feldspars, oxides, hydroxides, organic materials and non-crystalline phases (e.g. colloidal silica, iron hydroxide gel). (*Source: Dutch magazine for amateur geologists, mineralogists and paleontologists GEA, 1997, no 2; phyllosilicates: chapter 7*)

In this chapter, much attention will be paid to several kinds of clay and the reason why clay becomes plastic when you add water to it.

Clay is a *sediment*. In nature sediments are geological materials which were transported somewhere, e.g. by water and subsequently deposited or sedimented. They can be subdivided into fractions based on the grain size, which can vary from blocks with diameters > 630 mm to clay with grains < 2 µm. In between these two extremes we find boulders, stones, gravel and sand. The grain size is an aspect of the so-called texture, a collective of characteristic features among which are the shape of the individual grain, the grain size, the packing of the grains and the density of the mass. On The Internet I found the experiment “How to determine Soil Texture” in the Time Life..Project Directory.

Experiment:

Fill half of a glass vessel with a lid with equal mass quantities of soil and water. Shake vigorously. Allow the mixture to stand. The largest particles (sand) will sink to the bottom within one minute, silt requires an hour and clay a day. When the experiment has been performed correctly, three layers should be visible. By measuring the thickness of the three layers together and of each of the layers separately, you can express the composition of the soil in % (m/m) sand, silt and clay.

This composition is then plotted into a composition triangle (see Phase rule / ternary systems) in order to read off the name of the soil. An example is given in figure 8.1. Let us suppose that the result of the experiment was 40% (m/m) sand, 30 %(m/m) silt and 30% (m/m) clay. These numbers are transferred to the composition triangle by drawing three lines parallel to the sides of the triangle. Each line begins at the percentage in question on the triangle side of the substance in question and the intersect somewhere inside the triangle (figure 8.1).

The triangle is divided into areas with the names of the various

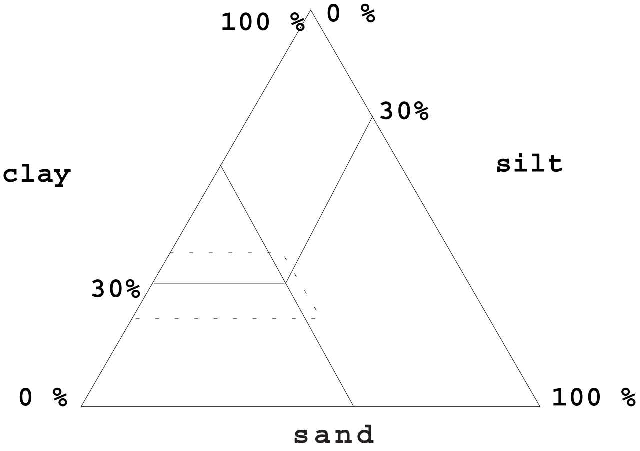


Fig. 8.1 Ternary compostion triangle for clay-containing soils.

soil kinds. When the soil for example roughly contains more than 60% (m/m) clay, less than 40% (m/m) silt and the rest is sand, then the it is called clay. In the example above the soil kind is a "sandy loam", as are all compositions within the area between the dotted lines.

8.2 GEOLOGY OF CLAY

Clay is found everywhere on earth, usually as part of the outer layer of the earth's crust, the lithosphere. In a few places clay is also found and mined below the surface. Clay is an erosion product of magma or sedimentary rock. Before entering into the phenomenon "erosion", first some information about the various kinds of rocks of which the earth's surface is built up. By now we know that the elements O, Si, Al, Fe, Ca, Na, K and Mg mainly occur in rocks (see Geology /Mineralogy).

Rocks are subdivided into igneous, sedimentary and metamorphic rocks according to the manner in which they arose. Only igneous and sedimentary rocks are of importance for the formation of clay.

ROCKS

I Igneous rocks

Igneous rocks are also called solidification, eruption or magma rocks. They are formed from the solidification of magma, a liquid rock mass in which gases can also be present. When this solidification process takes place in the earth's crust, we speak of effusive or volcanic rocks. However, when it takes place at the crust, so-called intrusive rocks or plutonites are formed. The most common igneous rocks are the granites, which comprise approx. 90–95% of the plutonic igeneous rocks and the basalts which determine the composition of volcanic igneous rocks for about 98%. The composition of the rocks and their names are represented in the by now familiar composition triangle. Because of the limitations of the diagram, only the three main components of the rocks are incorporated into it, namely :

quartz	SiO_2
alkali feldspar	general formula $X[(Al,Si)_4O_8]$
	X = Na, K, Ca or Ba
plagioclase	$Na[AlSi_3O_8]$ – $Ca[Al_2Si_2O_8]$

these minerals form the so-called mixed crystals and the above-mentioned formulas represent the pure minerals

In figure 8.2 the rocks with a composition as indicated by the shaded part are called “alkali granite”. The corners of this shaded area represent four mixtures whose compositions can be found in table 8.1.

II Sedimentary rocks (depository rocks)

Sedimentary rocks are produces by the weathering of preexisting rocks. In this way large deposits of unconsolidated particles (sediment) are

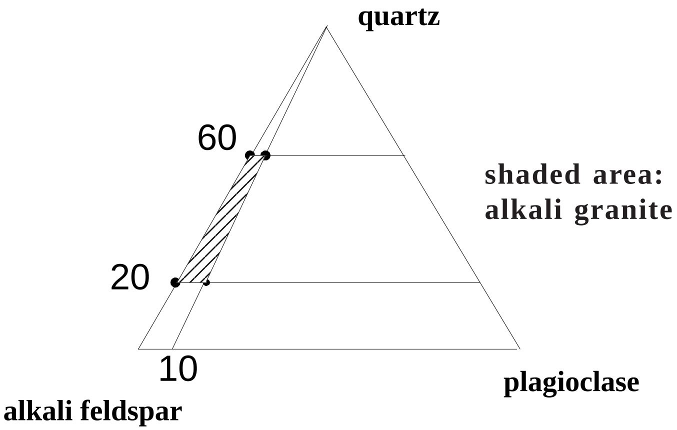


Fig. 8.2 Composition triangle of rocks containing the components quartz, alkali feldspar and plagioclase.

Table 8.1 Compositions of the systems which are represented by the four cornersof the shaded part in figure 8.2

mass% quartz	mass% alkali feldspar	mass% plagioclase
20	80	–
60	40	–
60	35	5
20	70	10

formed which are subsequently compacted to form larger units during diagenesis. With diagenesis we mean a sum of all processes like dissolving, precipitation and chemical reactions by which changes in a sediment are brought about after is deposition (i.e. particles stick together).

The clastic sedimentary rocks are the most common forms. They arise when an original rock wears down due to mechanical erosion and the weathering products are transported by gravity, mudflows, running water, glaciers and wind and eventually sorted by size deposited in various settings.

III Metamorphic rocks

Metamorphic variables result from the conversion of other rocks, which undergo a metamorphosis (see chapter 7).

8.3 THE FORMATION OF CLAY

Clay is an erosion product of igneous and sedimentary rocks. The weathering proceeds via mechanical and chemical processes. Its result depends on many factors, among which climate, vegetation and composition and texture of the rocks.

Mechanical erosion is influenced by temperature differences, plant roots, wind, water and glaciers. A well-known example is frost which not only affects nature but can also have annoying consequences inside, just think of frozen water pipes. In both cases the fact that water increases in volume when it freezes is the cause of all problems.

Chemical erosion on the other hand is a complex process which is influenced by many things, among which are the transport of – mostly dissolved – substances, the acidity of the water and the crystal structure of the minerals in the rocks. When dissolved in water, sulphuric acid and an acid produced by humus can cause a $pH < 7$. Sulphuric acid can arise from the oxidation of the mineral pyrite, FeS_2. Chemical erosion occurs according to the following fundamental reaction:

$$\textbf{primary minerals} + \textbf{supplied solution} \rightarrow \textbf{secondary minerals} + \textbf{drained solution}$$

Four kinds of chemical erosion exist; the ending “lysis” in the name means “separation”. The components of a rock are separated and new components can be formed.

1. *acidolysis*: under the influence of an acid. H_3O^+ ions play an important part in the erosion of minerals. Because of their minute dimensions they can easily penetrate a crystal lattice. In those cases a relatively large K^+ ion is replaced by a much smaller H_3O^+ ion, owing to which part of the stability of the lattice is lost and that is the start of the erosion process in an acid environment.

2. *salinolysis*: under the influence of a saline solution. This can apply to all possible salts.

3. *alkalinolysis*: under the influence of an alkalline solution.

4. *hydrolysis*: separation under the influence of water. This takes place when the water contains few ions and has a pH value of about 7.

Figure 8.3 is a simplified representation of how erosion in rock might take place. A mica is a clay mineral. The structure of this group of minerals will be discussed in paragraph 8.4 and is already partly discussed in the chapter about geology and mineralogy. At this moment the only thing which is important is the fact that the structure consists of one or more T(etrahedral) layers consisting of SiO_4 tetrahedrons and one or more O(ctahedral) layers, consisting of $Al(OH)_3$ octahedrons. Both in the T and in the O layers a number of central Si^{4+} or Al^{3+} respectively can be replaced by other cations. Between the layers water molecules and hydrated cations are present to compensate for the negative charge.

The erosion starts with the extraction of cations [1]. This involves the most mobile ions Na^+ and K^+ first and then in order the ions of

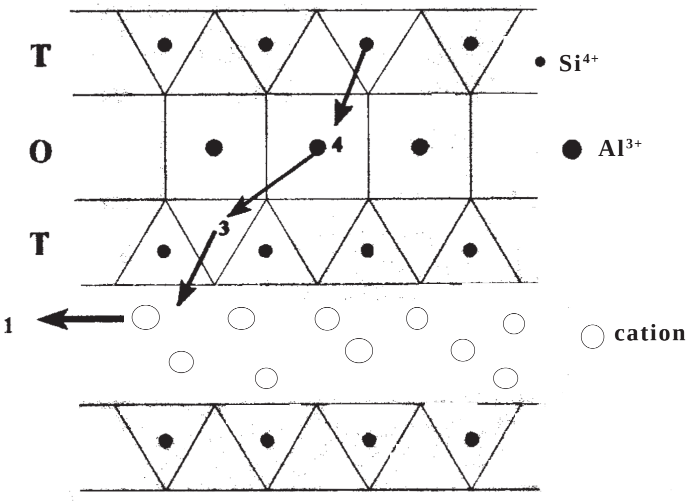


Fig. 8.3 Erosion of a mica. Source: Millot 1967).

Ca, Mg, Sr, Mn, Ni, Cu, Co, Fe, ……..Si, ……… and finally Al. In the intermediate layer a surplus of negative charge arises. This is compensated by cations of the O layer [2,3,4], initially Mg^{2+} and Fe^{2+}. The thus formed vacancy in the O layer is filled with a Si^{4+} from the T layer [4] or an Al^{3+} from the O layer. By now the disintegration has reached an advanced stage. An example of erosion in a chemical equation is the formation of the clay mineral kaolinite from orthoclase, an alkaline feldspar.

$$2K[AlSi_3O_8] + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2\,K^+ + 2\,OH^-$$

orthoclase kaolinite quartz potassium hydroxide in solution

Such a disintegration can only continue when there is an ample supply of water and when kaolinite, quartz and the potassium hydroxide solution are drained off. In such cases when the potassium hydroxide is not drained, the erosion mechanism follows a different path and the clay mineral illite is formed instead of kaolinite :

$$3K[AlSi_3O_8] + 2H_2O \rightarrow \underset{\text{illite}}{KAl_2(Al,Si_3)O_{10}(OH)_2} + 6SiO_2 + 2K^+ + 2OH^-$$

Under tropical circumstances, this erosion very often continues after kaolinite has been formed until boehmite [AlOOH] and possibly even gibbsite [$Al(OH)_3$] are produced. Both minerals are components of bauxite, the well-known aluminium ore.

At some moment in time the erosion can be interrupted by the transport of the partially weathered material. In such cases it is continued under different circumstances and this will result in other products.

It will be apparent from this paragraph that clay has a composition which is determined by numerous factors. In general you might say that there is a direct relationship between the lenght of time a material was exposed to weathering conditions and / or the distance over which it was transported and the complexity of its composition.

Experiment : It is possible to illustrate the erosion of a rock with a device which chemist use for the extraction of one or more substances from a mixture of solids: the so-called Soxhlet extractor.
(Source: Chemical Weathering of the Silicate Minerals, F.C. Loughnan, Elsevier)

The Soxhlet extractor (figure 8.4) is filled with fine grains of one of the two kinds of rock which are most common on the earth's surface, viz. basalt and granite. Next water is constantly passed through this rock mass and for a very long time. This results in a continuous extraction of materials from the rock; in other words: the rock is exposed to

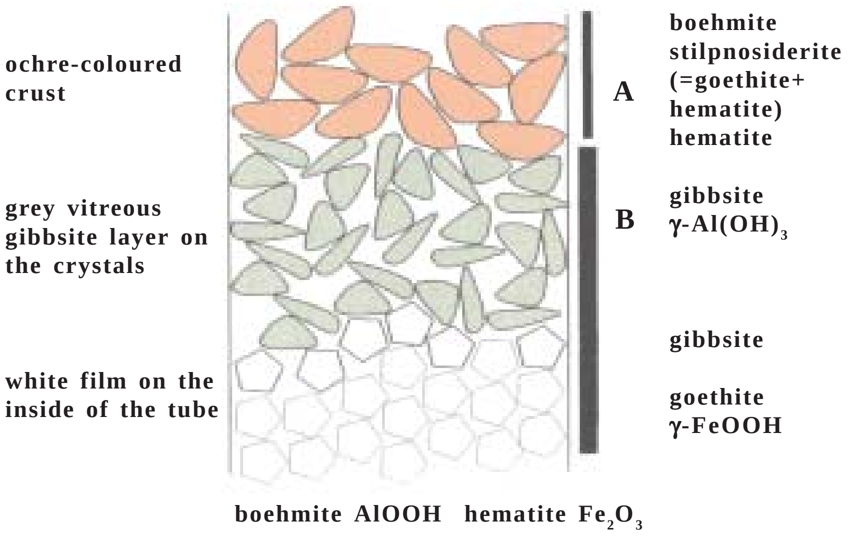


Fig. 8.4 Rock mass after extraction of a basalt.

weathering. Important parameter are the pH (acid rain!) and the oxygen and carbon dioxide content of the “rainwater”. When the water in the rock mass has reached a certain level, the surplus water will flow back to a reservoir. Make certain that the rock mass rises higher than the above-mentioned level! A part of the mass is periodically submerged. The flushed out (= extracted) elements and compounds end up in the water reservoir. At the end of the experiment you can determine the contents of the reservoir with the help of a series of chemical analysis.

Results of an experiment:

In one experiment *basalt* was used which contained the following materials (the minerals which were predominantly present are indicated with a *):

*	plagioclase	$(Na,K)[AlSi_3O_8]$
*	augite	$(Ca,Mg,Fe^{2+}, Fe^{3+}, Ti, Al)_2[(Si,Al)_2O_6]$
	hornblende	$(Na,K)Ca_2(Mg,Fe^{2+}, Fe^{3+}, Al)_5[(OH,F)_2/(Si,Al)_2Si_6O_{22}]$
	olivine	$(Mg,Fe)_2[SiO_4]$
	titanomagnetite	Fe_2TiO_4
	apatite	$Ca_5[(F,OH)/(PO_4)_3]$

When we call the rock mass through which the water perculates zone A and mass which is occasionally submerged zone B, then figure 8.4 represents the situation in the rock mass after the experiment has been completed (almost two years!)

8.4 THE COMPOSITION OF CLAY

The composition of clay is dependent on its “history”, i.e. the way it was formed and the events which took place afterwards. It is of vital importance for the composition of clay whether the clay was immediately deposited on the place where it was formed without having been altered under the influence of the environment or whether the clay was transported over a long distance. In this paragraph we will have a closer look at the composition of clay which is often quite complex and at how this composition can vary within a clay deposit.

The Dutch magazine KGK (Klei Glas Keramiek = Clay Glass Ceramics) reports the results of an extensive physical and chemical research of five clay deposits in the area between the rivers Rhine and river Meuse in the Netherlands. The chemical part involved both main and trace elements. The analysis of trace elements was carried out within the framework of an Act on the requirements for the environmental quality of soil materials in relation to, for example, the chemical composition of baked clay products. One of the things which have to be investigated in the baked product is the degree in which incorporated pollutions leach out (are extracted) under the influence of the weather, and especially under the influence of water. The analysis of one of the five deposits is represented in table 8.2.

Some of the mentioned trace elements have natural origins, others are the result of for example industries. The latter are only considered to be pollutants when their contents exceed a certain norm value. This subject is, however, beyond the scope of this book.

Table 8.2 requires some more details with regard to the main elements. In the field of ceramics it is customary to indicate these contents in the form of oxides. This might,however, imply that the clay is mainly built up of oxides and that is not correct. Chemists consider clay differently and would represent it composition as shown in table 8.3.

It should be born in mind that this is a overall clay composition. When we compare the representations of a clay composition in both tables, we notice that chemists apply the existing nomenclature rules (chapter 3, Chemistry). Furthermore the above represention proves that clay contains a number of silicate minerals. The structure of these silicate minerals and of quartz was already discussed in the chapter on Geology and Minerology. In the next paragraph we will concentrate on a certain group of silicates, the so-called clay minerals. Without these minerals clay would not possess its specific clay properties.

8.5 THE STRUCTURE OF CLAY MINERALS

We have already learnt that the building unit of the silicates is the SiO_4 pyramid. By linking these pyramids in various ways the different kinds of silicate anions are formed. The classification of the silicates is based on these kinds of ions. The silicate anions of clay minerals have a layered structure, the top view of which is again represented in figure 8.5.

The silicate “construction sheet” in figure 8.5 consists of tetrahedrons and is called *T-sheet.* Clay minerals also have a second building

Table 8.2 Analysis of a clay deposit

Unit of physical properties, 1st part of table: %(m/m) [unless specified differently]
Unit of analysis of main elements, 2nd part of table: %(m/m)
Unit of analysis of trace elements, 3rd part of table: mg/kg

depth of profile (m)	2.40
number of samples	21
course sand (>250 µm)	12.4
fine sand (63 × 250 µm)	12.6
loam (<10 µm)	44.0
humus	1.0
specific area	96 m^2/g
specific area (<10 µm)	44.0
SiO_2	73.0
TiO_2	0.71
Al_2O_3	10.1
Fe_2O_3	4.82
MnO	0.17
MgO	0.79
CaO (total)	0.55
CaO (carbonate)	0.5
Na_2O	0.36
K_2O	1.92
P_2O_5	0.12
loss on ignition	4.76
Barium (Ba)	301
Cobalt (Co)	<10
Chromium (Cr)	62
Copper (Cu)	<10

Gallium (Ga)	11
Lanthanum (La)	31
Niobium (NB)	26
Nickel (Ni)	39
Lead (Pb)	56
Rubidium (Rb)	90
Strontium (Sr)	69
Vanadium (V)	76
Zinc (Zn)	116
Zirconium (Zr)	368

stone which is built up of octahedrons of the mineral gibbsite [$Al(OH)_3$] or of brucite [$Mg(OH)_2$]. This is called the *O-sheet*. Figure 8.6 shows part of a gibbsite sheet.

In figure 8.6 every octahedron shares the four OH^--ions in the sheet with four neighbouring octahedrons, i.e. 1/4 of each of those four ions belongs to the octahedron. The OH^--ions above and below the Al^{3+}-ion fully belong to the octahedron. The formula of an octahedral unit in the sheet is thus $Al^{3+} + 4 \times 1/4\ OH^- + 2 \times OH^- = Al(OH)_3$. Now that we have been introduced to the O and T sheets, the next step is to link these sheets and in this way form clay minerals. This process in represented in figure 8.7.

For clarity's sake only one tetrahedron of the T sheet and one octahedron of the O sheet have been drawn in figure 8.7 and the charges of the ions are not indicated. During the linking an octahedron will release an OH^--ion. In this way the formula of the octahedron becomes:

$$Al(OH)_3 \quad - \quad 1\ OH^- \quad \rightarrow \quad Al(OH)_2^+$$

The formula of the tetrahedral sheet is $Si_4O_{10}^{4-}$

(Note that four tetrahedrons are represented in this formula)

In order to form a neutral entity four octahedrons must link with four tetrahedrons:

Table 8.3 Overall composition of clay

- organic material (humus)	0.5–2.5 % (m/m)		
- clay minerals (a certain group of silicate minerals)	15–100		
- quartz, tridymite and cristobalite	40–70		
- feldspars, amphiboles and other non-clay silicates	1–9		
- iron oxides and hydroxides:			
hematite	α-Fe_2O_3	maghemite	γ-Fe_2O_3
goethite	α-$Fe_2O_3.H_2O$	lepidocrocite	γ-$FeOOH$
magnetite	Fe_3O_4	hercynite	$FeO.Al_2O_3$
- aluminium oxide and hydroxide			
gibbsite	γ-$Al(OH)_3$	boehmite	γ-$AlOOH$
- water			
- other compounds			
- salts: among which	Na_2SO_4,NaCl, $MgSO_4$, $MgCO_3$ (magnesite), $MgCa(CO_3)_2$ (dolomite), $CaSO_4$, $CaCO_3$ (calcite and aragonite), calcium silicates, $BaSO_4$ (rare), FeS, FeS_2, $FeSO_3$, $FeCO_3$, Fe(II)/Al silicates and iron(II) silicates, rare strontium minerals, zeolites (certain group of silicates, which are not clay minerals)		
- oxides: among which	titanium minerals (rutile, anatase and brookite, all having the formula TiO_2)		

$$4\ Al(OH)_2^{+} + Si_4O_{10}^{4-} \rightarrow Al_4[(OH)_8 / Si_4O_{10}]$$

clay mineral kaolinite

This linking of one T and one O sheet to form a TO layer is the simplest way to produce a clay mineral. A crystal of kaolinite consists of extremely many of those TO layers. Between the TO layers no ordinary chemical bond exists. Water molucules and hydrated ions can be found there. These water molecules are bound to the TO layer by means of an ion dipole bond and the water molecules themselves are interlinked by means of H bridges. This collection of physical bonds keeps the TO sheets together. The different kinds of kaolinite which are found in nature exhibit different packings of the TO layers with respect to each other: directly above each other or shifted in position.

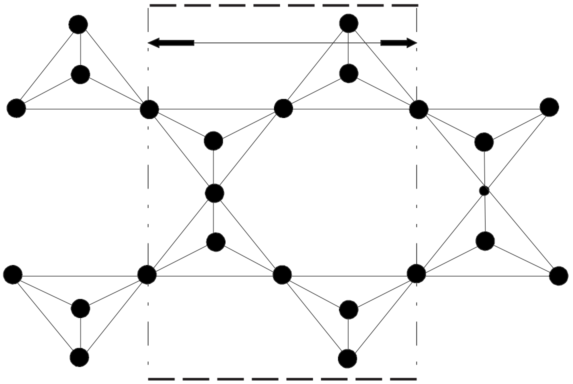


Fig. 8.5 The structure of a silicate ion in a clay mineral.

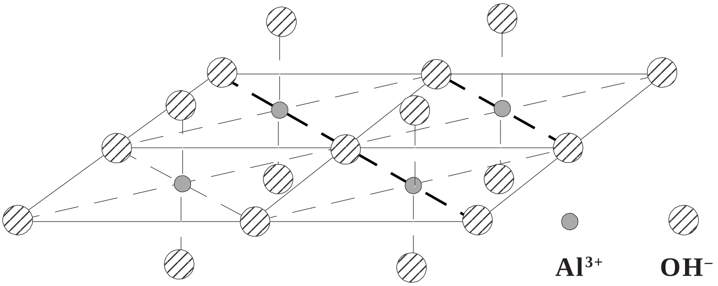


Fig.8.6 Part of a gibbsite sheet.

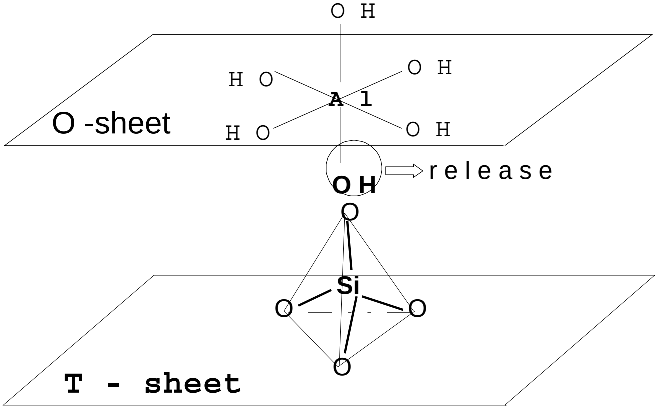


Fig. 8.7 The linking of an O- and a T-sheet.

When we use the basic structure of a clay mineral (the T and the O layer) as a starting point, the other clay minerals can be described in a simplified manner as follows:

1. An O layer can be "wrapped up" between two T layers.
2. T and O layers can be stacked in various ways, e.g. : TO..TO..TO.. in for example kaolinite; TOT..TOT..TOT.. in for example illite and montmorillonite.
3. The O layer can also contain Mg^{2+} or Fe^{2+} apart from Al^{3+}. In that case there is a shortage of positive charges which is compensated by taking up positive ions from the weathering process or during the transport in between the layers.
4. A number of Si^{4+} ions in the T layer can have been replaced by Al^{3+}. Again, there is a shortage of positive charges which is compensated in the same way as described in 3.
5. In most cases water molecules and ions occur between the layers. Especially the water is responsible for the elastic behaviour of a clay type.
6. There are clay minerals which only contain T sheets, e.g. chrysotile: $Mg_3[Si_2O_5 / (OH)_4]$
7. Some clay minerals exist which contain layers of different, stacked clay minerals, e.g. some layers of illite, alternated by some layers of montmorillonite.

An example of another clay mineral is montmorillonite with the chemical formula $MgNaAl_5(Si_4O_{10})_3(OH)_6$ which is represented very schematically in figure 8.8. Of the T sheets only the top of one pyramid is included and of the O sheets two OH groups of one octahedron. In addition the charges of the ions are not given.

In the O sheet of the montmorillonite an Al^{3+} ion of each six aluminium ions has been replaced by a Mg^{2+} ion. The shortage of one positive charge which is thus created is compensated by the sodium ion between the top two sheets. By adding up the formulas of the four sheets you can obtain the formula of montmorillonite.

8.6 TYPES OF CLAY

It is customary in the natural sciences to make classifications. Clays can be classified according to the geological period in which they were formed or according to properties such as texture, colour after baking, plasticity and rheology. When we consider the geology of The Netherlands for instance, we can distinguish four periods during which clay was formed and deposited.

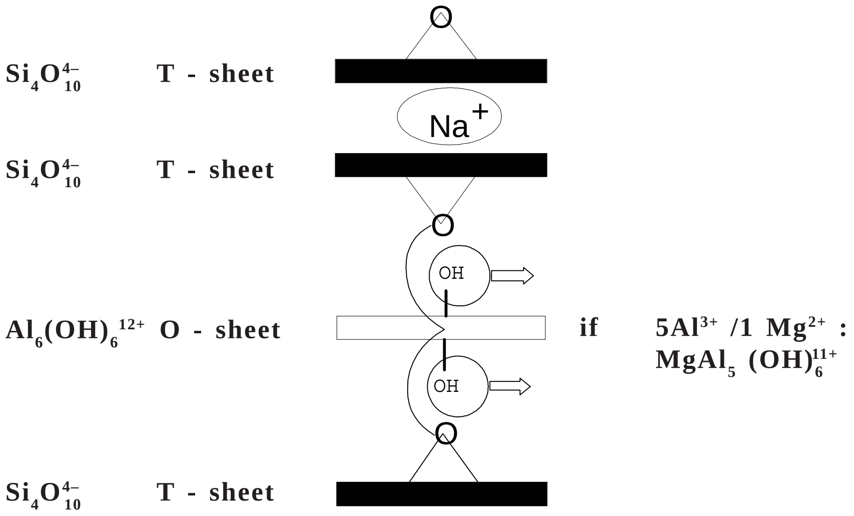


Fig. 8.8 Structure of the clay mineral montmorillonite.

It is important to realise that clay can be exposed to many processes after it has been depos-ited. The periods are the Miocene Epoch (26 - 7 million years old), the Pliocene Epoch (7–2 millions years old), the Pleistocene Epoch (2 million to 15,000 years old) and the Holocene Epoch (up to approximately 15,000 years old). In The Netherlands no primary clay deposits are found, i.e. all clay is secondary, i.e. formed elsewhere and transported by wind, ice or water.

Before elaborating on the different types of clay, it is important to clearly define the terms *clay* and *clay body*. A clay is a material with plastic properties, formed by natural forces and found in nature. Some examples are:

– primary kaolin or china clay: is found at the formation site and consequently extremely pure. Kaolin is named after a hill in China (K'ao-ling = high hill), the place where it was first mined. The clay has hardly been exposed to erosion and as a result its particles are relatively large and the clay is less plastic. It is mainly used for the production of expensive porcelain.

– secondary kaolin: is also called sedimented kaolin. This clay is somewhat less pure and a little more yellow than the primary type. All of this is the result of the fact that it has been transported. In addition, the particles are smaller and the clay is consequently more plastic.

– ball clay: is transported by water. It contains carbonate-like materials which often give it a grey or brown colour, whereas its baking colour is offwhite. Its particles are minute and as a result it is extremely plastic and exhibits the largest shrinkage of all clay types. A long time ago this clay was deposited together with layers of organic material which were later mined as coal. The name “ball clay” originates from the mines where the clay was removed from the coal deposits by rolling it into balls which were subsequently carried out of the mines by pack animals or in mine cars.

– fire clay: is transported by erosion and wind and redeposited. It contains metal oxides and free quartz due to which it can have different colours after baking. Fire clay is quite abundant, especially in mountains and deserts.

– stoneware clays: lie between ball clay and fire clay as far as texture, plasticity, colour, shrinkage and baking temperature ranges are concerned. It is quite rare in nature.

A *clay mass* is a mixture of clay and additives for a specific ceramic (processing) technique. The clay provides the plastic properties. Possible additives are a flux and a filler. Some examples of fluxes are potassium feldspar, bone meal, volcanic ashes and ground glass, all of which serve to affect the density and decrease the melting range. Fillers reduce the shrinkage as well as the sticky character of the clay.

8.7 THE MINING OF CLAY

It is possible that the mother rock is still present in places where clay is mined. This is for instance the case in Cornwall, Great Britain where clay was formed out of granite. Here clay is mined by means of high-pressure spraying pistols. This method results in a lot of slurry which is first segregated or subjected to a hydrocyclone treatment in order to separate quartz and feldspar.

In The Netherlands clay is supplied by rivers and the sea. Clay is deposited due the sedimentation of particles. The sedimentation rate depends on the mass of a particle. Consequently bigger particles already sink to the bottom in the lower reaches of a river. The smallest particles reach the sea. Sea clay is usually fat as a result. Older clay layers are often covered by sand.

Conditions for a viable mining of clay:

– Is the clay composition within a certain range? A clay whose composition deviates only little from the desired composition, i.e. the clay with the desired properties can be made suitable for production purposes by mixing it with a different clay type and / or other additives.

- It must be possible to mine clay in an economically sound way.
- The mining site should preferably be near the factory.

When a clay site is investigated, drills are carried out. Figure 8.9 is an example of a so-called drilling map, a map on which the drills spots in a certain area are indicated together with the analyses of the drilling samples in question.

On every sample six standard analyses are carried out: mass % coarse sand (> 250 µm), fine sand (63–250 µm) and loam (< 10 µm), iron (III) oxide, calcium oxide and humus. Based on the results of these analyses the expert can, among other things, draw conclusions concerning the suitability of the clay for moulding and its behaviour during drying and baking, the baking colour, which, as we already saw, is mainly determined by the ratio of the mass percentages of iron and calcium ions.

After the decision to mine a clay site has been made, a mining plan is set up. This is based on the analyses of the drilling samples. Because clay is geologically seen deposited in more or less horizontal layers, it is mined in thin, vertical layers. In this way an average clay composition is obtained. The top layer can contain a lot of plant remains and is therefore often dug up and stored separately. After the clay has been mined this soil can be used to cover the site and recultivate the area.

The clay is stored after mining. This storage is part of the pretreatment of the raw materials. Because clay is deposited in layers

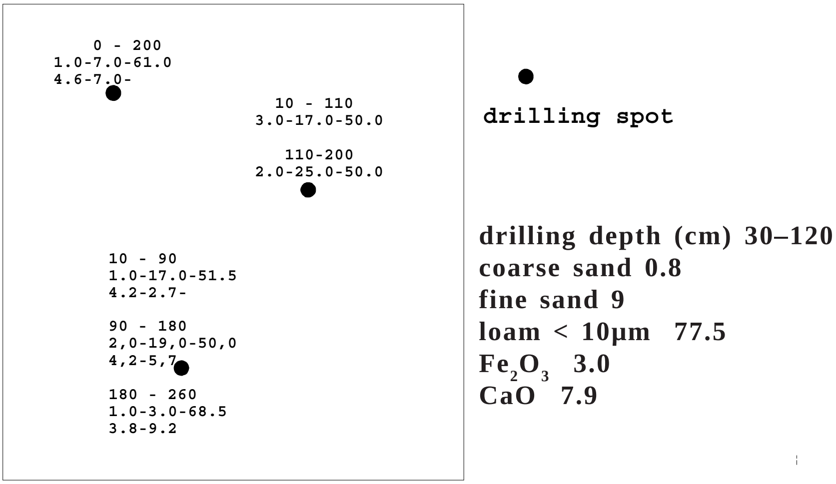


Fig. 8.9 An example of a so-called drilling map of a clay site.

and then mined vertically, it is mixed. During the storage plant remains will be digested by bacteria and this improves the clay quality. It is vital that the clay supply does not dehydrate, yet it should also not absorb too much water. For those reasons some clays are stored indoors.

In 1999 I visited the Westerwald, an area in Germany with approximately 25 clay quarries, which is discussed in chapter 12. In one of these quarries I received documentation on analysis data of 28 different clay types which can be supplied. In the table below the analyses of three of those types are presented to give you an impression of the large variety in composition and properties.

8.8 PROPERTIES AND ANALYSIS OF CLAY

In natural sciences, analytical methods are constantly developed which are based on the properties of substances. That is why both these subjects are treated in one paragraph. Analytical methods indicated with a *-sign are also discussed in chapter 13.

1. Colour before and after baking

Natural clays are coloured due to pollutions of the clay minerals. After baking the colour is strongly affected by the Ca/Fe ratio. When the baking colour is not white, this is caused by metal ions with d-valence electrons (see “glazings” in the paragraph Fine ceramics and “baking colour” in the paragraph Coarse ceramics).

2. Morphology or crystal form and crystal structure

Scanning Electron Microscopy (SEM) is a very suitable technique to study the morphology, the microstructure of solid objects. A resolution of about 1 nm is possible and this value almost equals the binding distance between atoms. Another advantage is the 3D image. Transmission Electron Microscopy (TEM) can also obtain extremely high resolutions and can supply images of lattice defects, crystalline phases, glass phases, grain boundaries, etc.

**3. Water absorption*

The water absorption of a clay can be measured by means of a certain grain fraction from the grain size distribution of a clay which has been dried for some hours at e.g. 50 °C. Fill a measuring cylinder to a specific level and add drops of a known quantity of water to the clay. Measure the rise of the clay level.

Qualities		**5123**	**5167**	**5199**
chemical analysis, calcined [%]				
SiO_2		58.70	74.64	90.63
Al_2O_3		33.00	17.55	7.30
TiO_2		1.48	1.35	0.81
Fe_2O_3		1.78	4.25	0.40
CaO		0.47	0.18	0.12
MgO		0.66	0.30	0.10
Na_2O		0.28	0.08	0.00
K_2O		3.66	1.60	0.32
Loss on ignition [%]		10.12	5.30	2.96
Whole carbon [%]		2.50	0.05	0.00
Fired colour 1200°C		light cream	light red	white
Particle size distribution [%]				
	> 200 µ	1.30	1.80	4.00
	> 63 µ	2.50	6.10	27.75
	< 1 µ	70.00	49.00	14.00
Firing shrinkage [%]				
	1050°C	7.70	1.87	0.00
	1200°C	11.30	5.01	0.96
Water absorption [%]				
	1050°C	7.80	13.98	15.00
	1200°C	0.20	6.35	12.90
Dry bending strength [N/mm²]		7.50	3.42	1.60

*4. Plasticity

With plasticity we mean the property of a substance to react to the influence of an external force with a lasting change in shape but without exhibiting cracks. This property is mainly caused by the sheet-like structure of the clay minerals as well as by the water which is both physically and chemically bound to these sheets. The sheets slide over each other. Furthermore plasticity is affected by particle size, water content, specific area (SA : m^2/gram). The surface charge of the clay particles and the presence of humus acids appear to increase the plasticity. In the chapter Ceramics in general / shaping, the plasticity measurement according to Pfefferkorn is discussed. A second method is the one according to Rieke. The plasticity number according to Rieke is the difference between the water content at the stick value and on the other side at the roll out value. An example of a calculation:

– the stick value indicates the water content at which the mass no longer sticks to the hands

mass at stick value	130 g
mass after drying	98 g
mass of water	32 g of 98 g = 33 %

– to determine the roll out value a clay mass is rolled out on a plaster plate until it begins to crack (the mass is dehydrated)

mass at roll out value	218 g
mass after drying	190 g
mass of water	28 g of 190 g = 15 %

Plasticity number according to Rieke = 33 - 15 = 18

*5. Grain size distribution

The simplest way to determine the grain size distribution is with the help of the sieve tower. This method is decribed in the chapter “Ceramic in general / mass preparation”.

6. Mineralogy

As we have already seen clay usually contains minerals like quartz, feldspars, calcite, dolomite et cetera. Especially the quartz determination is of importance in relation to the so-called quartz jump. During the firing process the quartz which is present can transform to a different crystal structure (modification) with a smaller density. Due to the resulting expansion the ceramic object can crack. The minerals are mostly determined by means of X-ray diffraction, a technique which is too complicated to be discussed within the framework of this book.

7. Drying behaviour

When drying a piece of shaped ceramics the ceramicist always takes the water content of the mass into account. In this way cracking owing to the formation of water vapour can be avoided. Extremely finely grained, and consequently plastic, clay is especially characterized by a high specific area and for that reason contains a lot of water. Cracks can also be avoided by adding sand and feldspar which will lead to more pores. An additional advantage of feldspar here is that it provides extra densification during the firing process. The various clay minerals exhibit large differences in drying behaviour, consequently research into this is necessary. Drying should take place gradually and slowly (see also the chapter Ceramics in general / heat treatment).

8. Texture

This property has been discussed elaborately in this chapter.

9. Rheology

See the chapters “Colloid chemistry” and “Ceramics in general / shaping”.

10. Firing behaviour

Firing behaviour is extremely clay specific and depends e.g. on the presence of quartz. The firing needs to take place carefully because volatile substances will evaporate. Shrinkage is * measured with a dilatometer, but also by means of techniques like DTA and TGA.

**11. Chemical composition*

**12. Adsorption and specific area*

9

Ceramics in General

9.1 INTRODUCTION

This chapter deals with the process from raw materials to finished products. In principle, this process is roughly the same for all ceramic branches of industry and we can distinguish five phases:

- choice of the right raw materials
- preparation of the raw material mass
- moulding
- heat treatment
- final treatment of the product

In every phase, the ceramicist can make a selection from the various treatments and techniques available. The total set of treatments and techniques eventually determines the properties of the product and consequently its applications. For that reason the ceramic industry is divided into seven branches of industry which will be discussed individually in chapter 11.

9.2 RAW MATERIALS

Clay

That clay is an extremely important raw material will be clear from the fact that chapter 8 is entirely devoted to it. This chapter explains how clay is formed in nature, which composition it has, the structure of important clay minerals and the properties of clay. One property is highlighted here and that is the very varied composition of clay and the relatively large number of substances – apart from the clay minerals – which are present in clay. For most products made of clay the complex composition of this clay poses no problems in the production process nor for the final product properties. In this respect, these clay products differ substantially from ceramic objects which are not made of clay. For the latter extremely pure raw materials are required.

Synthetic raw materials

In technical ceramics, also called non-clay ceramics, mainly synthetic raw materials are used. Sometimes these are complemented with clay or some naturally occurring silicates provided that these can be mined in an extremely pure form or can be purified simply and cheaply. Silicates can also be made synthetically by melting a mixture of oxides.

Synthetic materials are used for two reasons. First it is possible that the substance does not occur in nature with the desired properties, e.g. with the correct purity and/or grain size. Second some ceramic products require substances which do not occur in nature at all. Table 9.1 lists some commonly used synthetic raw materials.

As appears from the table, "exotic elements", i.e. uncommon elements are also used, e.g. Y (yttrium), Th (thorium), U (uranium) and Eu (europium). We already learnt in chapter 3 that the most electron-

Table 9.1 Some commonly used synthetic, ceramic raw materials

kind of raw material	examples
oxide	$Al_2O_{3,}$ ZrO_2 TiO_2 SiO_2 CaO BeO MgO B_2O_3 CrO_3 Y_2O_3 ThO_2 FeO
boride	TiB_2 ZrB_2 CaB_6 ZrB_{12} HfB_2 VB_2 TaB_2 MoB_2 W_2B_5 UB_4 EuB_6 LaB_6
nitrides	Si_3N_4 BN TiN AlN
carbides	SiC B_4C TiC
titanates	Al_2TiO_5 $MgTiO_3$ $CaTiO_3$ $BaTiO_3$ $PbTiO_3$
hydroxylapatite	$Ca_{10}(PO_4)_6(OH)_2$
silicates	forsterite $Mg[SiO_4]$ steatite $Mg_3[(OH)_2/Si_4O_{10}]$ cordierite $Mg_2A1[AlSi_5O_{18}]$
ferrites	collective for a large group of ferromagnetic oxidic materials, consisting of sintered mixtures of oxides of bivalent metals, especially Cu, Mg, Mn, Fe and Zn with iron (III) oxide

egative element is placed to the right in the formula of ionic and covalent compounds and is mentioned last in the name. The names oxide, boride, nitride and carbide are based on this rule. In chemistry the formula of a titanate is described as in the table. The compound is considered to be a salt which is built up of a metal ion and an acid rest. For instance: magnesium titanate is built up of Mg^{2+} and TiO_3^{2-}. The ceramicist bases the notation on the use of oxides and writes down the compound as $MgO.TiO_2$, a mixed oxide.

Some syntheses

Raw materials for ceramics are synthesized in many different ways. The way they are made will have affect their main properties, such as the particle size and the crystal structure. Some examples:

1. In nature aluminium oxide is mostly mined as the minerals bauxite and laterite, but these as extremely impure. Most bauxite is purified according to the Bayer process which removes the oxides of iron(III), silica and titanium. This takes place by autoclaving the bauxite with sodium hydroxide and sodium carbonate. The precipitated aluminium hydroxide is subsequently heated, or calcined. Calcination involves a heat treatment of a powder as a result of which the latter breaks down:

$$2\ Al(OH)_3 \xrightarrow{400\text{–}500\ ^oC} \gamma\text{-}Al_2O_3 + 3\ H_2O$$

2. Silicon nitride can be formed in the gaseous phase:

$$3\ SiCl_{4\ (g)} + 4\ NH_{3\ (g)} \rightarrow Si_3N_{4\ (s)} + 12\ HCl_{(g)}$$

3. Silicon carbide is prepared by heating a mixture of quartz sand and anthracite coal for several hours at approx. 2250 °C (figure 9.1):

$$SiO_{2\ (s)} + C_{(s)} \xrightarrow{\text{appr. } 2250\ ^oC} SiC_{\ (s)} + 2\ CO_{(g)}$$

As can be seen in figure 9.1 the reaction mixture is covered up to intercept and remove the formed carbon monoxide. Carbon monoxide is combustible and consequently can be used as a fuel. The produced SiC is extremely hard and we distinguish two qualities: i.e. a) hexagonal SiC, which is used as an abrasive and is a raw material in the ceramic industry and b) cubic ß-SiC, which is used as a deoxidator and carbon supplier in the cast iron and steel industry. When the reaction

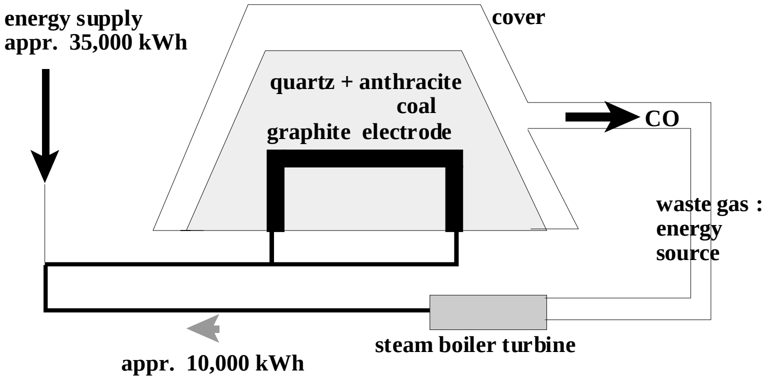


Fig.9.1 Synthesis of silicon carbide.

mixture is uncovered after the production process has been completed, the mass is dug up. Employees often find beautiful crystals then which are sometimes sold at mineral fairs. Of course expert collectors know that these are not real minerals, but will sometimes still buy them because they are so beautiful.

9.3 MASS PREPARATION

Before a mass of raw materials can be given a certain form, it must be subjected to certain pretreatments. We distinguish three groups of treatments, not necessarily in this order: a) treatments to alter the grain size and sometimes even the grain form, b) mixing of raw material components, possibly followed by drying them and c) producing one or more fractions with certain grain diameters from the raw material mass.

Grain size

Small to minute particles are needed to manufacture ceramic objects, especially for technical ceramics applications. There are two reasons for this: a) the raw material mass must be mixed with water and usually also with binding agents for the heat treatment. This mixing can only be optimal when the particles are small. b) during the last stage of the heat treatment, the sintering process (i.e. baking at high temperatures) it is better that the particles exhibit maximal surface contact for them to adhere to their neighbouring particles, obviously this is achieved when there are many minute particles present.

Altering the grain size mostly amounts to reduction and is accompanied by changes in the grain size distribution and the specific surface. This specific surface is a major ceramic property of raw materials

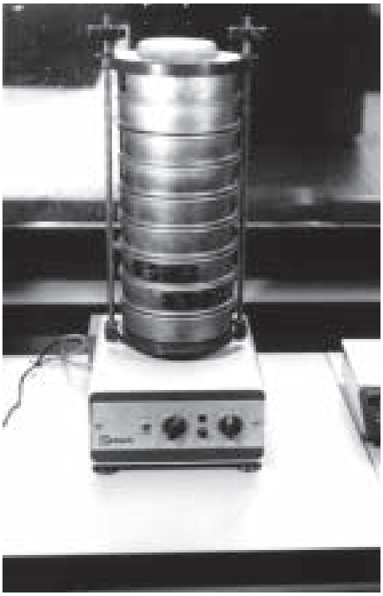


Fig. 9.2 Sieve tower (Retsch) (by Bovendorp, Sendon Van de Weerdt).

and is expressed in m^2/g. It goes without saying that when the grains are reduced in size, the area increases, as does the specific surface, whereas the mass remains the same.

With “grain size distribution” we mean the “number of grains” plotted in a graph as a function of the grain diameter. Obviously the grains are not counted. In a simple determination a certain mass is led through a number of sieves and then the contents of every sieve are weighed. So not the number of grains is plotted, but the mass of a portion of grains, expressed in a mass % of the total mass sieved.

In a laboratory the distribution is determined in a sieve shaker (figure 9.2). This consists of a number of stacked sieves and a container at the bottom. The sieves are mounted on a shaking device and the shaking time and frequency can be adjusted.

The top sieve has the largest and the bottom one the smallest holes. After a certain sieving time the contents of each sieve and the container are weighed and the mass as a percentage of the total mass as well as the grain diameter are plotted out graphically. This can take place in two ways, i.e. separately and cumulatively. In table 9.2 the weighing results of a sieving analysis are mentioned. Separately means that the mass per sieve is plotted as a function of the grain diameter. The cumulative mass % is the percentage of the total mass with a diameter smaller than the value mentioned.

Table 9.2 Results of a sieving analysis. Leeuwenborghclay Ltd. Sittard Laboratory for materials technology, 15 May 1992; Material: Clay from Overveen, sample no. 18b

sieve no.	diameter sieve pore (mµ)	separate mass %	fraction smaller than:	cumulative mass (g)
container		0.00	63 µm	0.00
1	63	1.50	90	1.50
2	90	6.26	125	7.76
3	125	10.41	125	7.76
4	180	50.20	250	68.37
5	250	20.59	355	88.96
6	355	7.61	500	96.57
7	500	2.10	710	98.67
8	710	1.33	1000	100.0
9	1000	0.00		

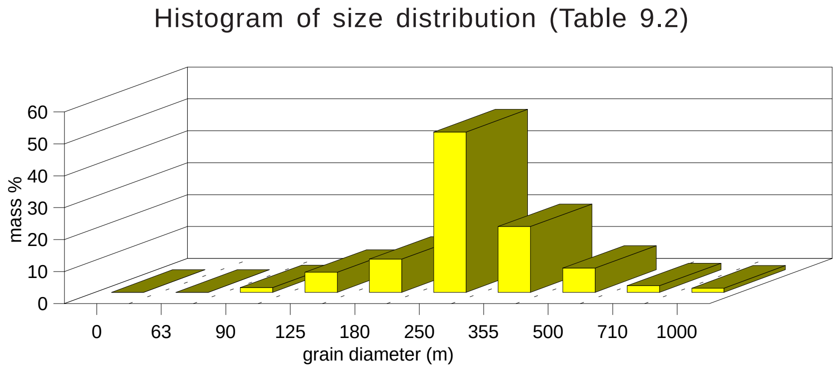


Fig.9.3 Histogram of a grain size distribution.

In figure 9.3 the results of table 9.2 are plotted as a histogram, i.e. the diameter of the sieve pore against the separate mass percentage.

In figure 9.4 the grain size distribution of table 9.2 is plotted cumulatively.

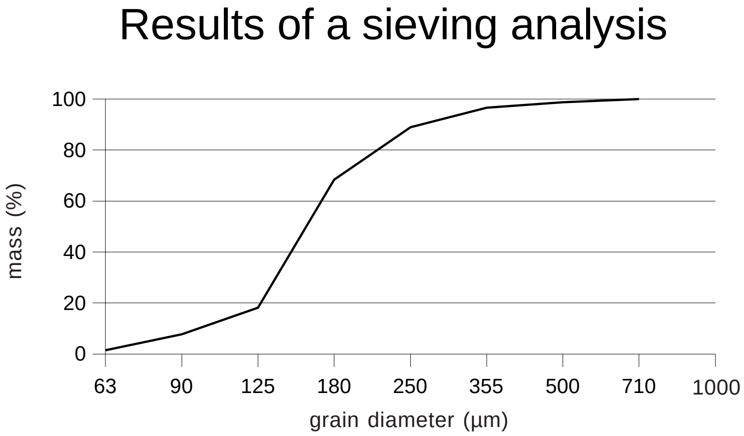


Fig.9.4 Results of sieving analysis.

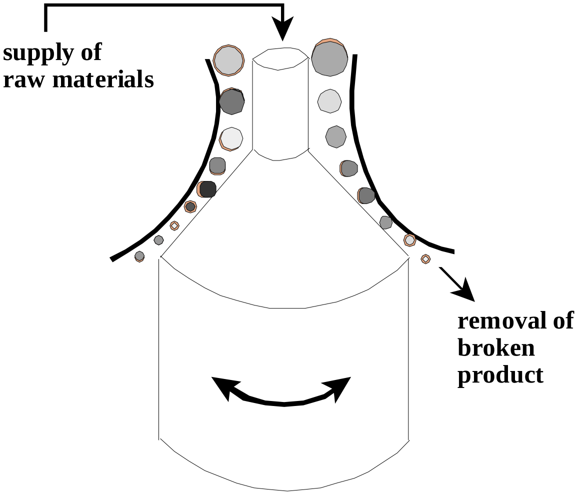


Fig. 9.5 Conical crusher.

Crushing

When the raw material is supplied in large fragments, these will first have to be crushed. In general hammers are used for this or the material is compressed. Two devices applied here are: the conical crusher (figure 9.5) and the prall mill.

Crushing is mainly applied for clay ceramics, e.g. in the case of chamotte, a baked clay which is sometimes added as a powder to unbaked clay in the manufacture of e.g. bricks. This is done to increase the dimensional stability during the baking process.

Grinding and mixing

During the grinding process the grains are reduced to specified values. The progress of the grinding process can be closely monitored by taking samples and carrying out sieving analyses at regular intervals. Grinding can be done wet or dry. A kollergang or a mill filled with ceramic balls made of aluminium oxide (figure 9.6) can be applied. A kollergang is built up of a round sieve on top of which two heavy wheels turn. When the material is poured onto the sieve, it is mixed by the wheels and also pressed through the sieve. It leaves the sieve shaped like sausages.

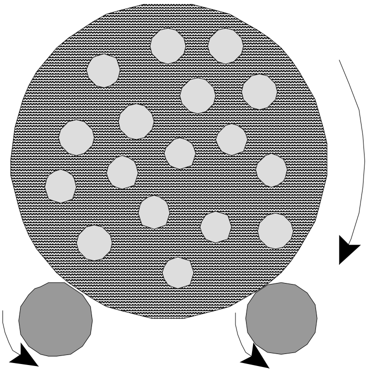


Fig. 9.6 Mill with ceramic balls.

In the case of crushing and grinding the grain shape is determined by the degree in which the material can be cleaved which usually occurs according to certain crystal planes. After a grinding process not all particles have the same grain size, but there is question of a grain size distribution which strongly affects the properties of the ceramic product. When the particle size is less than 5 m, the particles exhibit a relatively large tendency to agglomerate. An agglomeration has a porous structure which can easily be moistened by a liquid. The particles will immediately be dispersed throughout that liquid. When there is a tendency to agglomerate, it is advisable to grind wet. Very often this is done in a mill with ceramic balls and takes place in the presence of dispersing substances, also called deflocculants (figure 9.6)

The mass to be ground in placed in a porcelain container with grinding spheres which in its turn is situated on top of two rotating axes. The grinding spheres come in different sizes and degrees of hardness. Naturally the spheres must be harder than the the crystals of the mass. The result of the grain size distribution after the grinding depends on the diameter of the container, the amount of mass and the number of spheres (i.e. how much of the volume of the container is taken up by the spheres and how much by the mass), the diameter and the hardness of the spheres, the diameter and hardness of the crystals in the mass and the grinding time.

Granulating

Many dry-ground raw materials have a relatively low bulk mass, which means that a relatively small mass per volume unit is needed in a mould. When a powder is compressed into a mould, the highest possible bulk mass is required because then objects with the highest possible densities can be made. For this reason the powder mixture is made more compact, or in other words is granulated. The grainy mass is poured onto a slanting and rotating dish and at the same time a binding agent (e.g. water) is sprayed on the dish. Among other things the grain size is determined by the dish size, the rotating speed and the gradient of the dish.

Mixing

When the raw materials are mixed, it is important to try to produce a mixture with the highest possible homogeneity, because this will affect the subsequent moulding and heat treatment. Dependent on the nature of the mixture (dry, wet or plastic), many kinds of mixing techniques are available. It should be pointed out, however, that with some of the techniques discussed in the previous paragraphs mixing is also possible.

Separation into fractions

Sometimes it is necessary to separate particles with a certain grain size distribution from the raw material components or from the total raw material mass before mass preparation or the moulding can begin. This can for instance be done with sieves, spray driers and wind sievers. In figures 9.7 and 9.8 the latter two devices are shown.

In a spray drier the raw material slurry is nebulized. Hot air is blown into the spray drier tower In the opposite direction. The moisture from the droplets of the nebulized slurry evaporates and the product of this drying process, the spray dry granulate, consists of little soft balls of nearly equal size. Together with the air, granulate can also be drained off. After that it is intercepted in a so-called cyclone separator.

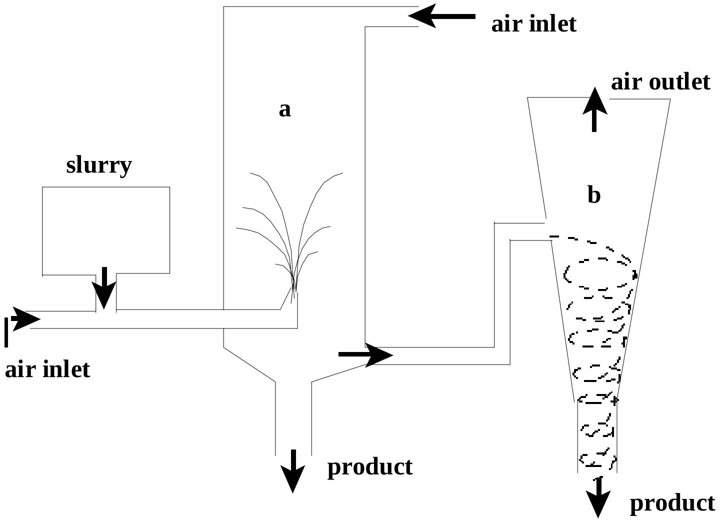


Fig.9.7 Spray drier (a) and cyclone separator (b).

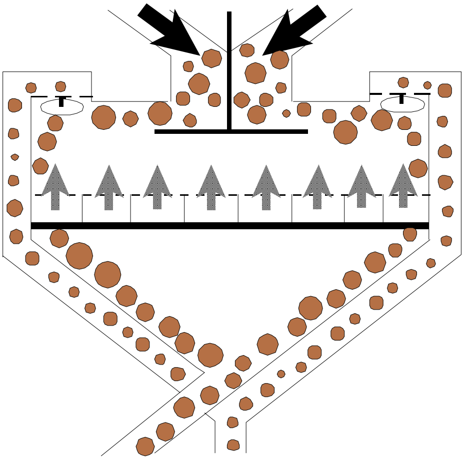


Fig. 9.8 Wind siever.

In a wind siever a powder with a large grain size distribution is introduced at the top and then falls onto a rotating disk . When the grains fall off the disk, they are swept away by an upward flow of air. The lighter particles are blown upwards and removed through two rotating blades in the left and right top corners. By adjusting the wind velocity a fraction with a narrow grain size distribution can be removed along the outer wall.

9.4 MOULDING

9.4.1 Kinds of moulding

The nature of the raw material mass to a large extent determines the way it is moulded. We distinguish the folling kinds of moulding:

- Plastic moulding
- Compressing of powder
- Moulding suspension
- Other moulding methods

9.4.2. Plastic moulding

We call a mass plastic when it undergoes a change in form under the influence of sometimes slight forces but without exhibiting cracks. Plasticity is affected by the following properties of the raw materials: the water content, the electrical charge on the particles, the size and shape of the particles and the organic components. Water can form plastic mixtures together with clay and clay minerals, but with hardly any other solid. The raw materials used for technical ceramics are not plastic at all. So in order to be able to apply plastic moulding techniques, large amounts (20–50 % v/v) of organic binding agents are added to the raw material mass. This has one major disadvantage: these binding agents must be removed during the heat treatment. This is extremely time-consuming and can give rise to many faults in the product, but more about this in the paragraph on “heat treatment”.

The reason why clay exhibits plastic behaviour can be found in the packing of clay sheets with water molecules and hydrated ions in between. At the surface of such a clay sheet the water molecules are tightly bound by means of H-bridges between the water molecules and the surface charge of the sheet. Further away from the sheet the water molecules are interconnected by means of H-bridges but these forces are weaker and consequently those water molecules can move more easily than the ones which are bound to the clay sheet. In that movement both the loose water molecules and the hydrated ions act as a “lubricant” between the sheets and can move parallelly in relation to each other: the plastic behaviour (figure 9.9).

Clay mostly already contains organic components which affect the plasticity in a positive way. The fine ceramics industry makes use of this fact in order to make masses more plastic, especially in the manufacture of thin-walled articles.

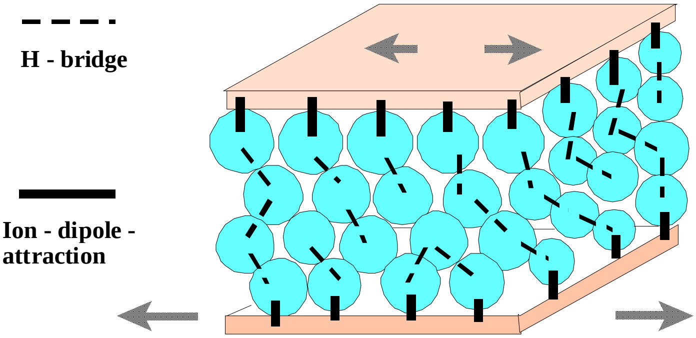


Fig. 9.9 The plastic behaviour of clay.

Measuring plasticity

Plasticity is measured in several ways. The starting point of one method is a moisture content at which the mass no longer sticks to the hands. Then the water content is reduced by drying until it is no longer possible to roll the mass in a strand and it crumbles. The difference in moisture contents before and after drying is a measure for the plasticity. Very well-known is Pfefferkorn's method which determines the degree of deformation as a function of the moisture content. A cylinder with a cross-section of 33 mm and a height of 40 mm is made of the mass to be examined. This cylinder is then placed on a metal plate and a metal disk with a mass of 1192 grammes is dropped onto the mass from a height of 186 mm above the base of the cylinder. The ratio between the starting and remaining height or the remaining height of the cylinder is plotted graphically against the water content and is a measure for the plasticity (figures 9.10 and 9.11).

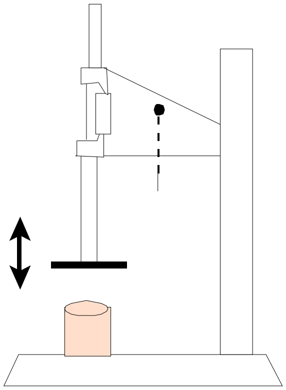


Fig. 9.10 Pfefferkorn's device.

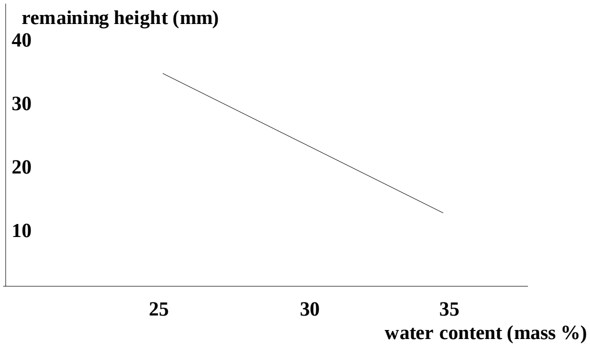


Fig. 9.11 Graphic representation of Pfefferkorn measurements.

Rigid masses have a remaining height of more than 25 mm and for soft ones it is less than 16 mm. In figure 9.11 you can read off the desired plasticity (remaining height) and the required water content. The desired plasticity differs for every product, table 9.3 supplies some examples.

Kinds of plastic moulding

Very occasionally bricks are still made by means of hand moulding. A lump of clay is forcefully thrown into a mould and then the surplus clay is removed. The result is a lively and variable product. When large quantities of bricks are produced the process does not differ much from that of hand moulding. However, now the clay is pressed into a mould and a rather uniform product is the result, e.g. the common brick.

In the extrusion process the plastic clay mass is forced through a die by a screw mechanism (figure 9.12).

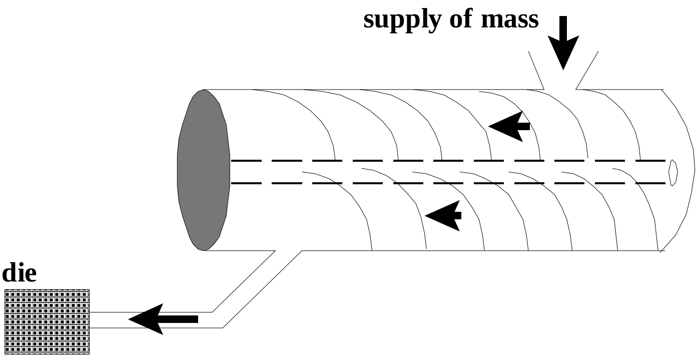


Fig. 9.12 Extruder.

Table 9.3 Pfefferkorn remaining height of some products

remaining height (mm)	
32	extruder products
25	
20	and roofing tiles
16	
12.5	potter’s wheel products
10	
8	
6.3	
5	moulded bricks
4	

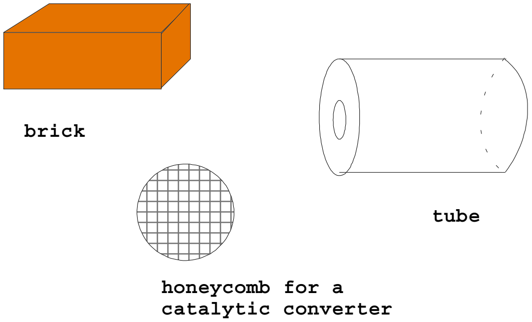


Fig. 9.13 Some extrusion products.

In figure 9.13 you can see a number of extrusion products, among which tubes which can be used as oven tubes, for high temperature processes, as protective cases for thermocouples and as filter tubes for e.g. waste and process water treatment.

9.4.3 The compressing of powders

In this way of moulding pressure is continously of gradually exerted on a powder in a mould. A binding agent and a lubricant are added to the powder. The mass must meet the following requirements: a) suitable grain size distribution, b) sufficiently strong grain, c) correct content of binding agents and lubricants and d) bulk density which is as high as possible, i.e. as much as possible mass per volume unit in order to obtain the densest product possible. This way of moulding

Extrusion of a ceramic tube (ECN-NKA, Netherlands)

is only suitable for mass production, because the equipment and powder preparation are relatively expensive. Articles manufactured in this way are e.g.: floor tiles, wall tiles, plates, refractory stones, magnetic materials, spark plugs, high-voltage insulators and nose cones for rockets. Three kinds of techniques can be applied: unaxial compression, biaxial compression and isostatic compression.

As you can see in figure 9.14 pressure differences occur in the mass due to uniaxial compression. As a result, the product is locally more or less dense and consequently not everywhere equally strong. This problem can largely be solved by compressing biaxially.

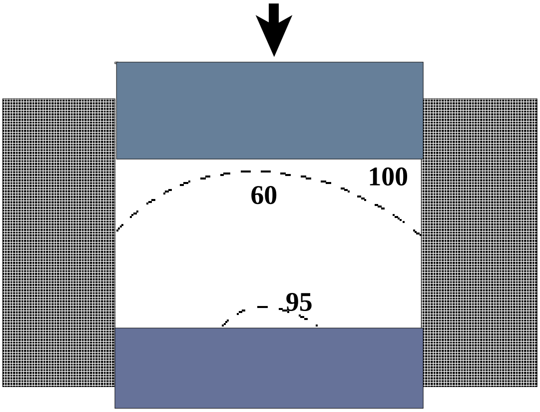


Fig. 9.14 Uniaxial compression of a powder (pressure variations are indicated in percentages of applied pressure).

In the case of *isostatic compression* the same pressure is exerted on the ceramic mass on all sides. The mass is contained in a rubber mould and this is immersed in a liquid inside a pressure vessel. By pressurizing the liquid you can apply the same pressure on the mould from all directions (figure 9.15). This method is especially used for fanciful and asymmetrical objects.

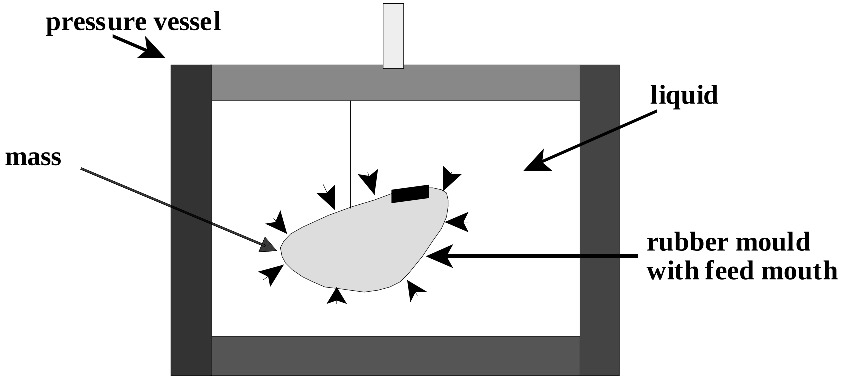


Fig. 9.15 Compressing powders isostatically.

9.4.4 Moulding suspensions

A suspension is a mixture which arises when solid particles are mixed optimally in a liquid. The suspended solid particles have a diameter of appr. 200–0.5 nm and the mixture is also called a “colloidal dispersion”. The liquid is the medium of dispersion. A clay suspension is suitable for the production of so-called hollow, non-rotation symmetrical articles, such as sanitary ware. Until the beginning of the 20th century these products were made by beating the clay into plaster of paris moulds, the so-called dies. Gradually people discovered not only the physically and chemical properties of suspensions but also how to change them and thus the technique of clay moulding developed and complicated shapes could be made. The science of colloid chemistry has been essential here. In the field of technical ceramics the moulding technique is also applied with other raw materials than clay.

Properties of suspensions

The solid particles in a suspension attract because of the Van der Waals forces and charged particles also attract due to Coulomb forces. The charge of the particles and consequently also the Coulomb forces can be affected by adding electrolytes. The relevant theory was already

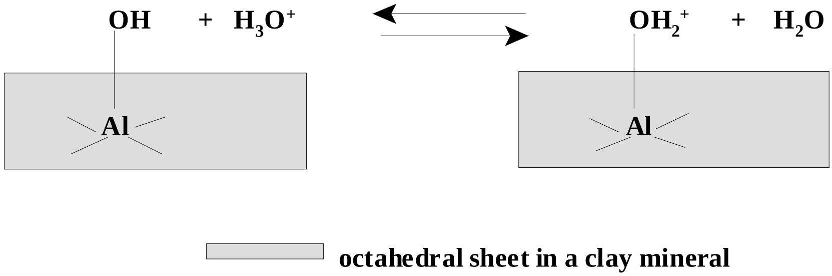


Fig. 9.16 A surface charge on a clay sheet.

discussed in the chapter “Colloid chemistry”, but let us have a look at yet another example. Suppose we add H_3O^+ ions to a clay suspension. At the surface of the clay sheets a positive charge can arise as indicated in figure 9.16.

In the reaction of figure 9.16 a proton is bound to an OH group. This reaction is reversible, which means that the structure on the right can be converted back into the one on the left by adding e.g. OH^- ions. These remove the proton and use it to form a water molecule. The addition of OH^- ions to the structure on the left causes a negative surface charge to be formed:

$$-\mathrm{Al}-\mathrm{OH} \;+\; \mathrm{OH}^- \;\rightarrow\; -\mathrm{Al}-\mathrm{O}^- \;+\; \mathrm{H_2O}$$

The surface charge of the suspended particles affects the viscosity of the suspension, but that was already explained in the chapter Colloid chemistry.

Viscosity

With the viscosity of a liquid mass we mean the flow behaviour and this depends on: a) the viscosity of the dispersion medium, b) the concentration of the solid, c) the shape and dimensions of the particles and d) the interaction between the solid particles themselves and the solid particles and the molecules of the dispersion medium.

The viscosity η (Greek letter èta) of a liquid mass is defined as a measure for the friction which arises when two parallel layers move at different speeds. To get a better idea of this, you can rotate a cylindrical body in a cylindrical vessel which contains a suspension. What you see then is that the suspension near the rotating object turns more quickly than it does near the vessel wall. In figure 9.17 the movement of parallel layers is shown.

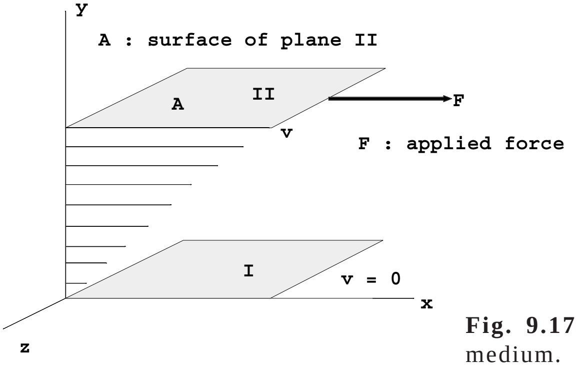


Fig. 9.17 Laminary flow in a liquid medium.

In figure 9.17 two parallel suspension layers are shown in a three-dimensional system of axes so as to create a spatial image. Layer I is at rest; the velocity $v = 0$. A force F is exerted on layer II, owing to which the plane moves with a speed v. The speed of the intermediate layers gradually decreases from layer II in the direction of layer I. The illustrated flow type is called laminary and will only occur at low speeds. At high velocities turbulence arises. The difference between these two kinds of flow can be clearly seen in a burning cigarette: from the tip of the cigarette the smoke first rises virtually straight upwards for appr. 15 cm, the laminary flow; then it falls apart, the turbulent flow.

The shear stress is indicated by means of the Greek letter τ (tau); in formula:

$$\tau = \frac{F}{A} \quad \mathrm{N\ m^{-2}}$$

When the shear stress is directly proportional to the shear velocity v, the mass exhibits Newtonian behaviour and the formula changes into:

$$\tau = \frac{F}{A} = \eta \times v; \quad \eta \text{ is viscosity}$$

or

$$\frac{\tau}{v} = \text{ constant} = \eta$$

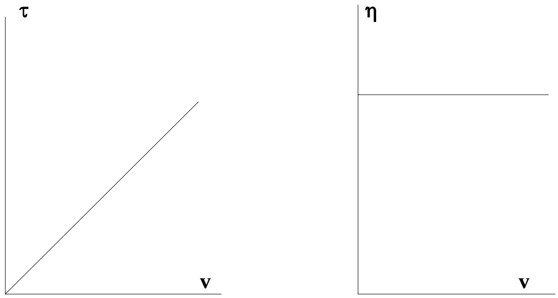


Fig. 9.18 Newtonian flow behaviour.

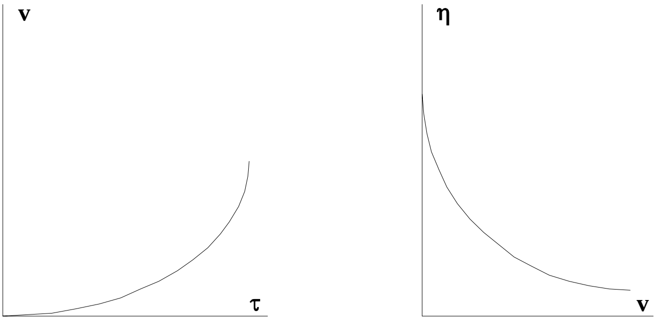


Fig. 9.19 Pseudoplastic behaviour of e.g. paint.

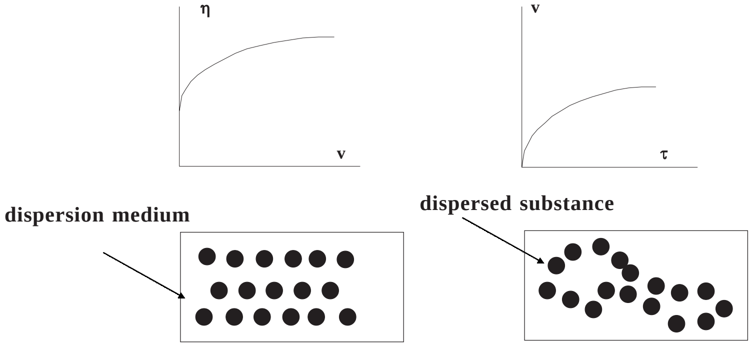


Fig. 9.20 Dilatant flow behaviour.

As we already know, viscosity is affected by four factors. These factors can be the reason that the flow behaviour is non-Newtonian; for those masses τ/v is not constant. Figures 9.18, 9.19 and 9.20 are graphic representations of Newtonian flow behaviour and some forms of non-Newtonian behaviour.

Some examples of Newtonian liquids are: water, light oils and other systems in which the dissolved subtance has a low mole mass, does not associate with other dissolved particles and only exhibits limited interaction with the solvent (dispersion medium).

In more complex systems, the answer to the applied shear stress is no longer linear.

In a pseudoplastic mass the shear speed increases together with the shear stress and the viscosity decreases. This behaviour can be seen in solutions of guar gum and alginates.

Suspensions with high concentrations of densely packed solids often exhibit dilatant flow behaviour. An example of this is a starch/water mixture (figure 9.20).

The dispersion medium water is indicated by the shaded area and the brown circles are the starch components. When you slowly stir a suspension, you feel a slight resistance, which increases as you stir more quickly. In the starch suspension the starch particles are densely packed at rest. (figure 9.20 a) with few water molecules in between. By stirring slowly, you allow the planes of suspended particles to slide along each other. In case of violent stirring the structure becomes less ordered and there is no longer question of planes which can slide along each other; the resistance (viscosity) increases (figure 9.20 b).

Slip casting

The most used forming process for suspensions is slip casting. The slip is usually poured into a plaster of paris mould. These last ten years they have been are researching the possibility of making moulds of plastic. The mould has to be porous for it to withdraw enough water from the suspension by means of capillary forces. All of this results in a so-called sherd at the side of the mould; this is a layer with a higher mass percentage of solids than anywhere else in the slip. After the desired wall thickness has been attained, excess slip is poured off and the mould with the so-called green product is air-dried. The product will shrink and in this way comes free of the mould wall. Figure 9.21 is a representation of the slip casting process.

Before the excess slip can be poured off, the wall must be strong enough and should not collapse due to its own weight. Moreover it

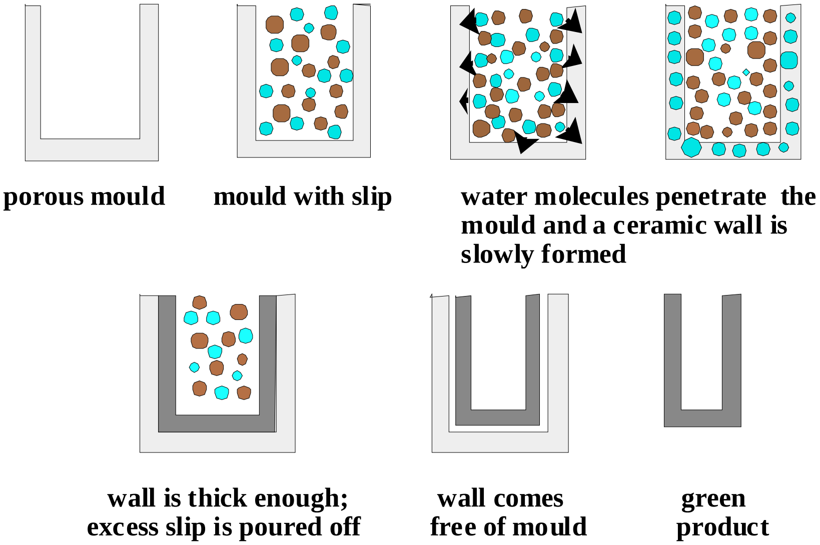


Fig. 9.21 Slip casting.

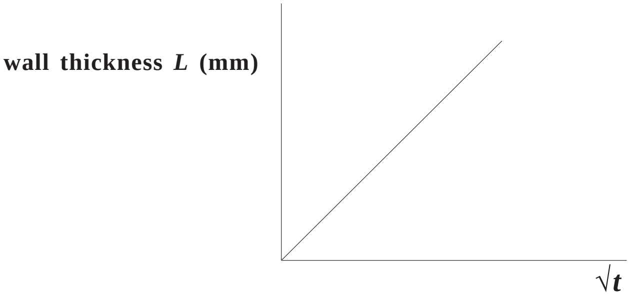


Fig. 9.22 Wall thickness as a function of the square root of the growth time.

must be transported to the oven. The strength of the wall is assessed by experience and is related to the content of solid material and the thick-ness of the wall. A relationship also exists between the thickness and the “growth time”. To determine the wall thickness as a function of time, a bottomless graduated cuvette is placed on a layer of the same plaster of paris as the mould. Some slip is poured into this cuvette and a stopwatch is started. Every minute for example the thickness is read. In figure 9.22 this thickness is plotted as a function of the square root of time; only when plotted like this is the relationship theoretically linear.

The following mathematical relationship appears between the wall thickness and the root of the growth time:

$$L = c \times \sqrt{t}$$

9.4.5 Other moulding methods

Quite a modern way of moulding is densifying ceramic masses by means of a shock wave created by explosives. The Technical University of Delft together with TNO (a Dutch research centre) are two institutes which have researched this possibility (see chapter 12). In order to obtain an extremely dense material, several thermal and mechanical methods are available. Sintering is the oldest method, but sintering alone does not produce a high density. Before the sintering takes place, the ceramic particles must be compressed; we already discussed some of the methods applied for this. Crystalline materials are difficult to compress and when you succeed, the result is mostly a change in the packing of the building blocks and an increase of the coordination number. This means that the number of particles grouped around a single particle increases. It is difficult to compress most ceramic materials (especially the technical ones) to deformed particles and also to sinter them due to their high melting points.

Dynamic densification by means of shock waves produces an extremely dense material, which in its turn reduces the sintering temperature required. The result of a shock wave is regroup-ing, plastic deformation and breaking of the particles.

The use of shock waves was imitated from nature, more specifically from meteorite craters. Among other things, unique forms of diamonds were found in there, i.e. hexagonal diamonds formed out of graphite. Furthermore the mineral stishovite was also found there.

Stishovite (density 4.28 g/cm^3) is a modification of quartz (density 2.65 g/cm^3) and can be made from the latter at a temperature of 1000-4000 °C and a pressure of 120–160 kbar.

9.5 HEAT TREATMENT

9.5.1 Introduction

The heat treatment of the green product takes place in three stages:

DRYING	the removal of water
FIRING	the removal of binding agents and lubricants
SINTERING	densifying the product by baking it

9.5.2 The drying process

For an optimal drying process three conditions must be met: a) the temperature of the drying air must be high enough, b) the airflow must have a sufficient speed and c) the drying air must have a relatively low humidity. These conditions might suggest that drying is a simple process; on the contrary! For many years now much research has been done into the drying of ceramic masses. The science of technical ceramics gladly avails itself of the experiences of classic ceramicists. In figure 9.23 the evaporation speed of water from a green product has been graphically plotted as a function of the humidity. The evaporation speed can be measured by subtracting the mass of the dry substance from the total mass of the moist, green product at regular intervals.

The drying speed from A to B is constant in figure 9.23. The pores are completely filled with water and the evaporated water can easily be replenished from elsewhere in the object: the water flows through the pores. Because the moisture disappears, the solid particles can move closer together: shrinkage occurs, the so-called drying shrinkage which is a phenomenon we already encountered in the paragraph on slip casting. From B to C the evaporation speed decreases because not all pores at the surface are filled with water anymore. After C water transport only takes place by means of diffusion. There is still water in the pores with minute diameters, but that water is strongly adsorbed, also because it is bound to clay particles. The diffusion process is extremely slow and the evaporation speed slowly drops to zero. When we increase the temperature, the evaporation speed rises again.

Inexpert drying can lead to cracks in the green product, the causes

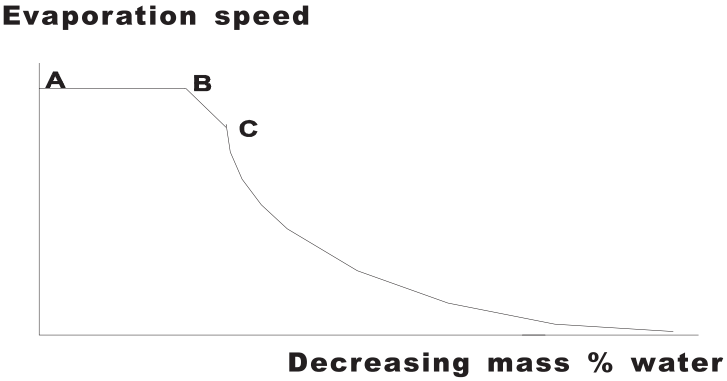


Fig. 9.23 Evaporation speed of water from a green product.

of which may be: too high evaporation rate, large differences in moisture content in different places of the product and insufficient drying. Due to insufficient drying, the moisture evaporates “explosively” during the heat treatment which follows.

Another negative side effect is that dissolved salts are deposited at the surface during the drying. This causes discoloration and will affect the glaze which may be applied to the product at the end of the ceramic route. The drying temperature and drying shrinkage are determined by means of analytic techniques like DTA, DTG and dilatometry. Figure 9.24 is a graphic representation of a drying installation for paving bricks.

9.5.3 Firing and sintering

Firing

After the drying process the product often still contains undesired components, e.g. binding agents and deflocculants. At the right temperature these substances decompose and / or burn and eventually evaporate. This firing must also be carefully controlled, since the decomposition and combustion products are gases which can cause cracking. This risk is especially large in the case of extruded or injection moulded products, because these contain up to 50% (v/v) binding agents; the concentration of deflocculants rarely exceeds 1%. Decomposition takes place between appr. 200 and 400 °C and combustion between appr. 400 and 600 °C. The temperatures for the above-mentioned processes are determined by means of DTA.

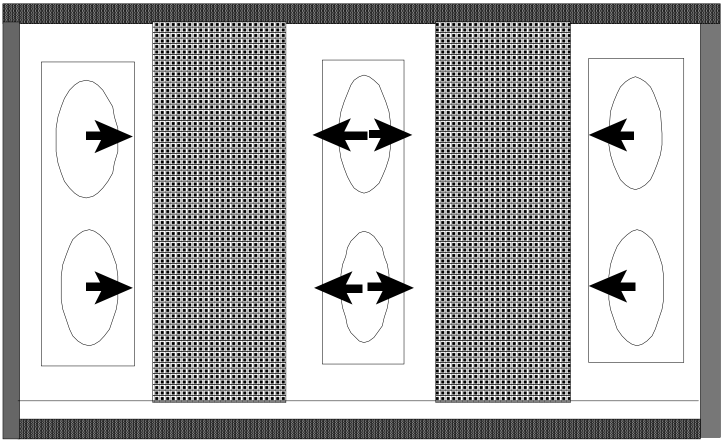


Fig. 9.24 Drying chamber for paving bricks.

Sintering

After the firing process the temperature is again increased and the sintering or baking process is started. For clay products the temperature is appr. 1200 °C and for technical ceramics temperatures of 1600 °C and higher are applied. During the sintering the green product with particles without much cohesion is converted into a firm product. The pores between the particles virtually disappear, solid bridges are formed between neighbouring particles and eventually the particles merge.

It goes without saying that material transport is required for the sintering process. The nature of this transport depends on the sintering method.

Sintering without liquid phase

The material transport e.g. takes by evaporation and condensation. This results in a so-called neck growth between the particles (figure 9.25)

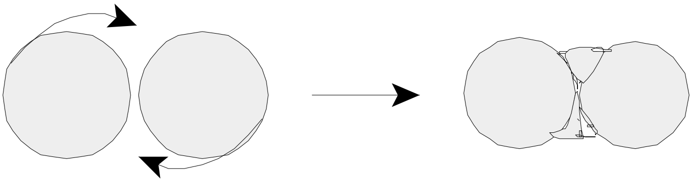


Fig. 9.25 Neck growth due to evaporation and condensation of the material.

Apart from via the vapour phase the material can also be transported to the neck via the solid phase; this is called diffusion. During this process the particles move through the solid, from their place in the lattice to an adjacent empty lattice place, a so-called vacancy.

Coffee cup before (left) and after (right) firing (by : E.Bormans)

Sintering with a liquid phase

Before this sintering method begins, one or more substances are added to the ceramic raw materials and they form a very viscous liquid during the sintering process, a glass phase. This glass phase ensure a speedy densification. This method is mainly applied in technical ceramics since the atoms in technical ceramic materials have little or no freedom of movement and diffusion is consequently virtually impossible. The glass phase consists of mixture of silicates with a composition in which the solid phase only dissolves to a limited extent. In addition it is vital that the glass composition is carefully controlled so that hardly any glass phase will be present after sintering and cooling. In general a glass phase is undesirable in ceramic objects because it negatively affects the high-temperature properties owing to softening. An example is the addition of yttrium oxide or a mixture of yttrium oxide and aluminium oxide before the sintering of silicon nitride. In figure 9.26 you can see the result of the sintering with a liquid phase after cooling.

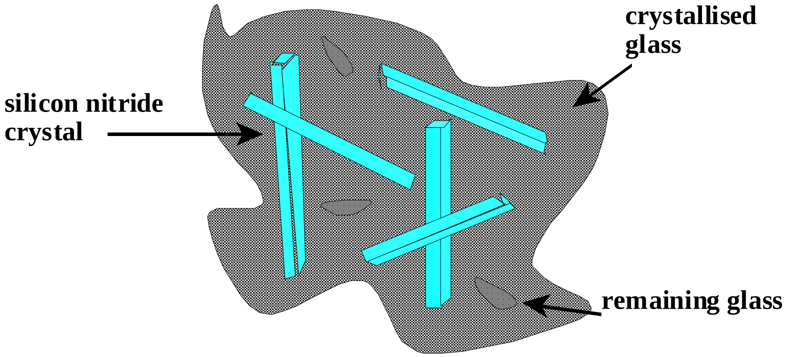


Fig. 9.26 Firing with a liquid phase (result after cooling).

Another method of sintering

In the previous two sintering processes only physical changes take place in the substance. In the case of reaction sintering a compound is formed during the sintering. A silicon nitride object can be manufactured in such a way. The starting material is a silicon powder which is processed and moulded. Then the object is placed in an oven in a nitrogen environment at a temperature which increases from appr. 1150 °C to appr. 1400 °C. The following reaction takes place in the object and at its surface:

$$3\ Si_{(s,l)} \quad + \quad 2\ N_{2(g)} \rightarrow Si_3N_{4(s)}$$

Sintering in this way ensures that virtually all pores disappear and only slight dimensional changes occur, i.e. less that 0.1 %. Consequently the main advantage of this method lies in the dimensional stability.

9.6 FINAL TREATMENTS

At the end of the production line a ceramic product is often characterized by insufficient dimensional reproducibility and inadequate surface quality. These drawbacks can be overcome to some extent by certain treatments of the green product or the final product or by applying a covering layer.

Treatment of the green product, so no final treatment, is possible after the moulding and before the sintering process. It can be successful when the solid particles are well bound, because otherwise the object will collapse under the mechanical strain. Treatments of the final product can be divided into three groups: a) mechanical treatment, b) chemical and thermal treatments and c) applications of coatings.

After sintering the object is extremely hard and it can only be mechanically processed with diamond tools, which accounts to a large extent for the high price of some products. However, the product is still quite fragile after sintering, i.e. it can break easily. But provided it is properly secured in clamps, it can undergo mechanical processing in the form of wet or dry grinding, drilling, turning, milling or sawing.

Ceramic objects are only rarely processed chemically; an example is the making of microscope slides.

Thermal processing involves extremely high temperatures locally and as a result the material will melt, sublimate or dissociate. For this a laser is used, which has the advantage that the object is not polluted, the tools do not wear and no mechanical forces are exerted on the object. This technique is excellently suited for cutting, drilling and scribing. Scribing is a method of cutting which is applied for brittle objects. Blind holes are drilled, i.e. you do not drill completely through the material. Then the material is broken by means of a shock wave or a bending stress is applied to it. It is also possible to remove a very thin layer of a ceramic material with a laser, but this technique present more problems than the above-mentioned ones.

A coating is applied to improve the surface properties. After sintering the surface of a clay ceramic object is dull, chemically instable, not very porous, nor wear resistant and it does not present an aesthetic exterior. That is why it is glazed. Glazes will be discussed elaborately in paragraph 11.1 Fine Ceramics. Because of technological progress, machine components and the materials from which they are made, have to meet increasingly higher requirements. When is material is not satisfactory - and mostly this involves its resistance to wear - a ceramic coating can be applied to it. The possibility to apply this coat by means of lasers are currently being researched. Some other techniques are discussed in paragraph 11.7 Chemical and Structural Ceramics.

In the field of bioceramics, paragraph 11.6, coatings of synthetic bone are applied to metal implants in order to ensure a better attachment to the body's bone.

9.7 PROPERTIES

The properties of ceramic materials depend on their structures and will be discussed separately for every branch of industry in chapter 11. In this paragraph some properties will be discussed which are measured in most branches of industry.Because the properties of ceramics differ in many aspects from those of metals and plastics and also because some knowledge of the last two is required, chapter 10 is devoted a comparison of these three material groups. In this paragraph they are only compared without going into the the structures of metals and plastics more deeply.

Density

As you can see in table 9.4 plastics exhibit relatively low densities. This is hardly surprising since their structures are much more wide-meshed than those of the other two material groups.

The density of a material is determined by the way the building blocks (atoms or ions) are packed in relation to each other, the length

Table 9.4 Densities (g/cm^3) of some ceramic materials, metals and plastics

ceramics			metals			plastics		
boron carbide	B_4C	2.5	magnesium	Mg	1.7	polyethene	PE	0.9
quartz	SiO_2	2.2	aluminium	Al	2.7			
aluminium oxide	Al_2O_3	3.9	iron	Fe	7.9	polyvinyl chloride	PVC	1.4
zirconium oxide	ZrO_2	5.8	silver	Ag	10.4			
tungsten carbide	WC	15.7	tungsten	W	19.4	polytetrafluorethene	PTFE	2.2

of the bonds and the mass of the building blocks.

The density of a ceramic or metal powder is determined with the help of a so-called pycnometer. The density of a piece of ceramic or metal material can be determined by measuring its mass and volume; in order to obtain the volume, the object is immersed in a liquid. For plastics a number of liquids with known densities are used and you determine whether a plastic floats, sinks or is suspended in a certain fluid. This will tell you that its density is less than, more than or equal to that of the liquid respectively.

So far our starting point has been that the mass whose density must be determined is not porous.

When a ceramic material (green or baked) is porous, we speak of true density and apparent density. True density is the density of a ceramic material without pores. In order to determine this, the mass of the object must be known as well as the volume less the pore volume. In figure 9.27 all of this is drawn and some calculations are given.

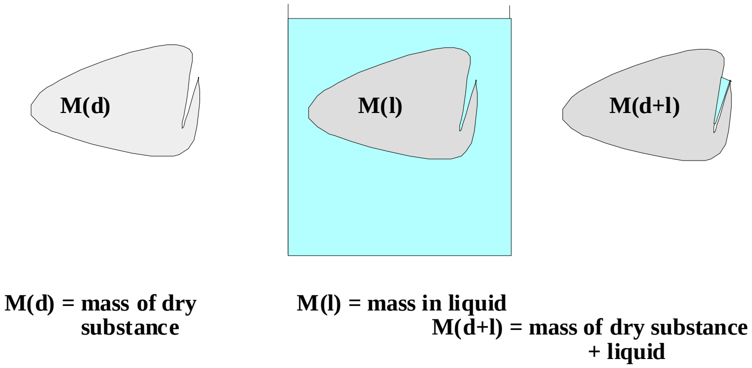


Fig. 9.27 Determination of the density of a porous body.

Archimedes' principle applies to the determination above "a body immersed in a fluid is subject to an upward force due to which its mass (apparently) decreases proportionally to the mass of the of the fluid is displaces". This means that:

mass of displaced liquid $m = M(d + \mathrm{l}) - M(\mathrm{l})$ g

density of displaced liquid $= D$ g / cm^3

volume of displaced liquid $v = \dfrac{M(d+1) - M(1)}{D}$ cm^3

density of the ceramic mass (without pores) $\rho = \dfrac{M\,(d)}{v}$ g/cm^3

With the help of figure 9.27 you can derive yet another formula for the percentage of open porosity, an important ceramic parameter. When a ceramic mass has been baked, it sometimes still possesses so-called open and closed pores. The open pores are in contact with the outside air and so can be filled with water. From figure 9.27 it appears that:

$$\text{open pore volume} = \frac{M\,(d+1) - M\,(d)}{D}\ \text{cm}^3$$

$$\text{total volume} = \frac{M\,(d+1) - M\,(1)}{D}\ \text{cm}^3$$

$$\%\ \text{open porosity} = \frac{\text{open pore volume}}{\text{total volume}} \times 100\% = \frac{M\,(d+1) - M\,(d)}{M\,(d+1) - M\,(1)} \times 100\%$$

Hardness

The hardness of a material is determined by its structure. For ceramic materials, this means that among other things the type of crystal structure and the firmness of the bonds can be of influence.

Two kinds of hardness can be measured: scratch hardness and indentation hardness. Special styluses are available to measure the scratch hardness. These are provided with a crystal tip which has a certain hardness. When a material is scratched with a certain stylus and no scratch is made, then the material has a higher hardness than the tip of the stylus. By using different styluses you can accurately determine the hardness. This method is often applied in mineralogy, e.g. by mineral collectors. Hardness is ranked along the Mohs scale, which is based on the hardness of minerals. In this scale talc is the softest mineral, which becomes clear when you rub it between your fingers.

When the indentation hardness is measured, a small sphere or the tip of a pyramid-shaped crystal of a material which is harder than the one to be tested is pressed in the surface. The depth of the imprint is a measure for the hardness. Especially in the case of porous material it is vital that the determination is carried out carefully to avoid that

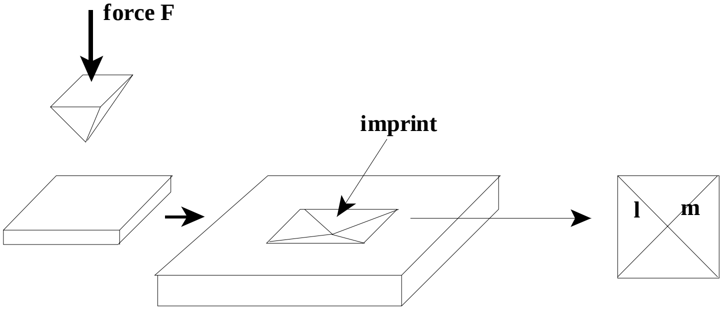


Fig. 9.28 Hardness measurement according to Vickers.

Table 9.5 Mohs hardness scale (H = hardness)

mineral	H	mineral	H
talc	1	feldspar	6
gypsum	2	quartz	7
calcite	3	topaz	8
fluorite	4	corundum	9
apatite	5	diamond	10

the test is done just above a pore. In ceramics the Vicker's hardness test is used to measure the indentation hardness (figure 9.28). The tester uses a square-based diamond pyramid indenter which is pressed into the material.

Suppose the diamond used has a top angle of 136°. Then the following formula applies to the area A:

$$A = \frac{a^2}{2 \times \sin 68^\circ} = \frac{a^2}{1.854} \text{ mm}^2, \text{ in which } a = \frac{l+m}{2}$$

In that case, the Vicker's hardness H_v is:

$$H_V = \frac{F}{A} \text{ kg/mm}^2 = \frac{1.854 \times F}{a^2} \text{ kg/mm}^2$$

Elastic modulus or modulus of elasticity

When a tensile force is exerted on a material, certain deformations occur within this material. The material is elongated and will eventually break. In practice the computer converts tensile force to tensile stress during an experiment by dividing the force by the cross-section of the object. The tensile stress is plotted in a graph against the relative stretch. When the material returns to its original shape once the force is removed, we speak of elastic deformation. When this is not the case, the deformation is plastic. In ceramic materials plastic deformations are hardly ever seen and once the elastic limit is crossed, the material will break. A material which cannot be deformed plastically is called “brittle”. Figure 9.29 shows the elongation diagram of a ceramic material and a metal. The diagram of a plastic is similar to that of a metal.

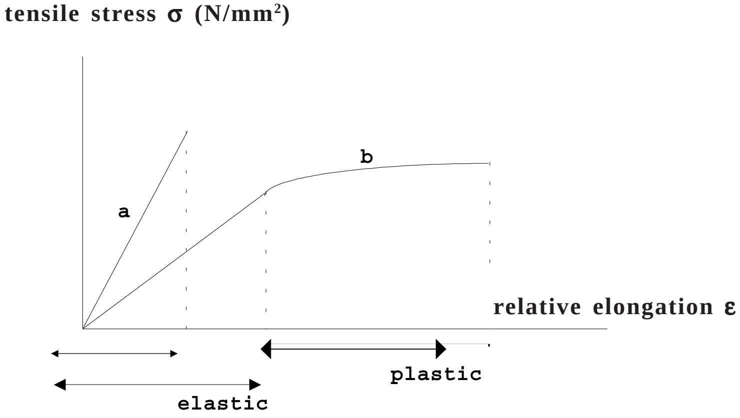


Fig. 9.29 Elongation diagram of a ceramic material (a) and a metal (b).

Fracture mechamics

Ceramic materials have strong ionic or covalent bonds and that is why sliding processes as occur in metals are not or only slightly possible. They lack the necessary plastic behaviour.

Consequently ceramics break easily, mainly because they are so brittle. Defects in the material result in cracks when loads are applied. The main defects are: porosity, foreign particles which have been incorporated and surface cracks resulting from the surface treatment of the baked product. For example: volume percentage and pore dimensions strongly affect the strength of the object (figure 9.30).

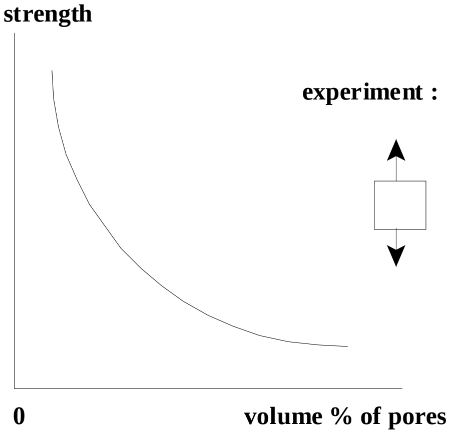


Fig. 9.30 The strength of a ceramic material as a function of the volume percentage of pores during a tensile test.

That is why we want to attain the highest possible packing of the dry substance during moulding, which is vital in the compressing of powders. The strength of pore-free ceramics depends on the grain size.

The stress on a ceramic object is concentrated in the areas around pores and cracks. As soon as the stress near a pore or crack reaches a critical value, a crack is formed which grows in size because the energy cannot be absorbed elsewhere in the object. A plastic material reacts much differently under strain. The material first starts to flow and then the crack will grow. In that case the energy which is exerted on the object is converted into deformation energy. Ceramics are brittle and cannot flow, so when the energy near the defect exceeds the binding energy between the atoms, the crack will grow. In the chapter on Ceramic Composites we shall have a closer look at how state-of-the-art ceramics are made less sensitive to cracking.

Finally we can conclude that the strength of polycrystalline ceramics depends on many factors, mainly on their chemical composition (a measure for the strength of the bonds between the atoms), their microstructure and their surface condition.

Fracture mechanics deal with the behaviour of materials which break easily. A measure for their strength is the fracture toughness, the maximum stress which can be applied to an object without breaking, i.e. the stress which the object with all its cracks can still withstand. This fracture toughness can be measured in a tensile test: test samples are provided with cracks of known dimensions and forms (figure 9.31).

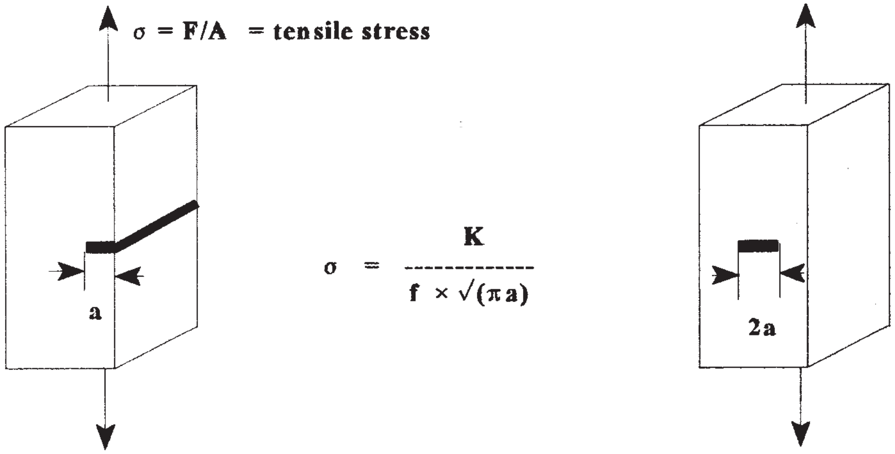


Fig. 9.31 Tensile test of a ceramic sample.

The formula of the tensile stress can also be expressed like this:

$$K = f \times \sigma \times \sqrt{(\pi a)}$$

or

$$K = f \times F/A \times \sqrt{(\pi a)}$$

where: K = stress intensity factor, σ = tensile stress, a = depth or width of cracks, F = tensile force, A = cross section of the sample, f is a factor which is determined by the shape of the object and the crack. It has a value of approximately 1, assuming the object has an “infinite” width.

One application of both formulas is calculating beforehand how deep the crack may be when a material is to bear a certain load in a specific construction.

As a result of the tensile test a critical value K_c is found for K which will lead to the extension of cracks and to the breaking of the object:

K_c = Critical stress intensity factor = *fracture toughness*

The fracture toughness depends on the thickness of the sample (figure 9.32).

In figure 9.32 K_{Ic} is the minimum value of K_c and in general this value is applied as a material value. Consequently, the formula of the previous pages changes into:

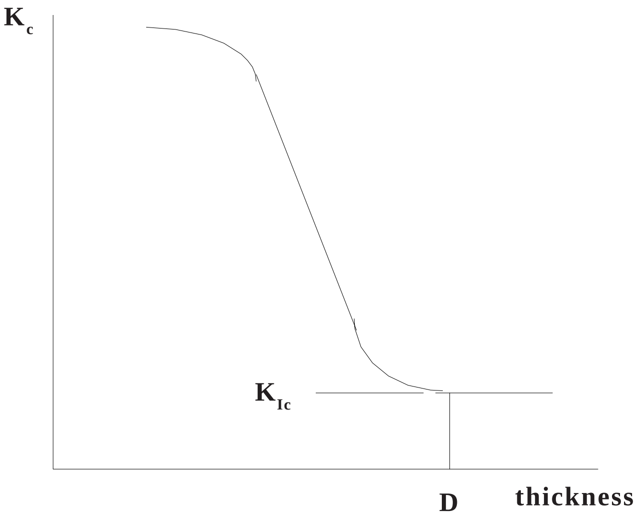


Fig. 9.32 The critical stress intensity as a function of the thickness of the sample.

$$K_{Ic} = f \times \sigma \times \sqrt{(\pi a)}$$

A calculation example:

A load of 300 MPa is exerted on a flat piece of zirconium. K_{Ic} = 11 MPa $\sqrt{m}$ f = 1.

How large can a crack be at most?

$$11 = 1 \times 300 \times \sqrt{(3.14 \times a)}$$

$$121 = 1 \times 90000 \times 3.14a$$

From this it follows that a = 0.43 mm. So a surface crack can be at most 0.43 mm deep and an internal crack at most 0.86 mm wide.

From the graph in fig. 9.32 it appears that K_c assumes the constant value K_{Ic} when the thickness of the sample exceeds the value D. Apart from these two K values, K_{IIc} and K_{IIIc} also exist. The latter two are applied for different ways of exerting loads (figure 9.33).

In practice, tensile tests on ceramic objects are hardly ever done because it is difficult to clasp them between the jaws of the testing equipment. The object is damaged by the jaw and a crack is very likely the result and this could be the place where the sample will break. The price of the test dumbbells is also a drawback of this type

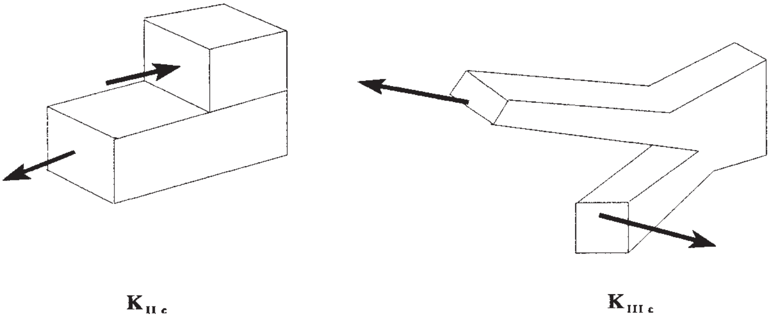


Fig. 9.33 Critical intensity factors for different ways of loading.

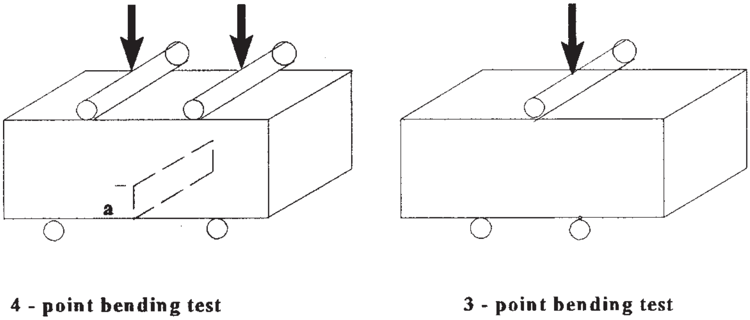


Fig. 9.34 Four- and three-point bending test of a ceramic object.

of experiment. Most of the time a bending test is done to measure the strength (figure 9.34).

A calculation example of a four point bending test:

$$\sigma = 300 \text{ MPa} \qquad K_{Ic} = 4 \text{ MPa} \sqrt{m} \qquad f = 1$$

Using this data, you can calculate that

$$a = 5.66 \times 10^{-5} \text{ m} = 56.6 \text{ µm } (1 \text{ m} = 10^{6} \text{ µm})$$

The E modulus of the material can also be determined with the three or four point bending test. The following formulas apply

three-point bending test four-point bending test

$$E = \frac{11 \times F \times l^3}{64 \times w \times h^3 \times d} \qquad E = \frac{F \times l^3}{4 \times w \times h^3 \times d}$$

Here F is the force which leads to the break, l the distance between the points on which the object rests, w, h is the width and height of the object, respectively, d is the distance over the centre of the object is moved.

10

Plastics, Metals and Ceramics: A Comparison

10.1 INTRODUCTION

No book on ceramics is complete without a comparison of the three main material groups: plastics (mostly mixtures of polymers and additives), metals and ceramics. The uniqueness of ceramics can only be fully understood when their properties are compared with those of other materials. This chapter again hints at the writer's educational background by posing the question: "How do I introduce such a comparison? What will be my starting point: the theory or the experiments?" Experience shows that an introduction with experiments is usually most successful. A simple experiment is heating a sample of each material in a blue flame. Most plastics will burn, either with or without producing soot-containing smoke. The metals of groups 1 an 2 of the periodic table will combine with oxygen and consequently burn. A good example of this is lighting a magnesium ribbon, only do not look into the flame when the ribbon burns! Most metals do not burn and have relatively high melting points owing to which they only become hot and then stay hot for a considerable time after having been removed from the source of heat. An object made of e.g. aluminium oxide can withstand extremely high temperatures without undergoing any noticeable changes. Another simple experiment involves the influence of organic solvents. Most plastics dissolve in correctly chosen organic solvents, but metals and ceramics do not. Metal, on the other hand, dissolve is correctly chosen acids. Even water can functions as an acid here, for example to dissolve calcium. Plastics and ceramics hardly do this. Based on the results of a number of simple experiments you can extrapolate a link between the behaviour of a certain material and its structure.

10.2 FROM RAW MATERIAL TO FINAL PRODUCT

You might ask yourself: “Why is one substance a ceramic, another a polymer and a third a metal?” This paragraph will answer this question by demonstrating that the individual forming processes (syntheses) are subject to certain rules and the nature of the product of the synthesis can be predicted to a large extent.

Synthesis of the raw material

During a synthesis the basic substances or reagents are mixed and consequently react under specific reaction circumstances to form products with usually totally different properties. With reaction circumstances we might mean high temperature or pressure, irradiation with ultraviolet light, the presence of a catalyst and many other possibilities.

What takes place during a chemical reaction can be highly complex, but a simplified representation will suffice here. The basic materials are built up of atoms, ions or molecules. These building blocks are linked by means of bonds and these bonds contain energy; after all, you need energy to break a bond. In a simplified model all bonds in the basic materials are broken during the reaction and this requires energy. When products are made, new bonds are formed and energy is released. If this reaction does not take place spontaneously, it must be activated by supplying the energy of activation $E_{A.}$ When it is necessary to supply this energy continuously, the reaction is called “endothermic”. Most organic synthesis reactions are endothermic.

A reaction is called “exothermic”when it is possible to remove the energy of activation after some time because the reaction proceeds with the help of the energy produced in the reaction. A good example of this is the so-called “volcano test”: some ammonium dichromate is shaped into a small volcano crater. A bright flame is held to the crater until the reaction starts: the volcano produces a green powder, chromium(III) oxide:

$$\underset{\text{ammonium dichromate}}{(NH_4)_2\,Cr_2O_{7(s)}} \xrightarrow{T} N_{2(g)} + H_2O_{(g)} + \underset{\text{chromium oxide (III)}}{Cr_2O_{3(s)}}$$

Among other things, the nature of the new bonds, and consequently the products, is determined by the energy balance. That is to say, each reaction aspires to use as little energy as possible in the formation of the main product in the case of an endothermic reaction and to produce as much energy as possible in the case of an exothermic

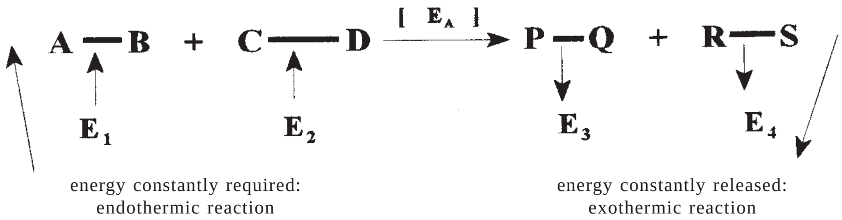


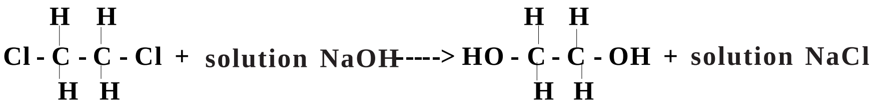
Fig. 10.1 Energy required (E_1 and E_2) to break bonds and energy released (E_3 and E_4) when forming bonds (E_A : activation energy).

one. In any reaction by-products are formed according to processes whose energy balances do not differ much from those of the main product.

When a product is a solid which can occur in several crystal structures (polymorphology), the reaction circumstances determine which structure will be formed. And thus some more factors can be mentioned which determine the nature of the product. A chemist is able to select these circumstances quite accurately and thus ensure an optimal yield of the desired substance in the synthesis. Afterwards it is very often necessary to purify the product, which often requires much more time than the synthesis itself.

The raw material

The raw materials for the syntheses of materials are often found in nature or made in the laboratory. In the case of plastics, petroleum products form the starting point and through some synthesis reactions these can be converted into the raw material for a polymer, the main component of plastics. For example: for the synthesis of PET (polyethylene terephthalate) of the well-known PET bottles, you need



$$\mathrm{Cl-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Cl} + \text{solution NaOH} \dashrightarrow \mathrm{HO-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OH} + \text{solution NaCl}$$

1,2 – dichloroethane **1,2 – ethanediol (ethyleneglycol)**

ethylene glycol, which in its turn can be synthesized as follows:

The raw materials for metals are ores found in nature. Iron is for instance mined as iron(III) oxide from which iron is obtained in blast-furnace processes:

Clay is the main raw material for the so-called classic ceramics. Its complex composition was elaborately discussed in chapter 8. For technical ceramics pure raw materials are needed (e.g. silicon nitride) which are often synthesized or the necessary raw materials are found in nature and subsequently purified very well, possibly after a chemical reaction has taken place.

$$\underset{\text{silicon tetrachloride}}{3SiCl_{4(g)}} + \underset{\text{ammonia tetrachloride}}{4NH_{3(g)}} \rightarrow \underset{\text{silicon nitride}}{Si_3N_{4(s)}} + \underset{\text{hydrogen chloride}}{12HCl_{(g)}}$$

The end product

The manufacture of a plastic starts with the synthesis of one of more polymers (chapter 3). Additives are added to the polymer or to a mixture of polymers and the plastic is ready.As mentioned earlier, metals are synthesized from metal ores. Some examples of ores are: haematite (Fe_2O_3), siderite ($FeCO_3$) and magnetite (FeO_4) for the synthesis of iron, pyrolusite (MnO_2) for manganese, chalcocite (Cu_2S) for copper, cassiterite (SnO_2) for tin and galena (PbS) for lead.

Ceramic raw materials are powders. Together with a mixture of additives these powders are moulded into a particular shape and subsequently dried and baked. After the baking or sintering process it is possible to apply a finishing coat if necessary and then the ceramic object is ready. The entire "route" from raw material to finished product was elaborately discussed in chapter 9.

10.3 STRUCTURE OF PLASTICS AND METALS

In the paragraph on "Organic chemistry" of chapter 3 some atten-

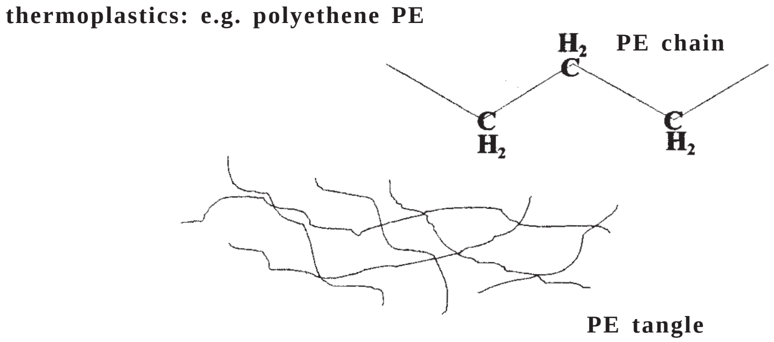


Fig. 10.2 The structure of polyethene (PE), a thermoplastic.

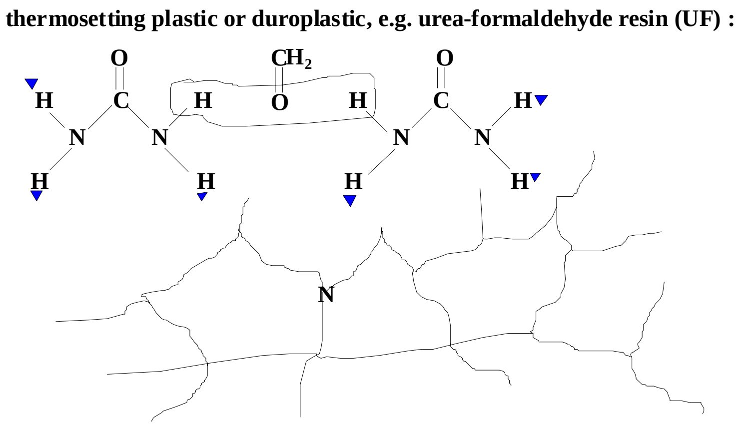


Fig. 10.3 The formation and structure of a urea-formaldehyde resin (UF), a thermosetting resin.

tion was already paid to polymers. The title "organic chemistry" indicates a group of substances, the so-called carbon compounds, which are molecules built up of branched or unbranched chains or rings of carbon atoms. Additives are added to these polymers in order to improve their processibility (e.g. lubricants or sulphur), their mechanical properties (e.g. rubber particles to increase the impact resistance) or other properties (e.g. pigments for the colour). Three kinds of polymers can be dis-

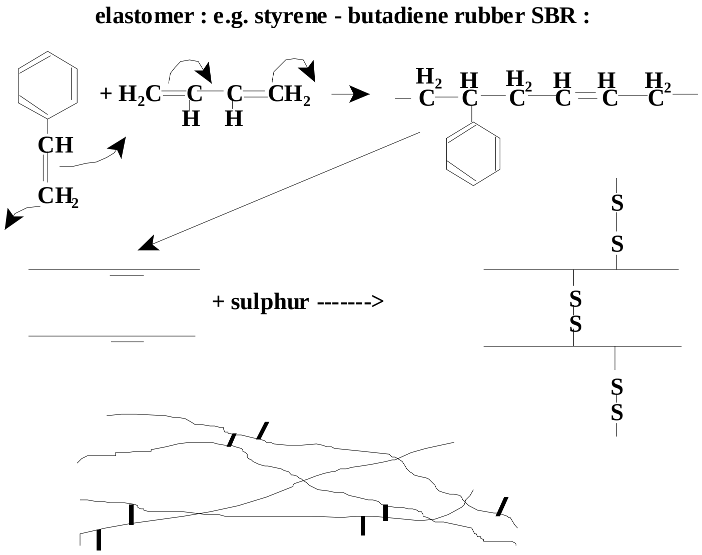


Fig. 10.4 The formation and structure of SBR, an elastomer.

tinguished and their structures are represented in the figures 10.2 up to and including 10.4.

Thermoplastics consist of long chains of molecules, in the case of PE these are unbranched. Many of these chains together form a tangle which is more difficult to unravel the more branched the chains are. The branches are like hooks which cause the molecules to catch. Under the influence of relatively small external forces chains and parts of chains can slide across each other. PE is for instance used to make containers, chemical tubing and blow-moulded bottles. Some other thermoplastics are polypropylene (crates), polyvinyl chloride PVC (pipes) and polystyrene (foam).

By means of chemical reactions thermosetting plastics form three-dimensional structures. In the example above the nitrogen compound urea reacts with formaldehyde (methanal), in which process three molecules combine and a molecule of water is formed. In this example two H atoms react, but all other H atoms (▼) enter into the same reaction. Since urea is a three-dimensional molecule, the network will also be three-dimensional. For instance switches and sockets are made of UF. Other thermosetting plastics are polyurethane PU (insulation) and melamine-formaldehyde MF (panels).

In the synthesis above styrene reacts with butadiene to form long chains while at the same time retaining a double bond per two molecules. Subsequently sulphur is added and sulphur bridges are formed between the remaining double bonds which interconnect the chains. These bridges are represented by small dashes. SBR is for instance used in the manufacture of car tyres. Another elastomer is polyurethane rubber PUR which is used as a foam in head rests.

The crystals of metals are built up as regular packings of positive ions among which an electron cloud of valence electrons moves.

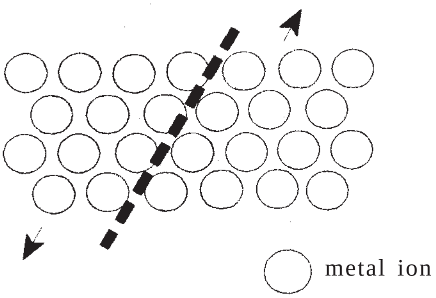


Fig. 10.5 Parts of the crystal lattice of a metal move along a crystal plane under the influence of external forces.

Furthermore the bonds in the crystal lattice are not strong and consequently parts of a crystal can slide along each other under the influence of external forces (figure 10.5). For that reason metals are flexible, unlike ceramics.

The result of the solidification of a liquid metal is mostly an unperfect packing, which means a crystal lattice with imperfections. These imperfections have already been discussed in chapter 4. An imperfection is a deviation from the perfect packing. For instance: a vacancy is an empty place in the lattice which should be occupied. It is also possible for a particle to end up in a place where it should not be. A foreign metal ion which is bigger than the own ions can upset the move of parts of the lattice in relation to each other. And then there are the faults which we call dislocations and which concern parts of the crystal lattice. For example when it seems as if a crystal is partly cleaved or both parts have shifted over one atom distance in relation to each other. Or the crystal is in fact partly cleaved, both halves move and the crack is filled with a layer of atoms.

The metallic elements are crystallized in one or more (polymorphology) of the following structures:

cubic closed packings (ccp):	e.g. Ca, Fe, Cu, Au, La, Al, Ni, Pt, Ag
hexagonal closed packings (hcp):	e.g. Ca, Ti, Co, Ni, Zn, Mo, La
body-centred cubic packings	this packing is a collection of cubes with a metal ion at every corner of a cube and in its centre: e.g. K, V, Cr, Zr, Mo, Fe, Ti, W

During the solidification of a liquid mixture of metals, alloys and/or intermetallic compounds can arise. When iron is mixed with more than 1.2% (m/m) C, the compound Fe_3C can be formed. In addition, iron can occur in the α, γ and δ structure. In the phase diagram of Fe/C you can see within which temperature and composition ranges the compound and the various crystal structures of iron are stable. Well-known alloys are bronze [Cu, Zn, Sn], pewter [Sn, Sb, Cu, Bi], stainless steel [Fe, Cr, Ni] and solder [Pb, Sn]. In an alloy foreign building blocks have been built into the crystal lattice of the “parent metal”, the so-called matrix which is the component which is present in excess. These foreign building blocks are the cause of the (desired) imperfections in the lattice and thus the required properties can be realised. As you can imagine, larger, foreign building blocks may make it more difficult for parts of the lattice to slide along crystal place in relation to each other. Crystal lattices of pure metals possess tetrahedral and octahedral cavities. When an alloy is made, larger metal ions will be introduced into the lattice of a parent metal. They occupy the cavities, but are often too big for them. For that reason the configuration in the neighbourhood of a cavity is disturbed and it will be more difficult to process the metal (alloy) than the parent metal; parts of the crystal lattice can no longer slide along crystal planes due to the earlier mentioned disturbances. The introduction of smaller atoms (e.g. C) increases the metal's resistance against deformation (process-ing). The smaller atoms do fit in the cavities, but they form bonds with the metal atoms and these bonds can cause disturbances.

10.4 PROPERTIES OF MATERIALS

The properties of materials can be divided into mechanical, physical and other properties. The last category comprises e.g. chemical properties. The nature of the bonds between the building blocks of a material and the energy present in these bonds are largely reponsible for the properties of a material. In general the bonds between ions with opposite charges are the strongest ones and the attracting Vander Waals forces between molecules (like e.g. thermoplastics) the weakest. Table 10.1 lists the bond or linkage energy of several bonds. This energy is needed to break the bond in question.

In this paragraph comparatively much attention will be paid to the curve in which tensile stress is plotted out in relation to relative elongation, because important properties can be inferred from this curve. One of these is the elastic modulus, a material property which was briefly discussed in chapter 9. This E-modulus often depends on the temperature and this relationship is represented in a log *E–T* curve. Next properties of the three groups of materials are compared in a table and finally some attention will be paid to "processing" and "corrosion".

TENSILE STRESS AND ELASTIC MODULUS

When a certain tensile force is exerted on a material, the object will experience stretching. The force which is needed to obtain a certain elongation varies for each material and will strongly depend on the bond strength (table 10.1). In practice the force is divided by the original cross-section of the sample and we apply the concept of relative

Table 10.1 Bond or linkage energy of several kinds of bonds

type of bond	bonding or linkage energy (kJ per mole)
ion bond	600 to 1500
covalent bond	500 to 1250
metal bond	100 to 800
Van der Waals bond	< 50

elongation and the following formulas:

$$\text{tensile stress } \sigma = \frac{F}{A_0} \text{ N (ewton)/mm}^2$$

A_0 is the initial cross-section of the object;

$$\text{relative elongation } \varepsilon = \frac{l - l_0}{l_0}$$

l_0 is the initial length of the object, l is the length under the influence of force F.

When σ is plotted graphically in relation to ε, then a graph arises which is characteristic for a certain material kind; a random example is shown in figure 10.6.

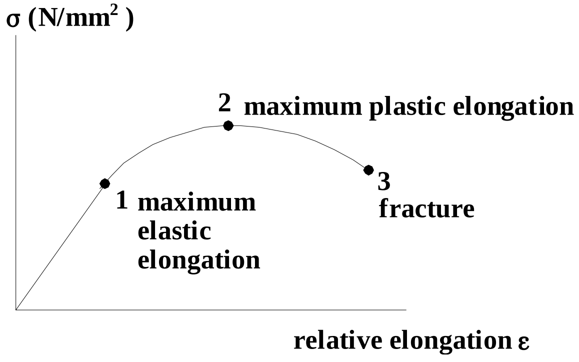


Fig.10.6 The tensile stress as a function of the relative elongation in a tensile test

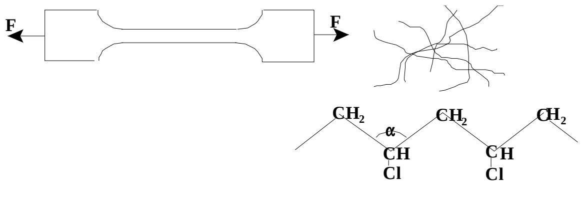
The first part of the graph is linear for most materials and is used to determine the elastic modulus or E-modulus according to Hooke's law; in formula:

E-modulus (or Young's modulus) $E = \dfrac{\Delta\sigma}{\Delta\varepsilon}$ N/mm^2

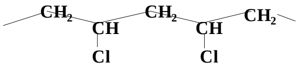
Up to point 1 in the curve the sample experiences an elastic elongation; i.e. when the stress is removed, the material returns to its original shape. Consequently the *E*-modulus is a measure for the elasticity and rigidity of a material.

What exactly takes place in a material during a tensile test?
We shall try to explain this on the basis of the thermoplastic PVC which is completely amorphous. The polymers chain form a tangle and each chain has the well-known zigzag shape of the carbon chain (figure 10.7). In figure 10.8 you can see the σ–ε curve of the PVC tensile test. Plastic tensile test specimens are flat and those of metals are often cylindrical.

During the initial phase of the tensile test the specimen experiences an elastic elongation or deformation and the carbon chains are elongated (figure 10.7). The narrow part of the specimen becomes narrower and longer. Then the elongated chains start to move along each other and at a certain moment the elastic elongation is replaced by plastic elongation. In the third phase mainly chains and possibly cross-connection situated in the centre of the specimen will break and the specimen will constrict. This constriction begins when the maximum of the σ–ε curve has been reached, i.e. a neck is formed



Tensile test specimen, polymer tangle and individual chain before the test



When a tensile force F is exerted on the specimen, the individual chains are first elongated, i.e. the bonding angle α increases

Fig. 10.7 The shape of a plastic tensile test specimen and the polymer chain before and at the beginning of the elongation of the carbon chain.

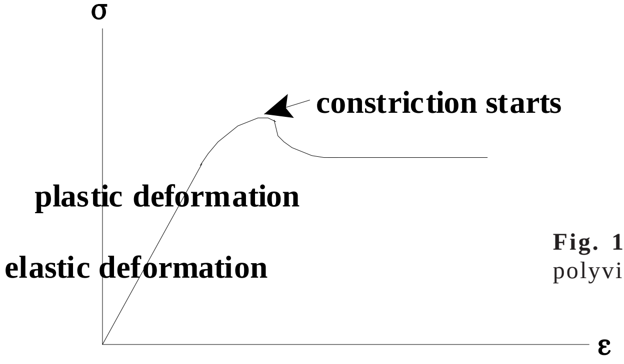


Fig. 10.8 The σ–ε curve of polyvinyl chloride PVC.

in the middle of the specimen. Once the process of constriction has been started, smaller forces are needed to continue the elongation. All of this is represented in figure 10.8.

When a metal specimen is subjected to the tensile test, the micropores around the centre of the dumbbell start to grow and combine. As soon as the metal wall which is initially still intact is no longer able to withstand the stress, the object tears. Apart from the above-mentioned growth of the pores, sliding processes in the crystal lattice also play a part in the formation of the fracture.

Fractures in ceramic materials are elaborately discussed in chapters 9 and 14.

Which properties can be inferred from the tensile test?

Three important properties can be inferred from the tensile test: i.e. elastic limit (i.e. the point of maximum elastic elongation), tensile strength and *E*-modulus. In many cases the transition point between the elastic and plastic deformation is not visible in the graph. For that reason it has been determined that this point is situated at an value of 0.002 and the accompanying tensile stress is determined as represented in figure 10.9.

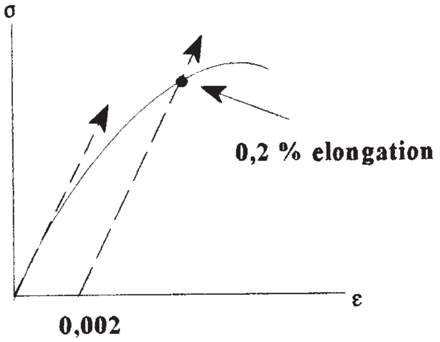


Fig. 10.9 Transition between elastic and plastic deformation (0.2% elastic limit).

Tensile strength is the maximum load that a material can support and this value can be found at the top of the curve.

A calculation example:

Suppose a specimen is cylindrical in shape and its middle has a cross-section with a radius of 6.4 mm. Calculate the tensile stress when the tensile force is 31136 N.

$$A_0 = \pi \times r^2 = \pi \times (6.4\,\mathrm{mm})^2 = 128.68\,\mathrm{mm}^2$$

$$\sigma = \frac{F}{A_0} = \frac{31136}{128.68}\ \mathrm{N/mm^2} = 242\ \mathrm{N/mm^2}.$$

A practical example:

Suppose a cylindrical aluminium rod in a construction will have to be able to withstand a maximum tensile force of 3×10^5 N. The engineer can use the σ–ε curve to determine that the safe tensile stress is maximally 170 $\mathrm{N/mm^2}$ with an accompanying $\varepsilon = 0.003$. The rod should at least be 5 m long and should not elongate more than 5 mm. What is the maximum length of the rod?

$$A_0 = \frac{F}{\sigma} = \frac{3 \times 10^5}{170}\,\mathrm{mm}^2 = 1756\,\mathrm{mm}^2$$

$$1756\,\mathrm{mm}^2 = \pi \times r^2 \rightarrow r = 24\,\mathrm{mm}$$

$$\varepsilon = \frac{5}{5000} = 1 \times 10^{-3}$$

However, at 170 $\mathrm{N/mm^2}$ ε is equal to 0.003 and, consequently, is much too high. That is to say that under the given circumstances the length of the rod can be at most:

$$l_0 = \frac{5}{0.003} = 1667\ \mathrm{mm} = 1.67\ \mathrm{m}$$

Comparison of the properties of plastics, metals and ceramics in the form of a table

Table 10.2 comprises a number of properties of the three mateial groups which serves as a comparison. The properties “corrosion” and “process-

Table 10.2

Properties	▦	▨	▩
	Plastics	Metals	Ceramics
Mechanical properties	deform both elastically and plastically under the influence of external forces	not brittle deform both elastically and plastically under the influence of external forces (◊)	hard, strong and brittle
Physical properties	TENSILE STRENGTH (GPa) (1 N/mm^2 = 1 MPa): PE............. 0.9–5.4 Styrene acrylonitrile (SAN) .... 10 - 12 MELTING POINT: PE .... 120 °C PS .... 70 °C THERMAL CONDUCTIVITY (W/m.K): PE .... 0.38 PS .... 0.13 THERMAL COEFFICIENT OF EXPANSION ($\times 10^{-6}$ cm/cm.°C): PE .... appr. 140 PS ....appr. 68	TENSILE STRENGTH (GPa) (1 N/mm^2 = 1 MPa): Mn steel... 102–1587 Al .... 69 W .... 408 MELTING POINT: Al .... 660 °C Cu ....1063 °C W ....3310 °C THERMAL CONDUCTIVITY (W/m.K): Al .... 247 Cu .... 398 THERMAL COEFFICIENT OF EXPANSION ($\times 10^{-6}$ cm/cm.°C): Al .... 24 Cu 17	MELTING POINT: Al_2O_3 .... 2050 °C SiO_2 .... 1650 °C THERMAL CONDUCTIVITY (W/m.K): Al_2O_3 .... 30 SiO_2 .... 2 THERMAL COEFFICIENT OF EXPANSION ($\times 10^{-6}$ cm/cm.°C: Al_2O_3 .... 9 SiO_2 .... 0.5
Other properties		Good conductor of heat. Conductor of electricity. Relatively high melting points. Opaque.	High heat capacity. Low heat conduction. Electric insulator or semiconductor or superconductor. Sometimes magnetic.
	Corrosion sensitive ◊ ◊	Corrosion sensitive ◊ ◊	Corrosion resistant

ing" will be further discussed later in this text. Please note that the filling-in above the individual columns symbolizes the structures of the material groups in question. In addition the reader should realise that most of the mentioned properties apply to the majority of the material group. In every group there is a grey area with properties which can occur in more material kinds.

Sometimes pure metals are used, but mostly alloys are applied because specific combinations of properties can thus be achieved. Most ceramic applications are discussed in chapter 11.

(◊) Processing materials

The mechanical properties of materials are of enormous influence on the way these can be processed. After a molten metal has cooled to a solid, the solid metal is mechanically moulded into the desired form. The way of cooling and the final shape to a large extent determine the properties of the product. By means of a heat treatment it is possible to alter the properties of some metals. In this process the polycrystalline material is converted to a less polycrystalline form and eventually a state is reached which comes close the the ideal state, i.e. the metal is nearly monocrystalline (figure 10.10).

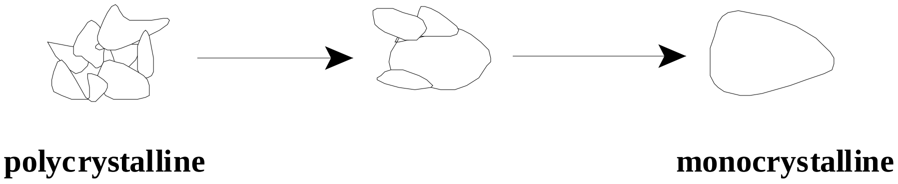


Fig. 10.10 The change from a polycrystalline to a monocrystalline form.

A polycrystalline material consists of a number of small crystals with an identical crystal structure, but they randomly oriented in relation to each other. A monocrystalline material, however, only consists of one crystal. Small-grained metals are stronger, but less ductile because sliding movements within the crystal are impeded during the processing. It is possible to see grain boundaries with the help of a simple microscope. In that case the metal surface is ground, polished and chemically etched respectively. The grain boundaries are etched more strongly than the rest of the material, because they exhibit a relatively larger surface and the crystal structure is interrupted there.

(◊ ◊) Corrosion

With chemical corrosion we mean the decay of a material under the influence of a corrosive substance. When brass contains more than 15 % (m/m) of zinc, the zinc and copper ions dissolve in an aqueous environment at a high temperature. Subsequently the copper ions are deposited on the metal surface. Nitric acid is able to selectively dissolve iron out of certain ceramic materials. Molecules of a solvent can penetrate a non-crystalline thermoplastic resin when the temperature is higher than a characteristic temperature value for that thermoplastic material, i.e. the so-called glass transition temperature. At this temperature the plastic converts from a vitreous, brittle state to a rubber-like one. As soon as the molecules of the solvents penetrate the plastic, it will start to swell.

Another example of corrosion is electrochemical corrosion. A well-known example of this is the rust formation on the body of a car. Such a process requires two electrochemical elements, transport of electrons and a closed “circuit”. Suppose two steel tubes are connected by means of a copper fitting and water flows through them. In that case electrons from the iron atoms in the steel will move in the direction of the fitting and the thus formed Fe^{2+} ions will be given off to the flowing water. The tube “decays”.

11

11.1 Fine Ceramics

11.1.1 Introduction

The name *fine ceramics* is based on the grain size distribution of the hard components in the ceramic mass. This rather differs from the distribution as it is seen in the ceramic branch of industry which produces for instance bricks, the coarse ceramic industry. Another difference is that all fine ceramic products are provided with a protective and in some cases also decorative coating, a so-called *glaze*. In this section much attention will be paid to glazes because this technique is rather unique for fine ceramics and because it offers the possibility to explore the subject 'glass'and some important physical and chemical properties of materials.

11.1.2 Raw materials

The raw materials for the sherd are: clay, kaolin, feldspars, quartz, carbonates, these are roughly the same ones as are used in coarse ceramics. In addition a number of 'unique' raw materials are applied in the glazes of fine ceramics, but more on this later. More water is used in fine ceramics than in coarse ceramics, mainly due to the mass preparation systems which are applied to obtain a homogeneous composition: slip casting, wet and dry moulding, the latter of which is preceded by spray drying. *Clay* is a plastic component. Other raw materials are added to it in order to adjust the plasticity of the clay to a specific product or production process. In addition, drying, firing and application properties are optimised. Before firing *the feldspars* make the clay less fat and during firing they act as a flux. They gradually transform from a tough smelt to a slightly liquid state and are among the first components to start to melt and subsequently incorporate other components into the smelt. Their contents vary form 5–20% (m/m) in sanitary ware and pottery to 20–40% (m/m) in porcelain. *Quartz* also make the clay less fat and it prevents warping of the product during drying and reduces shrinkage during drying and firing.

When a product is being fired, changes of quartz modifications occur which can lead to volume changes and damage to the green form. In order to prevent these changes as much as possible, quartz is preferably added in an amorphous form, e.g. in the form of flint. *Carbonates* are added to bind the amorphous SiO_2 which originates from the clay minerals and is redundant after firing, to form anorthite $Ca[Al_2SiO_8]$. The oxides which are formed of the carbonates and the anorthite act as a flux. The *aluminium oxide* which is present in the clay for instance increases mechanical strength, temperature resistance, and fire resistance.

11.1.3 Moulding techniques

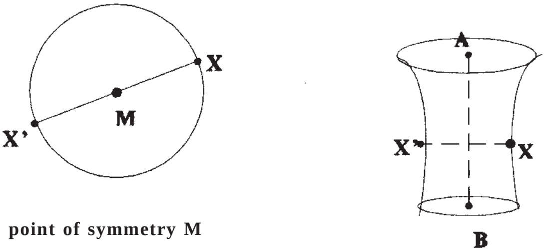
As moulding techniques turning, casting and pressing are applied. Casting (nowadays pressure casting) and pressing have already been discussed in chapter 9, Ceramics in general. Casting requires relatively much time and consequently results in a relatively low production speed. The method is only applied when turning or pressing is not possible, for instance in the manufacture of jugs and sanitary ware. Crockery and tiles are mostly pressed.

Turning takes place on a potter's wheel and is only suitable for so-called *rotation symmetric shapes*. This means that the objects which are made, such as plates, dishes and vases, are symmetric along an axis or point of symmetry.

As you can see in figure 11.1.1 each point X on a rotation symmetric object has a mirror image X' with respect to the axis or point of symmetry.

11.1.4 Drying and firing

After it has been moulded, the green product must be allowed to dry. Before the firing process can take place the green product must be



point of symmetry M

axis of symmetry AB

Fig. 11.1.1 Rotation symmetric objects.

nearly completely dry. The water which is bound to the clay minerals is not removed during drying. The drying result and consequently also the shrinkage during drying are determined by the composition of the mass, the size of the grains and the densification, the moisture content, the sherd thickness, the drying temperature and drying speed. When the green product still contains too much moisture, this can negatively affect the final product. During firing the object dries quickly at the surface, causing the surface pores to shrink and almost disappear. When the trapped water subsequently evaporates, cracks are formed because the water is unable to evaporate through the pores. Drying ceramics is a science in itself and involves the use of many different machines, instruments and techniques.

After the product has dried, the firing process follows. The product completes a certain temperature curve in a kiln. The atmosphere inside the kiln is of great importance; by heating in a reducing or oxidising atmosphere you can affect the colour of both glaze and sherd. First the remaining water evaporates. A temperatures of 400 °C and higher the crystal water is removed from the kaolinite. After that the mass can no longer be plasticized by absorbing moisture. At temperatures between 900 and 1000 °C sintering takes place and the material acquires its strength. Like the shrinkage during drying, the shrinkage during firing can also be determined dilatometrically in a firing experiment. Many types of kilns and heating techniques are applied.

11.1.5 Glazes

Introduction

In this section glazes will be discussed intensively as the subject offers the opportunity to elaborate to the material glass, which is closely related to glazes. In chapter 9, Ceramics in General, glazes were already mentioned briefly as a type of coating on certain types of ceramics to protect the surface and improve the aesthetic value of the product. Well sintered clay-ceramic objects mostly have a dull and rough appearance after firing. The reason for this lies in the fact that crystalline components are present in the top layer. You can improve the product by applying a glassy coating.

Historically seen the oldest coatings consist of finely grained, plastic clay types and are called *engobes* or clay coatings. The raw material of red and brown engobes is a colour-firing clay and multicoloured engobes are made with white-firing clay to which for instance 6% (m/m) iron(III) oxide for a red-brown colour and 3–10% (m/m) chromium(III) oxide for a bright to dark-green colour have been added.

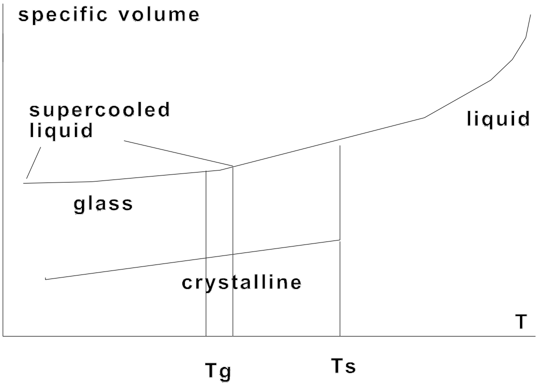


Fig. 11.1.2 Specific volume versus temperature for a glass.

Why these compounds produce these specific colours will be explained elsewhere in this section.

The so-called ‘terra sigillata’ (pottery with small decorations) from Greece and later also from the Roman Empire is an example of ceramics with engobes. Later people also started to use oxides and mixtures of oxides, the *glazes*.

In literature opinions differ on the use of the first glazes. These are dated between appr. 4000 and 3300 B.C. According to A. Avgustinik and I. Metreveli a mass production of domestic earthenware with alkali or lead glazes existed in Egypt in about 4000 B.C. It is assumed that the discoveries of glazes and glass were serendipitous and took place nearly simultaneously at several places in about 12,000 B.C. The firing condition at that time were quite primitive and consequently it was unavoidable that impurities (often oxides) came into contact with the products to be baked. Glazes resemble glass and so let us first have a look at some theoretical aspects concerning glass.

Glass

Starting point for the manufacture of glass is a mixture of oxides and possibly compounds which form oxides at high temperatures. This mass is first mixed vigorously and then molten. The result is an extremely viscous mass. When this mass is cooled down quickly, a material is formed which is mainly amorphous, a glass. By cooling it more gradually you get a more stable, mainly crystalline mass. So glass is in a so-called metastable state. This is represented in figure 11.1.2.

T_g is the so-called glass temperature and this varies according to the cooling speed. T_s (T_{solid}) is the temperature at which the solid is formed.

UNDER WHICH CIRCUMSTANCES IS A MIXTURE CAPABLE OF FORMING A GLASS?

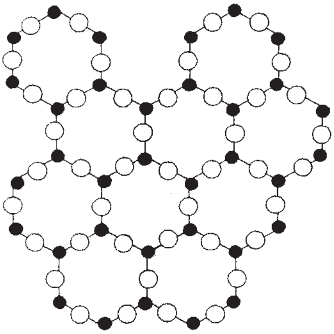
There is a possibility of glass formation when a mixture of compounds crystallizes with difficulty. In general this condition is met by substances which, in a liquid form, are built up of complicated, irregularly built structures that cannot easily be fit into an ordered crystal lattice. In addition rapid cooling increases the viscosity and this is at the expense of the freedom of movement of the building blocks; thus the formation of a regularly packed lattice is severely hindered. Quite often these substances form networks in their liquid phases. In organic chemistry resins are examples of substances which exhibit this phenomenon. In inorganic chemisty some examples are the elements O, S, Se and Te, the halogenides BeF_2 and $ZnCl_2$, the sulphides and most importantly:

$$B_2O_3 \qquad SiO_2 \qquad P_2O_5 \qquad P_2O_3 \qquad GeO_2$$

These compounds are called *network formers* and they already form large networks of molecules in the smelt. During this formation tetrahedral groups are strived for, like

$$BO_4 \qquad SiO_4 \qquad PO_4 \qquad BeF_4$$

As a rule every anion O^{2-}, F^-, etc. is not bound to more than two



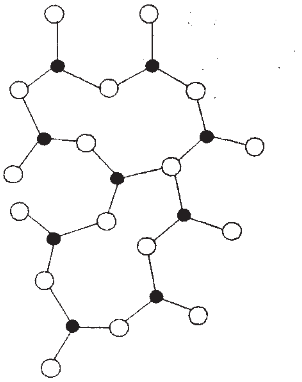


Fig. 11.1.3 Organized quartz structure.

Fig. 11.1.4 Unorganized structure of quartz glass.

cations. When the temperature drops the networks become more extensive and as a result of the increasing viscosity they are no longer capable of forming a crystal lattice. In figure 11.1.3 and 11.1.4 the organized structure of quartz and the unorganized structure of quartz glass can be seen . For clarity's sake the Si–O distances are larger in figure 11.1.4 than in figure 11.1.3.

When other components are added to the quartz smelt with a structure as shown in figure 11.1.4, a glass with a different network will be formed. The alterations in the networks are caused by the added cations and these are consequently called *network alterers*. They make sure that the network corners are broken. Where the breaks occur, places with a negative charge are formed and these must be compensated by the positively charged network alterers (figure 11.1.5).

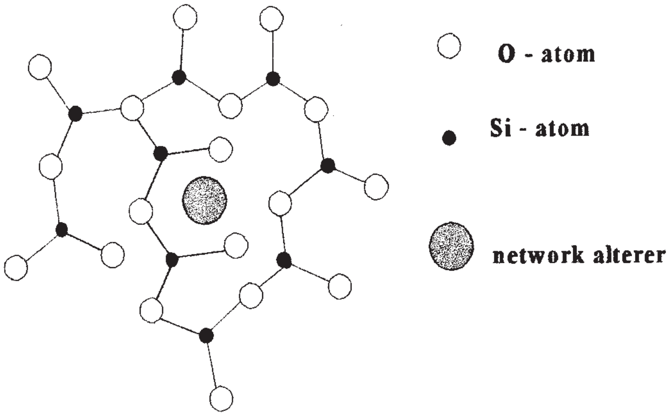


Fig. 11.1.5 Network alterers in quartz glass.

Examples of network alterers are the oxides of alkali and alkaline-earth metals which often ensure a disruption of the tetrahedral coordinations and then form octahedral coordina-tions at various places. By introducing network alterers you can change the properties of the glass, which can be illustrated with the following example:

— *Borosilicate glass* mainly consists of SiO_2 and B_2O_3:
  ** free of alkaline-earth metals %(m/m) SiO_2>80%, B_2O_3 12–13%
  –high chemical resistance, so suitable for syntheses
  –limited expansion
  ** containing alkaline-earth metals appr. 75% (m/m) SiO_2 8–12 % B_2O_3 at most 5% alkaline-earth metals and Al_2O_3

–slightly softer glass type
–higher rate of expansion
** 15–25 % (m/m) B_2O_3, 65–70 % SiO_2, rest: alkali + Al_2O_3
–very good insulator
–low chemical resistance
–use: oven-proof dishes

Raw materials for glass

One of the most important raw materials for glass is *sand*, which is mostly not pure enough and often contains coloured oxides, such as iron (III) oxide. For that reason silver sand is used for optical glass as it contains less than 0.001% (m/m) Fe_2O_3 and has a proportionally low TiO_2 content. The melting point of sand can be reduced by adding sodium oxide in the form of sodium carbonate. At a sufficiently high temperature potassium carbonate breaks down into the required *potassium oxide* and carbon dioxide. As *network formers* and *network alterers* CaO, MgO, Al_2O_3 and ZnO are used. *Feldspars* supply aluminium oxide. It forms AlO_4 groups in the smelt which enclose the alkali ions and thus close the open spaces in the network. Higher percentages of *lead (II) oxide* increase the melting temperature. The mineral witherite, $BaCO_3$, is the source of *barium oxide* in optical glass. Sodium and calcium borates which can be found in nature are used as raw materials for *boron oxide*. And finally glass can be coloured by compounds of for instance:

copper	black, blue
chromium	green, yellow
manganese	violet
iron	yellow, brown, blue, green
cobalt	blue, green

Raw materials for glazes

The raw materials for glazes are almost identical to the ones for glass. Aragonite $CaCO_3$ and dolomite $CaCO_3.MgCO_3$ both break down into CaO. The properties of glazes are strongly influenced by the kind of raw material used due to the different melting properties and the chemical activities during melting. Even slight pollutions can affect the glaze – for example, nowhere in the world can two identical kinds of argonite be found and the same goes for all minerals.

We also need additives for the production of glazes. 35–50% of the mass consists of water. When the glaze contains clay minerals, even more water is needed. The amount of water and the quality of both the water and the additives affect the reological behaviour of the glaze sludge. The hardness of the water is also of vital importance. This hardness is often expressed in degrees of German hardness (°D), where 1 DH is equal to 10 mg CaO in every litre of water. Dissolved gases and salts are also of influence. For example calcium hydrogen carbo-nate ($CaHCO_3$) is deposited in the form of carbonate during the drying of glazes. When the product is then fired, the carbonate can release carbon dioxide and thus cause bubbles in the glaze. Soluble, toxic or gas-forming minerals are often pre-melted to form a more or less stable glass.

The composition of glazes

The composition of glazes is represented on the basis of three groups of oxides and according to the Seger formula. The most used oxides, divided into three groups, are listed in table 11.1.1.

Table 11.1.1 Oxides as raw materials for glazes

alkaline oxides		amphoteric (or neutral) oxides	acid oxides
Na_2O	CaO	Al_2O_3	SiO_2
K_2O	ZnO	Cr_2O_3	TiO_2
Li_2O	BaO		ZrO_2
MgO	PbO		SnO_2
	SrO		B_2O_3

The composition of the glaze is expressed as a mole proportion. The Seger formula applies when the mass of the alkaline substances is 1 mole. Some examples:

** An example of the Seger formula is: 1.0 PbO, 0.1 Al_2O_3. 1.0 SiO_2. For this we need:

for PbO : 1/3 mole Pb_3O_4 = 229.0 g Pb_3O_4
for Al_2O_3 : 0.1 mole kaolin $Al_2O_3.2\ SiO_2.2H_2O$ = 25.8 g kaolin
for SiO_2 : 0.8 mole quartz = 48.0 g quartz
(0.2 mole of SiO_2 was already introduced through the kaolin!)

180 g PbO (M = 229 g/mole)	25.0 g dolomite $CaCO_3.MgCO_3$ (M = 184.4 g/mole)	60.0 g KALIVELDSPAAT $K_2O.Al_2O_3.6SiO_2$ (M = 556 g/mole)
0.786 mole PbO	0.136 mole CaO 0.136 mole MgO	0.108 mole K_2O 0.108 mole Al_2O_3 0.648 mole SiO_2
0.786 mole PbO 0.136 mole CaO 0.136 mole MgO 0.108 mole K_2O .... + 1.166 mole	0.108 mole Al_2O_3	0.648 mole SiO_2
Of the individual oxides, the number of moles of substance must be divided by 1.166 since the number of moles of alkaline oxides must be equal to 1.0000 in the Seger formula. Consequently, the Seeger formula is as follows:		
0.674 mole PbO 0.117 mole CaO 0.117 mole MgO 0.092 mole K_2O	0.0926 mole Al_2O_3	0.556 mole SiO_2

** The table on the following page illustrates the conversion of a glaze composition in grammes to the Seger formula in the last row of the table.

The colours of glazes

In order to explain the colour of glazes we first have to return to the atomic model, which is much more sophisticated than the Bohr atomic model mentioned in chapter 3, Chemistry. In that chapter we saw that all electrons move around a nucleus in regular orbits, the K shell, L shell, M shell etc. This model gave the impression that the distance between the electron and the nucleus is always the same. However, in reality the atomic model is much more complicated than that which means for instance that:

– electrons do not orbit the nucleus in circular paths but in so-called orbitals and they do not exhibit a constant distance to the nucleus. Such an orbital is a theoretical volume with a certain shape in which the electrons move. The simplest type of orbital is the s orbital; only one type of this is known, i.e. the sphere. In addition there are the *p*, *d* and *f* orbitals, the latter two in more than one form. In figure

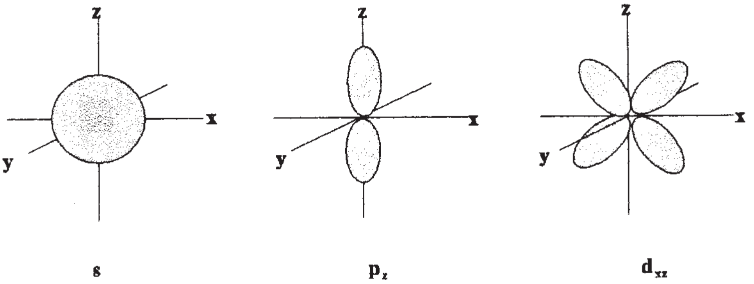


Fig. 11.1.6 Three types of orbitals.

11.1.6 three orbitals have been represented in a three-dimensional system of axes. The indications *x*, *y* and *z* behind the letter of the type of orbital indicate the position of that orbital with respect to the axis in question.

So naturally the electron distribution over the K, L, (etc.)shells according to Bohr will now become the electron distribution over the orbitals. In Fig. 11.1.7 this distribution is represented. As mentioned earlier, the letter *s*, *p*, *d* and *f* indicate the type of orbital. The numbers 1, 2, etc in front of the letters refer to the 'old' K, L (etc.) shells. In order to interpret this figure correctly you should know that each orbital can only contain a maximum of two electrons. Moreover it is important to mention that there are three p orbitals, i.e. p_x, p_y and p_z and five *d* orbitals.

An atom is built up by filling the orbitals with electrons, starting with arrow 1 in the filling plan. An example in which the 'new'

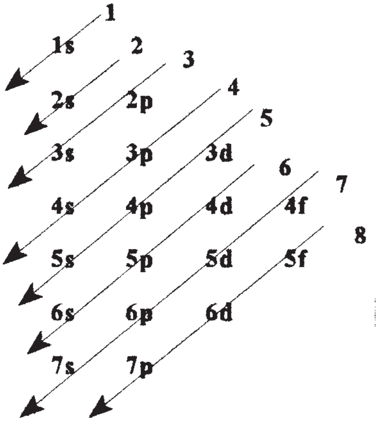


Fig. 11.1.7 Filling plan of the atomic orbitals.

atomic model is compared with the Bohr model:

electron distribution of ${}_6C$ according to Bohr: K2 L4
according to the new method: $1s^2$ $2s^2$ $2p^2$

This means that the two electrons of the K shell are now in the *s* orbital and the four electrons of the L shell are distributed over one *s* and two *p* orbitals. A more detailed electron distribution would be: $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$ as there are three *p* orbitals and the available electrons should be distributed evenly over those orbitals.

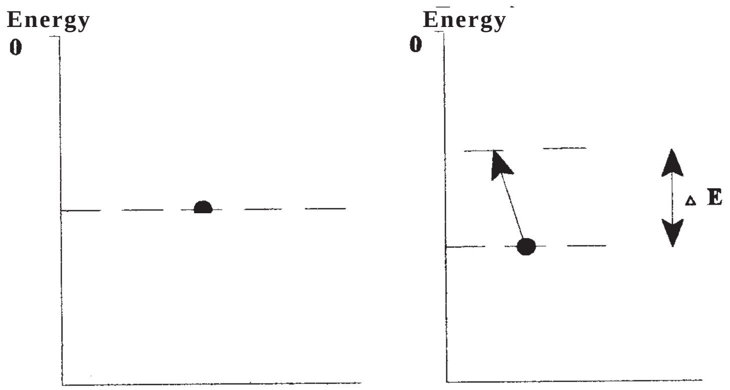
electron distribution of ${}_{28}Ni$: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^8$

Don't forget that $2p^6$ is in reality $2p_x^2\ 2p_y^2\ 2p_z^2$ and that the eight *d* electrons have been evenly spread over the five *d* orbitals according to 2 2 2 1 1.

Now that we have seen that the electrons are situated in certain areas (orbitals) surrounding the nucleus, let us have a closer look at the distance between an electron and a nucleus and also at the accompanying gravitational force. The closer the electron is to the nucleus, the larger this force is and the more energy is required to release the electron from that force. In the physical formulas (which we will not mention here) the charges of the nucleus and the electron must be multiplied and the result will obviously be negative. Consequently an electron close to the nucleus has a large negative energy value and electrons at a greater distance from the nucleus have a smaller negative energy value.

And now back to the coloured compounds and thus also to the coloured glazes. A *coloured glaze usually contains one or more compounds of metal ions from group 3 up to and including 12 of the periodic table and these elements usually have valence electrons in d orbitals.* Around these metal ions other particles have been arranged, the so-called ligands. We are already familiar with these compounds, e.g. the water-dissolved Cu^{2+} ion. The blue colour of this solution is caused by the $[Cu(H_2O)_6]^{2+}$ particle, a hydrated copper ion with six water molecules as ligands. The dark red colour of ruby and the green colour of emerald have the same origin. Ruby is a variation on corundum (Al_2O_3), a mineral which is colourless in a pure state. A pollution of at least 1% (m/m) chromium(III) oxide will already colour corundum red.

In figure 11.1.8 you can see an energy diagram with in it a valence electron in the *d*-orbital of a random metal ion from one of



Electron in a *d*-orbital of a metal ion without ligands

Electron in a *d*-orbital of a metal ion with ligands

Fig. 11.1.8.

the groups 3 up to and including 12. When the metal ion is not yet surrounded by ligands it does not matter in which *d*-orbital the electron is situated; the energy value will be the same in all cases. However, when we place ligands around the ion, such a ligand can assume a position close to an electron in a d orbital or at some distance from such an electron. Should a ligand end up in the vicinity of an electron, the energy value of that electron will increase and the energy values of the other electrons will decrease. As a result an energy difference ΔE is created and when no energy is supplied to the particle (ions and ligands), the electron will find itself in the lowest energy level.

When a metal ion with ligands is exposed to daylight, the particle will absorb a certain amount of energy ΔE and one or more electrons will move from a low energy level to a higher one:

$$\Delta E = h\frac{c}{\lambda}$$

where h is a constant, c is the speed of light, λ is the wavelength of absorbed radiation

From this formula it appears that: the larger ΔE is, the smaller the wavelength of the absorbed radiation will be. ΔE is determined by the combination of metal ions and ligands. When you remove a colour (which is a particular wavelength) from the daylight, the human

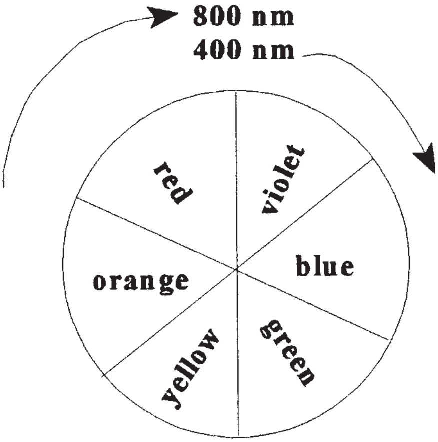


Fig. 11.1.9 Colour circle.

eye will perceive the radiated sample as having the so-called complementary colour. Figure 11.1.9 is a colour circle which is the so-called visible part of the spectrum with wavelengths of 400–800 nm (1 nm = 1 nanometre = 10^{-9} m). In it, the complementary colours are diametrically opposed.

For instance: when a sample absorbs radiation with a wavelength of 520 nm from the green wavelength area, it has a red colour.

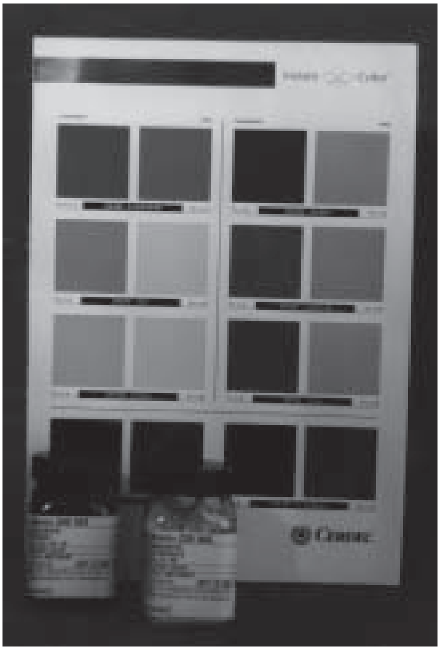
The (simplified) theory of coloured compounds with metal ions from groups 3 up to and including 12 described above can be applied to solids and liquids. In this chapter. it serves to explain the colours of glazes and in chapter 11.2 Coarse Ceramics it explains the red colour of certain bricks.

A change in colour can easily be demonstrated in a solution as there is question of simple particles here. In a solid this is most of the time much more difficult because a change of ligands means that the crystal structure will have to be broken down and rebuilt again, either partially or completely.

Some experiments:

Solid copper(II) sulphate.pentahydrate with the formula $CuSO_4.5H_2O$ has a blue colour because $[Cu(H_2O)_4]^{2+}$ particles are present in the crystal lattice. When this substance is heated, the water molecules are released and it turns white.

A solution of nickel(II) sulphate is green. This colour is caused by the presence of $[Ni(H_2O)_6]^{2+}$ particles. When we add acqueous ammonia to this solution, there will be a change of colour to blue/violet due to the formation of $[Ni(NH_3)_6]^{2+}$.



Example of a glaze colour chart (Cerdec) *(by E.Bormans)*.

Properties of glazes

The following major properties will be discussed respectively: viscosity, surface tension, expan-sion, hardness and chemical resistance.

Glazes do not have a melting point. When they are heated they pass through a number of stages of decreasing viscosity before they become liquid and flow freely (figure 11.1.10). The composition of the mixture to a large extent determines the intensity of the network formation and consequently also the *viscosity*.

Viscosity cannot be calculated on the basis of composition. However, some rules of thumb exist about the relationship between viscosity and the presence of certain components. Thus viscosity increases as the mass percentage of network formers (e.g. SiO_2) increases, whereas it decreases when the mass percentage of components which loosen the network (e.g. alkaline-earth metals) increases. Actually users are only interested in the viscosity during firing; this should not change too drastically. A glaze with the correct viscosity at a firing temperature of appr. 1000 °C may need to undergo a change in composition in order to achieve the same viscosity at 1400 °C. Among

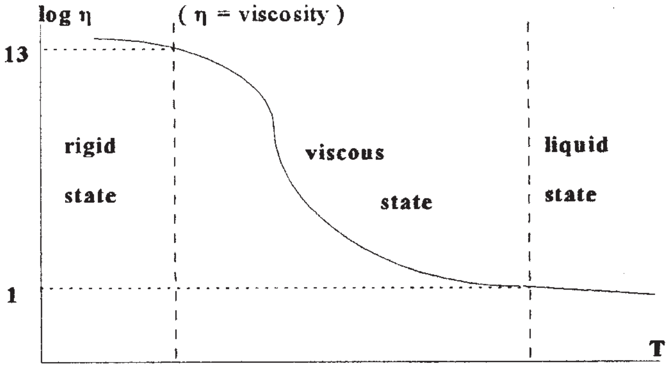


Fig. 11.1.10 Viscosity of a glaze as a function of temperature.

other things it is difficult to predict the chemical reactions which occur in the glaze during firing and they can give rise to changes in viscosity.

The *surface tension* of a smelt or liquid is based on the fact that the particles at the surface are only attracted by particles which are situated next to them. Particles well inside the liquid are attracted equally in all directions by the surrounding particles. Everyone is familiar with the surface tension of water, which can be viewed as a resistance to area expansion. It is as if the water has a skin. This can easily be demonstrated with the help of a tissue and a paper clip bent in a circular shape. Place the paper clip on the tissue and then carefully float both on water. The tissue will absorb water and sink, but the paper clip will be supported by the surface tension of the water and float.

Gnats can walk on water. The surface tension resists the expansion of the area which would occur if the gnat would push its legs through the surface. And finally, two water drops which make contact form one new drop. So apparently there is a constant tendency to minimize the area.

A too high surface tension in a glaze is mainly due to a firm, compact network. Glass bubbles which want to escape the sherd during the firing process are prevented from doing so by the glaze and this results in glaze faults.

The *expansion* and *shrinkage* of a glaze need to be finely tuned, especially during the simultaneous firing of sherd and glaze. When the glaze shrinks more during cooling than the sherd, cracks will form. However, when the amount of shrinkage exhibited by the glaze is less than that of the sherd, the result will be scaling. An object might even warp as a result of an excess difference between the shrinkages of glaze and sherd.

A number of designations are used in relation to *hardness*, all of which are based on different measuring methods. For instance, when you measure the mass which is required when a diamond produces a scratch with a certain width, this is called scratch hardness. It is a measure for the chemical and physical binding forces in the network of the glaze. In order to determine the imprint hardness, a diamond sphere is pressed against the glaze and the depth of the imprint is measured. Finally a glaze must be *resistant* to *chemicals*, notably moisture, diluted acids and bases, detergents and sanitary ware cleaning agents.

Glaze faults

Why an entire section on glaze faults? After all a ceramicist wants the glazing to run smoothly. And again this book proves its educational value: you can learn a lot from faults. A number of them can be linked to the glaze properties as described above. A coloured fleck is a black or brown impurity in the raw material. Dry spots or curled up glaze arise as a result of attachment defects due to dust or grease on the sherd. An kiln creep is a chip of oven material which has fallen on the glaze. Furthermore we distinguish holes or dents, bubbles, craters, decoration faults. From an educational point of view it is very interesting to introduce glaze faults on purpose.

A little bit of iron powder causes brown black flecks and copper powder green/blue ones. Wood and other organic particles result in dents, holes and craters and a grease stain on the sherd surface in a dry spot.

11.1.6 Some fine ceramic products

In Maastricht in The Netherlands two fine ceramic factories can be found: **SPHINX** which has three divisions: SANITARY WARE, TILES and TECHNICAL CERAMICS and **MOSA** which produces PORCELAIN.

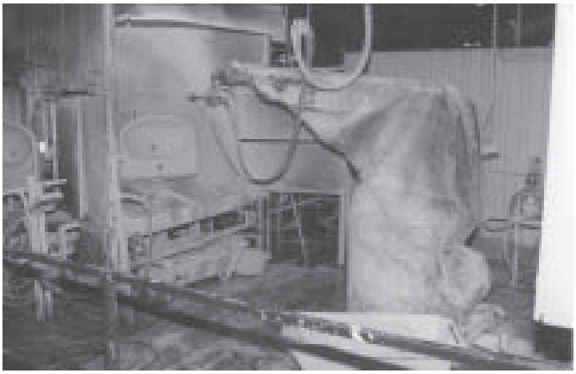
Among other things *Sphinx sanitary ware* manufactures washbasins and lavatory pans by means of slip casting. The moulds must be able to absorb a lot of water, for example 3 to 4 kg for a single basin.

That is why they are dried intensively after casting and can then be used several times a day. The average life span of a mould is about

Pouring clay suspension in a mould for producing a wash basin at Sphinx sanitary (by J.Aarsen).

Drying green toilet at Sphinx sanitary (by J.Aarsen).

100 castings. Then they are worn and will be rejected. When a lavatory pan is taken out of its mould it is still soft and difficult to manage. The green product will first undergo a partial drying process and before it can be further processed. The latter means that cast joints are removed and little imperfections are touched up. Subsequently the drying continues until the product is white. Next the glaze is sprayed. This is done twice because in order to ensure a proper bond the glaze needs to be applied in thin layers which should dry in between applications. Then the products to be glazed are transported to a tunnel kiln where the firing takes place.



Glazing a wash basin by robot at Sphinx sanitary (by J.Aarsen).

Wash basins on their way to the oven at Sphinx sanitary.

Closets in the oven at Sphinx sanitary (both pictures by J. J.Aarsen).

With sanitary ware the baking or firing process is a so-called single process. This differs from the firing process of tiles and pottery in which case the biscuit is fired first and then the product is subjected to glaze firing. In a tunnel kiln there is room for about 55 wagons and each 23 to 25 minutes a new wagon enters the kiln and another leaves it. In total each wagon is in the kiln for 21 to 23 hours; we call this the kiln cycle. The kiln's temperature curve can be seen in figure11.1.11. On leaving the kiln the fired products have a temperature of appr. 150 °C. They are subsequently cooled by ventilators.

The sanitary product must meet a number of requirements, most important here are dimensions and performance. The requirements as far as dimensions are concerned will be obvious. The products must fit certain, often small, spaces and they must be connected to standard service pipes and drains.

Showroom Sphinx sanitary at Maastricht, Netherlands (by J.Aarsen).

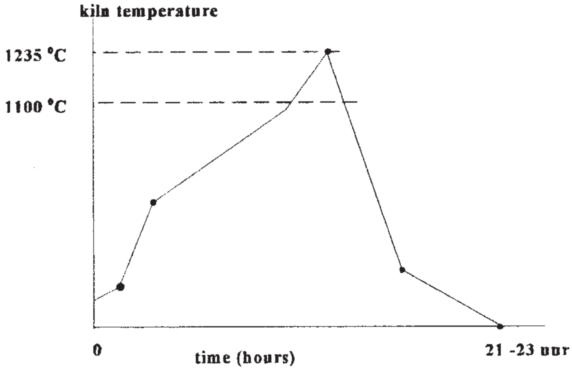


Fig. 11.1.11 Firing curve of sanitary ware.

Mainly lavatory pans and combinations of pans and cisterns are tested on their performance by means of a number of experiments. In the saw dust test the pan is sprinkled with 20 grammes of saw dust 5 times. By flushing once you should be able to remove most of the saw dust. In another test sponges shapes like faeces are placed in the pan and flushed away. The splash test is used to determine the amount of splashing water during flushing and whether or not it all ends up in the pan.

At *Sphinx tiles* wall and floor tiles are made. The mass for *wall tiles* is manufactured by grinding and mixing the hard materials sand, sherds, marls and coarse ball clay with the soft materials fine ball clay and china clay. These raw materials are mostly imported, because the clays found in The Netherlands are not fine enough. The hard materials are ground in a ball mill for appr. 5 hours. After that soft materials are added and the grinding continues for another hour. The resulting slip is sieved under constant stirring to avoid sedimentation. Then it stirred by blowing air into it.

In the next phase a spray drier converts the slip into a powder which is the raw material for pressing tiles at a pressure of more than 175 kg/cm^2. The moisture content is then reduced to 0–0.5 % (m/m) in a tunnel oven with a temperature of appr. 130 °C.

After the drying the firing process follows. We distinguish two types of processes here: double firing (for wall tiles) and single firing (for floor tiles).

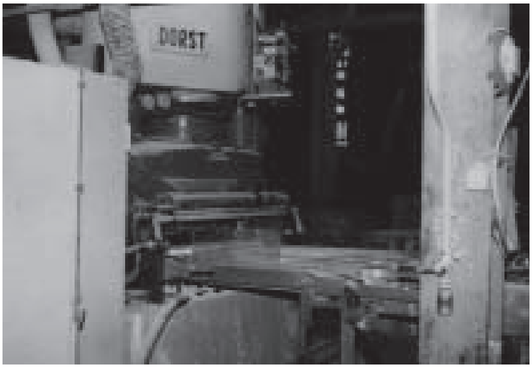
The first phase of the double firing is the so-called biscuit firing. This takes place in an appr. 100 metre long tunnel kiln at a temperature of appr. 1120 °C, The tiles remain in this oven for about 55 hours.

Then long conveyor belts transport the tiles through a glaze curtain and the tiles are decorated by means of serigraphy. Because of the high water absorption of the tile the water of the glaze easily penetrates the sherd. Homogenized, ground, coloured and unmolten glass remains behind on the tiles. The tiles enter the glaze kiln in this state. This oven is appr. 80 metre long and at most appr. 1060 °C hot. The glaze melts and is solidified again in the cooling zone and a glass-tight layer is formed. Tiles only remain in this kiln for 12–16 hours. Then they are ready for packaging and dispatching.

In case of single firing the sherd and glaze are fired in a simultaneous process. This is applied for floor tiles and traditionally takes place in a tunnel oven or in a quick firing process at a temperature of about 1170 °C. In case of a quick firing process the tiles are not transported through the oven in a compact way as in the tunnel oven, but in a single layer over ceramic or metal rollers. The duration can vary from appr.30 minutes to appr. 60 minutes. The requirements as far as purity of the raw materials is concerned are less strict due to the dark mass. A floor tile needs to be sintered much longer for the pores to close and the water absorption level to be low (< 2% (m/m)). For that reason melting agents are added, e.g. feldspars. Densification means mechanical reinforcement and this also prevents water penetra-tion, thus making the tiles frost resistant.

The glaze of a floor tiles differs substantially from that of a wall tile because the former must meet higher requirements as far as hardness is concerned. This is necessary to avoid wear as much as possible. Glazes of wall tiles are smooth at lower temperatures, which is consistent with their composition. The proportion of network formers and network alterers is higher in floor tile glazes. Their greater hardness and resistance to wear are determined by the nature, fineness and density of the crystalline structure which are mainly properties of lustreless glazes containing e.g. barium aluminium silicates or calcium aluminium silicates.

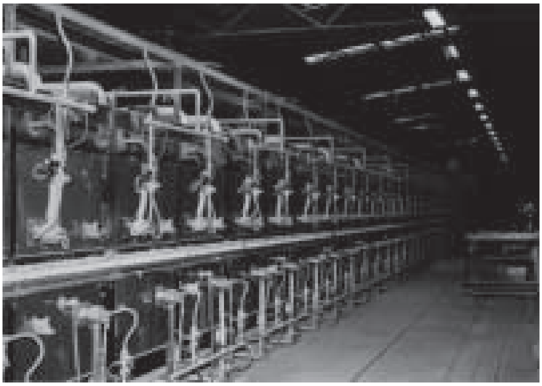
Grinding raw materials



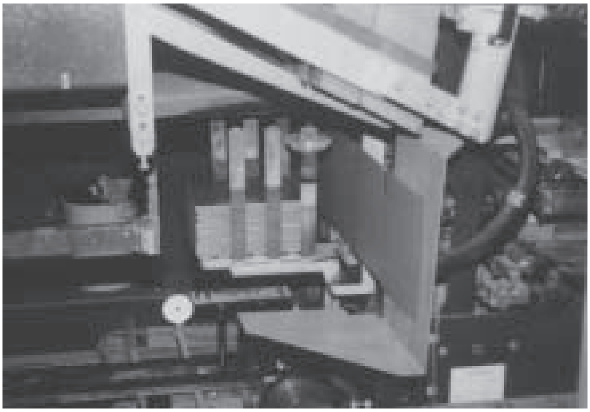
Pressing tiles

Glazing tiles

Decorating tiles



Outside of the oven



Sorting and packing tiles

Tile production at Trega International BV (Sphinx Tiles) Maastricht, Netherlands

11.2

Coarse Ceramics

11.2.1 Introduction

The difference between fine and coarse ceramics is based on the grain size of the hard components in the ceramic mass. In the case of fine ceramics this grain size is less than 100 μm and for coarse ceramics the grain size can be as much as 5 mm with a large range in grain diameters in between. Glazing is not a typical difference, although glazes are applied much more in fine ceramics than in coarse ceramics.

Some *products* of the coarse ceramic industry are: bricks, hollow building bricks, paving bricks, roof tiles, drain pipes, vitrified clayware products and insulation materials.

Vitrified clayware is sintered stoneware which is hardly porous and can withstand chemical and mechanical outside influences. For those reasons vitrified clayware is used for sewers, as a coating for vessels, reactor inlets, pipes, valves and pumps. Plastic clay with a relatively high content of aluminium and alkali metals and a low lime content is used as raw material

For the synthesis of insulation materials organic substances are added to the clay mass. During the firing the combustion products from those substances are responsible for the formation of cavities in the material.

Raw materials

In *The Netherlands* locally found clay is almost exclusively used as main raw material. The most important clay deposits for (paving) bricks are found along the river banks of Holland's main rivers. River clay from the polders is mostly fat to very fat and deficient in lime; consequently it is used in the production of e.g. roof tiles. We call a clay type "fat" when it contains a high percentage of minute particles. The Dutch coarse-ceramic clay is a sediment, appr. 45 % of whose particles have a diameter of < 10 μm. The coarser sand and silt fractions contain quartz and flint fragments, feldspar ($\leq$ 15 %), mica ($\leq$ 10 %) and lime grains ($\leq$ 25%).

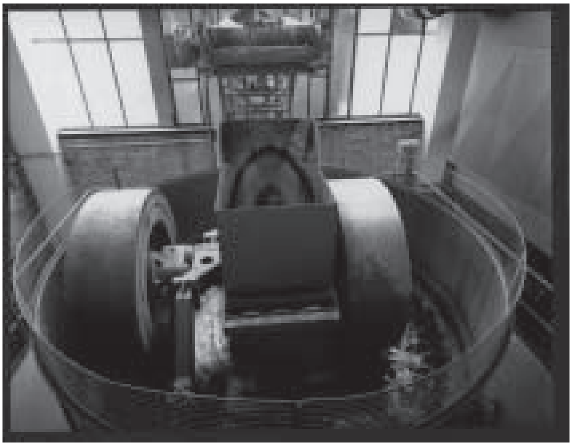
For some years now the brick industry has been researching the use of substitute raw materials, e.g surplus substances from other industries. A good example is the processing of mine-stone in a number of brick factories in the south of The Netherlands. Apparently prospects are good for the so-called Euroclay, which is made of clean dredge spoil from the Europoort area in Rotterdam, The Netherlands. Another alternative is a by-product in the processing of building and demolition waste. This slip results from the washing of rubble. When using substitute raw materials it is important to monitor a number of important factors carefully to ensure good product qualities. However, the employees' health and economic factors should also be considered. In addition it is important that the material will be amply available for a considerable period of time and that its composition is constant.

From a depot the clay is transported to the plant to undergo a *pretreatment* which varies for every branch of the ceramic industry. Conveyor belts or lorries then transfer the clay to a supply box, the Kastenbeschicker. As the German name already indicates, Germany is the cradle of the ceramic industry in Western Europe. This Kastenbeschicker contains a buffer stock and acts as a dispenser. Should this be necessary, it can be equipped with a stone and metal detector. The entire unit consists of a rectangular steel container, ~1.25 m wide and 5–10 m long. Its floor is a slowly moving conveyor belt which transports the material at a variable speed towards an open end with rotating arms. The scraping movement of these arms homogize the mass and the material is subsequently transported to the next unit.

Now the so-called *additives* are added. These improve the quality of the product and sometimes contribute to its colour. In coarse ceramics the clay mass is converted into a homogeneous, plastic mass by means of kneading and mixing. The various production sectors add different substances to the clay, often only minute quantities because the clay already contains the required additives in its natural form. These additives have little or no plastic properties. They may serve to regulate the plasticity and affect the drying and firing properties as well as the colour of the baked bricks. The most used additives are feldspars, quartz and lime. Feldspars are minerals which constitute appr. 60 % of the earth's crust. They are mixed crystals of orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$). Feldspars have relatively low melting points and retain their viscosity when they do melt. When the ceramic mixture is sintered, the feldspars form a glass and thus they bind the components which only melt with difficulty. They are mainly applied in sanitary ware and in stoneware masses. Quartz makes the clay less fat. As a result the mass is lighter, products do not warp as easily during drying and they shrink less. In coarse ceramics, quartz is considered to be inert. Calcium is added in the form of limestone, chalk or marl with the formula $CaCO_3$, calcium carbonate. During the firing the active calcium oxide (CaO) is formed which can start all kinds of reactions. Lime and the iron which is already present in the clay are responsible for a yellow colour in coarse ceramics; an well-known application is the production of yellow bricks. Very often water and / or steam are added to the clay during the pretreatment. The water makes the clay plastic and the steam raises the temperature, as a result of which the clay obtains even better plastic properties and its drying behaviour improves.

After the Kastenbeschicker several other machines carry out the subsequent pretreatment.The type of raw material and factory procedures determine which machines are used. Some of these machines are: clay rasp or Kollerwalze, differential rollers, Kollergang and pregrinder. Let us have a closer look at the Kollergang.

Kollergang: This machine can process both dry and plastic materials. Two heavy rotor discs move across a circular floor plate part of which is provided with sieve openings. The clay is pressed through the sieve which results in intensive mixing. The material behind the discs is continuously scraped loose.



Kollergang (Rieter–Werke Händle, Konstanz, Germany).

11.2.2 Bricks

History

When man still depended on the hunt, he lived in caves. He was not compelled to remain in one particular area, because wildlife was plentiful everywhere. Yet he made the change from hunter to farmer and as a result had to rely on certain fertile areas. So quite logically he needed a house to live in. First this was made of branches and twigs and subsequently the skeleton was covered with loam and clay. Loam is lean clay. Here ‘lean’ means less plastic than clay owing to a higher mass percentage of sand. Figure 11.2.1 is a phase diagram of the differences.

Later man started to build with blocks of dried clay. The first (baked) bricks were found in and near the area which is now called the Middle East. Catal Hüyük used to be a city on the Anatolia plateau in the centre of Turkey. According to archeologists it probably dates from approximately 8300 BC. For reasons as yet unknown the city was abandoned at around 5600 BC. Its houses had cornerposts of wood and cross beams. The rest of the wall consisted of loam bricks. However, loam has the annoying property that it disintegrates easily in a humid atmosphere. For that reason the houses needed to be repaired after every rainy season. At approximately 8000 BC a people in Jericho built round houses of hand-made loam bricks which were dried in the sun. Around 7500 BC people already knew how to make mortar. They probably heated limestone and mixed the thus formed burned lime with sand and water. In that case the following reactions occur:

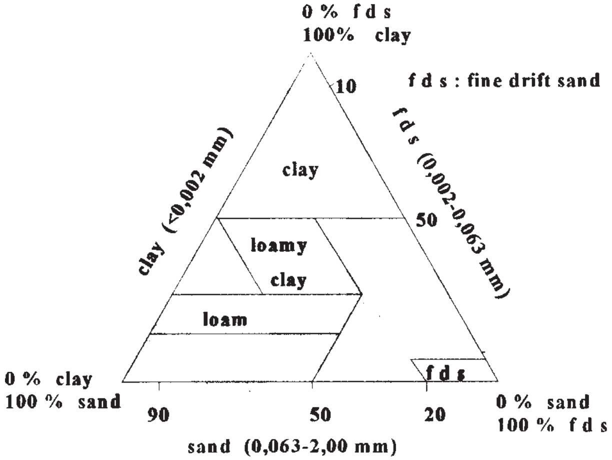


Fig. 11.2.1 Phase diagram of loam, clay and sand.

$$\text{limestone } CaCO_3 \xrightarrow[\text{heat}]{} \text{burned lime } CaO + \text{carbon dioxide } CO_2$$

$$CaO + H_2O + SiO_2 \rightarrow CaSiO_3$$

During the second reaction the bricks are ‘cemented’ together.

Experiment: The synthesis of ‘ancient mortar’ mentioned above as well as checking its working are quite simple experiments and consequently excellently suited for educational purposes.

They also found bricks with a fish bone design. The purpose of this design was probably not only to indicate the place of the brick in the wall but also to improve the bond between the brick and the mortar.

A ziggurat was a religious centre and the most important one is at Ur in the salt desert of South Iraq. It was built of loam brick and covered with brick joined together with asphalt.

About 4000 years ago the city of Moenjo-Daro perished. It was one of the first modern cities and was situated in the Indus valley, approximately 5000 km north of the present Karatchi in Pakistan. The city was very advanced. Its houses were made of weather-proof bricks and the bathrooms inside had water-proof tiling. There were even open, brick sewers connected to the drains of the houses.

In about 4000 BC the technique of baking clay for the manuafacture of utensils was well known in Mesopotamia and Egypt. In Assyria and Babylon, the two areas which - together with Mesopotamia - form a large area extending from the Persian Gulf between and on both sides of the Tigris and the Euphrates to approximately the city of Haran, buildings made of baked bricks dating from about 1000 BC were found. This area extends even further across what we now call Jordan and Israel and is also referred to as the Fertile Crescent. In the Euphrates, Tigris and Nile valleys history took an important turn in about 3200 BC with the advent of urban civilization. Around the cities irrigation channels and reservoirs were built for agricultural purposes and inside the cities a social organization developed. The first states arose and a system of symbols was developed to document trade in clay tablets. By elaborating this system man was able to record ideas, thoughts and events. This resulted in the first script.

In about 2500 BC an urban civilization starts to develop in the Indus valley in what we now call Pakistan. This civilization is approximately equally old as the one in Mesopotamia. Important cities were Mohenjodaro and Harappa which had rectangular houses along 8 metre wide streets. The cities were equipped with an extensive sewer system and the houses had bathrooms and brick toilets.

Brick production in Madagascar (by J.Aarsen).

In my own country, The Netherlands, the history of the brick starts in the 12th century. At that time the clay was shaped by hand and baked in so-called field ovens. During his holiday in Madagascar, my friend Jeroen made photographs which prove that bricks are still made in such a 'primitive' way to this very day.

The brick production

In the industrial world bricks are mostly made in an automated production process. After the raw materials have obtained the correct composition and plasticity, the *forming process* follows. In The Netherlands hand moulding, press moulding and extrusion moulding are applied in coarse ceramics. Occasionally the stamping press is still used, mainly in the manufacture of roof tiles.

Hand moulding is the oldest method. Wooden moulds with six or seven compartments of the desired size are used. First these are cleaned and then lubricated with sand to prevent the clay from sticking. A lump of clay is then rolled through sand or sawdust and forcefully thrown into a compartment. With a piece of wire, excess clay is removed from the top of the mould. Next the mould turned upside down and the shaped bricks fall out and are ready for transport. The baked bricks are characterized by an non-uniform texture. Nowadays handmoulding is often done mechanically.

In the *press process* the clay is pressed into a mould. Clays with low plasticity can be used and mostly sand-struck (paving) bricks

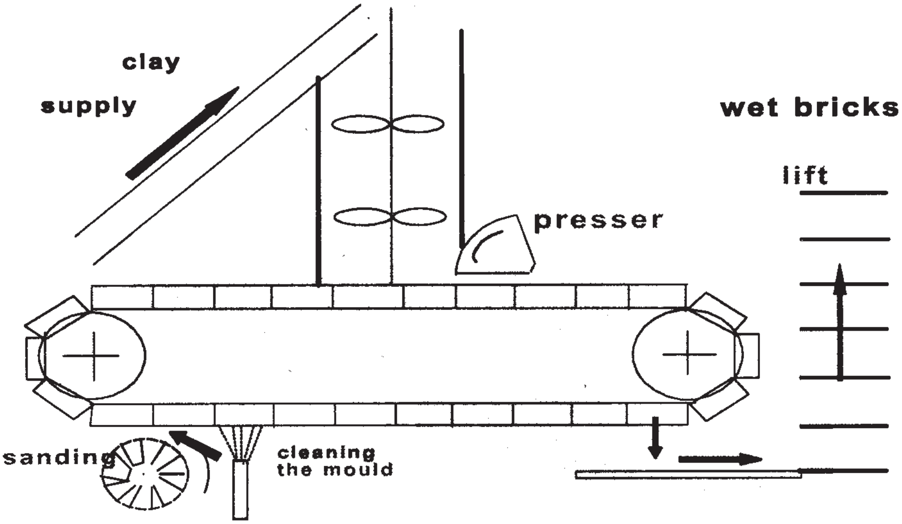


Fig.11.2.2 Press moulding. (source: Koninklijk Verbond van Nederlandse Baksteenfabrikanten [Eng.:Royal Association of Dutch Brick Manufacturers])

are produced thus. The biggest presses can manufacture 38,000 bricks per hour. The finished product is characterized by a smooth surface and sand on five of its six sides (figure 11.2.2).

In its simplest form an *extruder* consists of a body with a rotating axis equipped with blades, the so-called worm which extrudes the clay through a die, an opening with a special shape and construction which varies according to product requirements. During this extrusion the pressure on the clay is gradually increased to a maximum value. Near the die the pressure drops to zero when the clay is extruded.

The die produces a column of clay with the desired form and a steel wire cuts it in individual parts. Products made by an extruder: bricks (both perforated and not), hollow bricks, large building blocks, drainage pipes, sewer pipes, riven slabs, tiles and roof tiles. The extruder requires the use of a plastic clay. The baked product is characterized by its square shape and smooth surface.

After the forming process, the drying process follows. In earlier times bricks were dried outside and consequently people were dependent on the weather. Nowadays brick production is a continuous process and the bricks are dried in drying chambers. Hot air, partly from the cooling phase of the ovens, is transported to those chambers and ventilators ensure a proper air circulation.

Although a dried brick is quite firm, it obviously does not yet have the desired ceramic properties. These are obtained by *firing* it. This

MVC extruder (Morando Impianti).

is also the moment when the desired colour is formed. This firing takes place at temperatures of 1000 to 1200 ^{o}C and according to a firing curve (temperature plotted against time). A lot of research is needed to determine this curve whose form depends on the kind of raw material used and the product desired. There are two general types of kilns, continuous and periodic.

In the Netherlands, the continuous kiln is mostly applied. We distinguish two principles here: the bricks pass through the fire or the fire moves across the stationary bricks. The former principle is applied in tunnel kilns. Nowadays these are about 100 metre long and up to 8 metre wide.

Firing colour

When the clay is baked, the colour of the product, the so-called baking colour, can differ much from that of the clay. Bricks and roof tiles are available in various colours. Most colours are caused by components of the raw materials, but by adding certain ‘colouring components’ an even larger range of colours can be made. For instance by adding some percentages or more of manganese(IV) oxide, also called braunite MnO_2, to clay containing iron and calcium, you can produce a dark grey to greyish black firing colour. However, we shall restrict ourselves to the influence of calcium and iron ions on the firing colour; both components can be found in clay.

Generally said, the iron content is responsible for the red firing colour and the calcium content for the yellow colour. When the iron content is low and enough aluminium oxide is present, the free iron(III) oxide will bind with the silicates to form yellow compounds. Table 11.2.1 lists the baking colour as a function of the proportion of the iron(III) oxide, aluminium oxide and calcium oxide masses.

The theoretical background of these colour is similar to that of the colours of glazes, which means that colour is determined by the crystal structure and the combination of suitable central metal ions and the surrounding particles or ligands. The most commonly found iron oxides in clay are:

FeO black to greyish black

and α- Fe_2O_3 haematite: bright red to dark red.

In unbaked clay this oxide often contains chemically bound wa-

Different baking colours of bricks (by J.Aarsen).

Table 11.2.1

MASS PROPORTION Fe_2O_3 / Al_2O_3 IN CALCIUM-POOR CLAY	**FIRING COLOUR**
> 0.33	bright to dark red or purple
0.33 × 0.20	light red to pink
0.20 × 0.10	bright to light yellow
< 0.10	cream to white

MASS PROPORTION Fe_2O_3 / CaO IN CALCIUM CONTAINING CLAY	**FIRING COLOUR**
> 0.8	red
0.8 × 0.5	greyish
0.5 × 0.3	dark yellow to greyish yellow
< 0.3	canary yellow to cream

ter, owing to which the colour varies from yellow to brown and ochre. It has the corundum structure i.e. the O^{2-} ions form a hexagonal close packing and two thirds of the octahedral sites are filled with Fe^{3+} ions.

Under ideal circumstances these oxides can react to form: Fe_3O_4 magnetite: this compound is a mixed oxide containing iron(II) and iron(III) ions. The O^{2-} ions form a cubic close packed structure with the Fe^{2+} ions in the octahedral sites and half of the Fe^{3+} ions in tetrahedral and the other half in octahedral sites.

During the firing process a number of chemical reactions occur, among which:

$$CaCO_3.MgCO_3 \text{ (dolomite)} \rightarrow CaCO_3 + MgCO_3 \quad \text{(up to 400 °C)}$$

$$\rightarrow MgO + CO_2 + CaCO_3 \text{ (400–900 °C)}$$

$$\rightarrow MgO + 2\,CO_2 + CaO \text{ (above 900 °C)}$$

$$6\,Fe_2O_3 \rightarrow 4\,Fe_3O_4 + O_2$$

In addition, the various iron oxides interreact and the atmosphere and temperature determine which oxide is preferably formed and consequently which baking colour the product will have (in calcium-poor clay!):

$$\begin{array}{lccccc} & \mathrm{FeO} & + & \mathrm{Fe_2O_3} & \rightleftarrows & \mathrm{Fe_3O_4} \\ & \text{grey / black} & & \text{red} & & \text{grey} \\ \text{mass\% O} & 22 & & 30 & & 28 \end{array}$$

Firing in an oxidizing atmosphere at temperatures < 1100 °C results in a red product. Oxidizing means ‘adding oxygen’ in which case the present FeO and Fe_2O_3 are partially converted into the compound with the highest mass % of oxygen, i.e. Fe_2O_3. The reversed process, firing in a reducing atmosphere, produces a grey to greyish/black colour. This colour is also formed in oxidizing firing above 1100 °C when the temperature is so high that the iron(III) oxide releases oxygen (see last but one reaction).

Research on bricks

First the samples to be researched are conditioned, which means that they are tested in dry or wet conditions or vacuum saturated and these conditions are then normalised. For instance, a wet sample is obtained by storing it for a certain period of time under water. When the sample absorbs water in a vacuum, the minute pores can also be filled.

After conditioning various tests are carried out, depending on the functions the bricks will have in a construction and on the conditions under which these functions will have to be met. Bricks always need to have a certain strength and they must be able to withstand the influence of the weather. Furthermore, they must be easy to work with. In order to measure the strength we determine e.g. the fracture strength (figure 11.2.3) and bending strength.

Whether or not a brick is frost-proof is measured by allowing the brick to absorb water and subsequently storing it at temperatures below freezing. When cracks are formed the brick is not frost-proof. An important aspect as far as processing is concerned is the absorption of water. When a brick absorps too much water this is abstracted from the mortar and as a result the bond between the brick and the mortar will be less strong.

11.2.3 Roof tiles

History

Ceramic roof tiles are thousands of years old. It is assumed that the first roof tiles were baked of clay in China. The ancient Romans and Greeks first applied roof tiles on a large scale in Europe.

In the area of Tegelen in the south of The Netherlands a very old

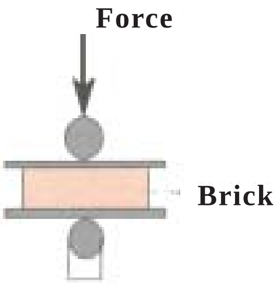


Fig. 11.2.3 Measuring the fracture strength of a brick.

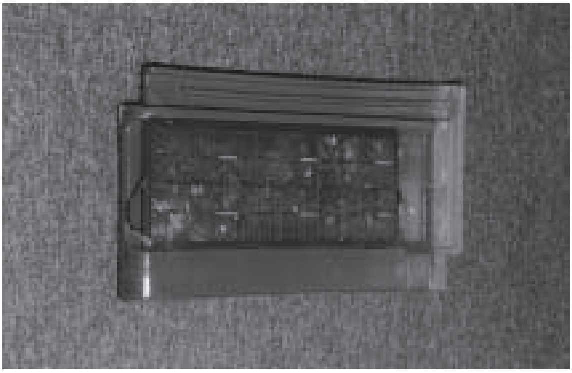
roof tile industry exists. It is hardly surprising that an exhibition on ‘2600 years of ceramic roof tiles’ was held in the centre of this region in 1995. It was organised by the Stichting Historie Grofkeramiek (Society for Historical Coarse Ceramics). The ‘tegula’ to which Tegelen owes its name, is a certain kind of tile which dates from appr. 630 BC and whose original design is Greek. The Romans adopted this design and spread it all over Europe. When I visited the exhibition I was struck by the large variety of roof tiles: the old Tegula tile from Roman times, monks and nuns, pigeon tiles (pigeon entrance to dovecot in attic), ventilation tiles, roof tiles with incorporated solar cells and even english tiles you can use to create flowerbeds in the garden.

The production of roof tiles

A stamping press is used in the manufacture of roof tiles. This is a machine which compresses a plastic clay mass between two moulds to obtain the desired shape. This compression technique is only rarely applied in coarse ceramics.

Research

In the roof tile industry as in the brick industry, research mostly means quality control. This is mainly aimed at: textures and finishes, dimensions, mechanical properties (e.g. breaking strength) and physical properties (e.g. water-tight and frost-proof).



Roof-tile with solar cells

Old Roman roof-tile (about 630 BC)

Roof-tile with entrance for pigeons

Pictures of roof tiles (by H.Raadschelders).

11.3
Refractory Ceramics

11.3.1 Introduction

Refractory ceramics are applied in the construction or coating of installations which are operative at high temperatures for long periods of time. In Dutch these products are called “vuurvaste producten” and in German “feuerfeste Erzeugnisse”. Both can be translated with “fireproof products”. However, these products are more than just fireproof and that is why the word “refractory” is a much better choice: a substance which is especially resistant to heat, corrosion, etc. At the outside of the installation it acts as an insulator. Bricks are used for this purpose, but also ceramic paper, string and even masses which are stamped or cast into the desired shape. The inside of the coating usually comes in contact with chemical products and thus must be resistant to high temperatures as well as to chemical and mechanical attack.

11.3.2 Definition

Refractory materials are materials and products – with the exception of metals and alloys – which can resist temperatures of at least 1500 °C. According to the Dutch refractory industry this definition is not very good, but apparently there is no consensus on a new one yet.

The temperature in a kiln can be measured with a so-called *Seger cone*, which was named after the German chemist Hermann August Seger. In 1885 he was director of the Chemisch-Technischen Versuchsanstalt der Königlichen Porzellan-Manufaktur zu Berlin and at the turn of the year 1887 he presented his cone for temperature measurements in kilns (figure 11.3.1).

The cone has a known chemical composition. After use we measure the angle of the cone’s curve. The combination of angle and composition is a measure for the ambient temperature of the cone in the oven.

Is the Seger cone still of importance nowadays? An article in the Keramische Zeitschrift of 1986 reports the production of 5 to 9 million cones annually at the Staatliche Porzellan Manufaktur in Berlin. At Sphinx, Technical Ceramics in Maastricht, The Netherlands Seger

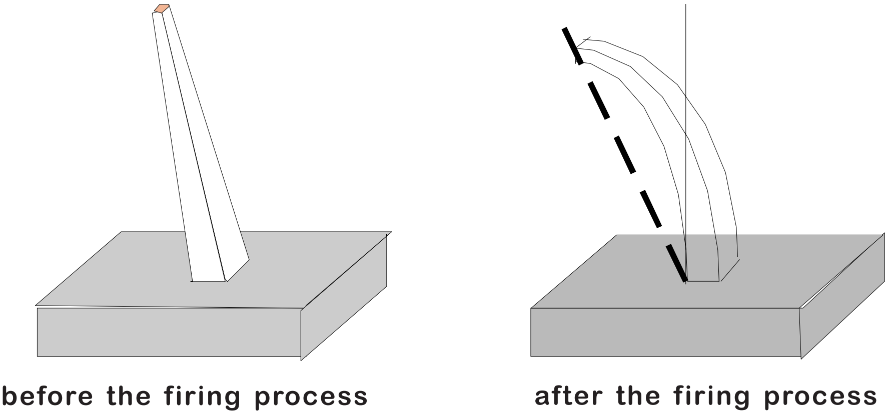


Fig. 11.3.1 The application of a Seger cone.

cones were no longer used by the year of 1997. Until recently they used *Buller rings*, but these have now been replaced by *Philips temperature control rings* (the so-called PTCRs). After firing, the diameter of the ring is measured with a micrometer and it is a measure for the maximum temperature to which the ring has been exposed.

11.3.3 Kinds of refractory materials

Refractory materials can be divided into three groups, i.e. a) insulation materials, b) refractory concrete and mortar and c) refractory bricks. The last group is not discussed in this paragraph but in a later one.

Insulation materials

We distinguish two kinds of insulation materials: fibre materials and insulation bricks. I received information on this subject from the American firm BNZ Materials Inc. and its Dutch subsidiary INSULCON. They manufacture insulation bricks which are called Marinite.

As an option these bricks can be reinforced with graphite fibres, making them tough and resistant to breakage. Their density is low, about 0.75 g/cm^3. This indicates that they are very porous. In addition the firm produces a bulk mass which consists for appr. 50% (m/m) of SiO_2 and for appr. 50% of Al_2O_3. This mass is excellently suited for the production of insulating blankets, paper, boards, textile and rope. The so-called Duraboard 1200 is a high temperature board which is extremely resistant to fire, chemicals, changes in temperature

Samples of fireproof stones.

Ceramic isolation materials.

Isolation stones (all three pictures by J.Aarsen).

and breakage at low and high temperatures. Its density is about 0.26 g/cm^2 and it is used for temperature seals and in the walls of some kinds of kilns. Ceramic paper roughly has the same composition as this board and is e.g. used to insulate the doors of the cokes ovens in blast furnaces. And finally there are the blankets which are composed of long ceramic fibres interlinked longitudinally and cross-sectionally without the use of a binder. They are used for protection against fire, for example.

Insulation materials contain more air and have an lower apparent density than ordinary refractory materials. In the case of insulation bricks the desired porosity is obtained by making use of additives which produce gases when heated (e.g. calcium carbonate), or of porous raw materials. In figure 11.3.2 the effect of the appplication of insulation bricks is represented.

In figure 11.3.2, λ (the Greek letter lambda) stands for the heat conduction coefficient. This is part of the following formula in which φ (phi) stands for the heat current through the brick.

$$\varphi = A \times \lambda \times \frac{dT}{dx}$$

A is the area through which the heat current passes, *dT* is the temperature difference between the outer and inner walls, *dx* is the thickness of wall

Consequently, a low λ value means a slight heat current through the wall. For the sake of comparison some λ values are mentioned in table 11.3.1.

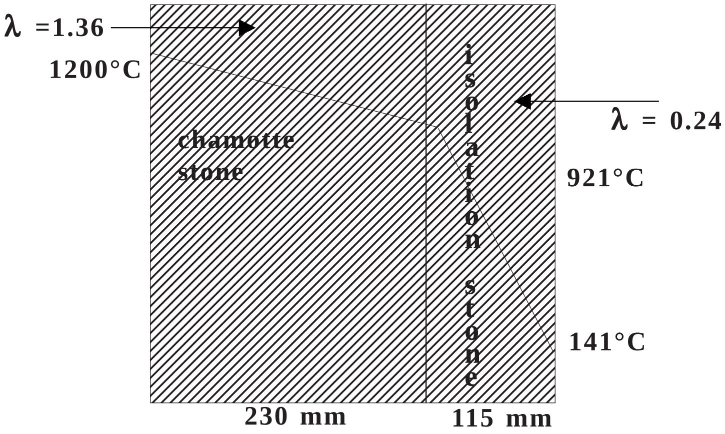


Fig. 11.3.2 The effect of insulation bricks.

Table 11.3.1 Heat conduction coefficient of some materials

Material	λ value
copper	40
brick	0.4
PVC (polyvinyl chloride, a plastic)	0.2
air	0.02
polymer foam	0.02–0.03
chamotte stone	1.35
insulation brick GI·23 produced by Gouda Vuurvast, the Netherlands	0.25

An experiment: Mix an amount of plastic clay with calcium carbonate in the mass proportion 90%–10%. Fill a rectangular mould with the mixture and store it for 24 hours at room temperature. Then dry the mass for about 6 hours in an incubator, thereby gradually increasing the temperature to 100 °C. Remove the bar from the mould and bake it for about 4 hours at appr. 850–1000 °C. Again allow the temperature during the baking to increase gradually, i.e. about 100 °C per hour. After baking drill three longitudinal holes in the bar to a half its length in order to place thermometers in them. Drill the holes at 1/10, ½ and 9/10 of the length. Place a small screen against one end of the bar with in it an opening of the same dimensions as the bar itself and heat the clay bar with an IR lamp. The three thermometers measure the development of the temperature in time.

A recipe from Vuurvast Gouda: 70% chamotte 0.2 mm +30% refractory clay 0–0.2 mm baked at a minimum temperature of 1100 °C.

Refractory concrete

Some knowledge of concrete is required to understand that refractory concrete needs to have a different composition from ordinary concrete. The melting point of ordinary concrete is higher than that of several kinds of refractory concrete. However, the fact that the

Portland cement which is present in ordinary concrete dehydrates at temperatures above 250 °C is a major drawback. This takes place according to the following reaction:

$$Ca_3Si_2O_7 \cdot 3H_2O \xrightarrow{T > 250°C} 3\,CaO + 2\,SiO_2 + 3\,H_2O$$

After cooling, the calcium oxide which is formed in the reaction reabsorbs water and expands, causing the concrete to crack.

	$CaO + H_2O$	$\rightarrow$	$Ca(OH)_2$
density (g/cm^3)	3.30		2.24

The cracks are caused by the formation of a material with a smaller density; consequently the material expands.

Ordinary concrete also contains sand and gravel, components which melt at high temperatures. They contain a high percentage of free quartz which transfers form a quartz to ß quartz at 570 °C; this process involves an increase in volume. When the earlier mentioned temperature is exceeded, the concrete will crack and burst. From all of this it is easily concluded that refractory concrete will have to have a different composition from ordinary concrete. A comparison:

Ordinary concrete	Refractory concrete
Portland cement	aluminium cement
sand and gravel	chamotte, andalusite, bauxite or corundum

11.3.4 Refractory bricks

In The Netherlands refractory bricks are manufactured by a firm called Gouda Vuurvast Ltd. and some of its customers are:

blast furnaces: wind heaters, steel ladles, blast furnace drains
aluminium industry: oven coatings made of bauxite bricks
refuse incinerators: oven coatings containing SiC materials
cement industry: coatings of certain parts of the rotating oven
petroleum and chemical industry: coating of thermal and catalytic cracking plants

This list is far from complete. The glass industry, ceramic industry, manufacturers of fire places, etc., could also be added to it.

Each branch of industry is characterized by specific (production) processes with their corresponding requirements for refractory products.

In an **oil refinery** petroleum is cracked, a process in which petroleum fractionswith high boiling points (hydrocarbon molecules) are decomposed by heat (thermal cracking at appr. 400 - 800 °C, in the liquid phase at 50 -70 atm. or in the gas phase at 5 - 15 atm.) or in the presence of a catalyst (catalytic cracking, at appr. 550 °C and a low pressure in the gas phase) into smaller molecules. Among the catalysts used is kaolin activated by mineral acids. The major advantage of catalytic cracking is that it is more selective, i.e. fewer products are formed and their nature is more of less predictable.

In the case of **refuse incinerators** a distinction must be made between the combustion of household and the incineration of chemical waste. Burning household waste involves steam generators used to generate electricity. The combustion chamber is provided with steam pipes which have to be protected against corrosive gases by means of SiC-containing materials.

In addition the walls of the combustion chamber must also be shielded from corrosive slag. Chemical waste is mostly incinerated in a rotating tubular oven coated with chromium-containing corundum stone or phosphate-bound corundum stone.

Different problems occur in the **aluminium industry**. The smelting of aluminium may be accompanied by serious damage to the refractory coating. Molten aluminium is a powerful reducing agent which can be oxidized in two ways, i.e. by oxygen from the air and by oxides like SiO_2 and TiO_2 in the refractory bricks.

With oxygen from the air the following reaction occurs both at the surface and inside a refractory brick:

$$\begin{array}{lll} 4\,\mathrm{Al} + 3\,\mathrm{O_2} \rightarrow 2\,\gamma\text{-}\mathrm{Al_2O_3} & \rightarrow \text{(from \textasciitilde 800 °C)} & 2\,\alpha\text{-}\mathrm{Al_2O_3}\ \text{(corundum)} \\ \qquad \rho = 3.5\ \mathrm{g/cm^3} & & \rho = 3.97\ \mathrm{g/cm^3} \end{array}$$

At the transfer from the γ to the α form, shrinkage occurs. As a result narrow channels are formed in the stone and these are filled with black, hard masses.

The reaction of molten aluminium with SiO_2 is as follows:

$$4\,\mathrm{Al} + 3\,\mathrm{SiO_2} \rightarrow 2\,\mathrm{Al_2O_3} + 3\,\mathrm{Si}$$

and at 800 °C the γ-form of the aluminium oxide is changed into the α-form again.

Finally it should be noted that when aluminium is alloyed with zinc, this metal speeds up the conversion of γ- to α-Al_2O_3.

Development of refractory brick

In the development of a refractory brick many questions play an important part, such as “Is the brick able to withstand the chemicals it will come into contact with?” and “How temperature resistant is the brick?”

In the aluminium production described above bricks come into contact with liquid aluminium at high temperatures. By means of the aluminium cup test you can determine whether or not this contact runs smoothly. A cylindrical cavity is drilled into the brick and filled with liquid aluminium. Next both components are allowed to interact. As you can see in the photographs the material in question is not suitable. The phase rule is an excellent aid in answering the second question, as can be concluded from the phase diagram of the system SiO_2 / Al_2O_3 in figure 11.3.3)

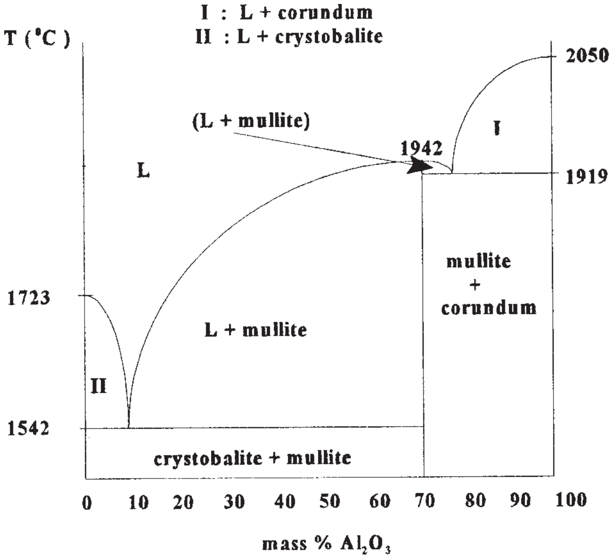


Fig. 11.3.3 Phase diagram of the system SiO_2 / Al_2O_3.

The phase diagram indicates the existence of a smelt (L) and three crystalline phases, i.e. crystobalite (a certain crystal structure of silicon dioxide), corundum (a certain crystal structure of aluminium oxide) and mullite, a congruently melting compound of both oxides with 71.79 % (m/m) Al_2O_3 and a melting point of 1942 °C. Moreover it appears that the melting point of crystobalite (1723 °C) can be strongly reduced by adding small amounts of Al_2O_3 and that, as a general rule, the fire resistance is directly proportional to mass % of Al_2O_3.

Result of a aluminium cup test (by Gouda Vuurvast, Netherlands).

Raw materials

Because refractory bricks are nearly always applied in high temperature environments and in direct contact with oxygen from the air, high-melting oxides are preferably used as raw materials (table 11.3.2).

Refractory bricks are divided into two groups according to their chemical composition, based on commercially interesting stones and clays in their natural forms:

I Bricks whose main component is SiO_2 and / or Al_2O_3
II Bricks whose main component is MgO, CaO and / or Cr_2O_3

In this phase of the chapter it will be clear that the process in which the refractory brick comes into contact is decisive for the

Table 11.3.2 Commonly used oxides for the production if refractory bricks

Oxide	Melting point (°C)
SiO_2	1710
Al_2O_3	2050
MgO	2810
CaO	2570
Cr_2O_3	2275

requirements the brick must meet. Very often the components present in the raw material will affect the properties of the brick and it goes without saying that a manufacturer must choose his raw materials extremely carefully.

Examples of *raw materials used for the manufacture of group 1 bricks* are: fireclay and mullite.

** Quite often *fireclay* is burnt to chamotte at the place where it is found. The most common clay mineral in fireclay is kaolinite with the ideal formula $Al_4[(OH)_8/Si_4O_{10}]$, or in the notation applied in world of ceramics: $Al_2O_3.2SiO_2.2\ H_2O$. Kaolinite contains chemically and physically bound water. When you heat it to about 1500 °C, the physically bound form is first released and subsequently the chemically bound one. In the last phase chamotte is formed:

about 110–150 °C	physically bound water is released product: $Al_2O_3.2SiO_2.2\ H_2O$ [39.50% (m/m) Al_2O_3]
500–1000	chemically bound water is released product: $Al_2O_3.2SiO_2$.
1000–1500	formation of chamotte (mullite + free SiO_2) products: $3\ Al_2O_3.2SiO_2$ + $4\ SiO_2$ [45.90% (mm/m) Al_2O_3] mullite crystobalite

When the kaolinite is heated, the content of aluminium oxide increases. Ideally the chamotte will contain 45.90 % (m/m) Al_2O_3 and 54.10 % SiO_2. In practice these values lie between 30–45 % and 51–64 % respectively and small amounts of TiO_2 , Fe_2O_3, CaO + MgO and Na_2O + K_2O are also present. The last four components are mentioned in sets of two because they are determined together analytic chemically and unlike SiO_2 have the property that they produce a glass which is much less fireproof than mullite: mullite (**) melts at 1942 °C and K_2O can for instance form a smelt with SiO_2 at a temperature of 985 °C and higher. The silicon dioxide which is produced in the firing of kaolin can be incorporated in this glass phase either completely or partially.

** *Mullite* only rarely occurs in nature and derives its name from the island Mull in Scotland. The mineral has a low expansion coefficient and great resistance to sudden temperature changes. It has a fibre-like crystal structure and forms a lattice which liquid slag can only break down with great difficulty. Mullite is formed during the firing of clay, andalusite or bauxite, but can also be used as synthetically manufactured mullite grains.

Production of bricks

After the raw materials have assumed the required grain shape they are mixed and transported to the press. The pressed bricks are conveyed through the oven tunnel by wagons and thus complete the usual process of heating, firing and cooling. The parameters grain distribution, press pressure and firing temperature mainly affect the quality of the product; they determine e.g. the porosity, gas permeability, temperature fluctuations resistance, shrinkage, softening under pressure, mullite content and the percentage of glass phase.

11.3.5 Damage to refractory products

Refractory materials can be damaged by high temperatures and by reactions with gases, liquids and solids. *At high temperatures* a brick can contain so much melt phase that its strength becomes too small. In addition abrupt expansion can occur which is caused by the conversion of a mineral in the brick into another allotropic form.

Most *gases* do not affect refractory bricks. Under high pressure hydrogen gas can reduce silicon dioxide. At appr. 400–800 °C, carbon monoxide is converted into carbon and carbon dioxide. The carbon is deposited on the brick and this may lead to brick's compression. However, a solution has been found. The decomposition of carbon monoxide appeared to be stimulated by certain iron compounds. By firing the bricks at a sufficiently high temperature, you can convert these iron compounds into iron silicates which do not act as catalysts.

The effect of a *liquid* can for instance be seen in a glass oven. The glass melt is acid and consequently the oven wall should not contain any alkaline bricks or the coating will dissolve. *Solids* cause mechanical damage. In a blast furnace, for instance, a mixture of ore and cokes moves along the bricks. Only bricks with hard, well-sintered grains can withstand this.

11.3.6 Research on refractory products

In table 11.3.3 some tests are mentioned which can be carried out on refractory products.

Table 11.3.3 Tests on refractory products

chemical analysis
mineralogical analysis
creep under the influence of temperature, time, pressure
deformation under pressure
hot bending strength
temperature fluctuations resistance
gas permeability
density and porosity
cold compression strength
Seger cone heat resistance
pore size distribution
resistance to wear
damage caused by slag
expansion coefficient
heat conduction

11.4

Electroceramics

11.4.1 Introduction

It will be apparent from the contents page that the paragraph on electroceramics is one of the most elaborate of chapter 11: Seven Ceramic Branches of Industry. The main reason for this can be found in the large number of applications but also in the fact that the market for electroceramic materials is expected to grow considerably. This marktet, in its turn, is propelled by the strong desire to make electrical components of devices increasingly smaller. Table 11.4.1 shows a 2 thousand million dollar turnover for sophisticated electroceramic materials in Europe in 1995. It is expected that this amount will increase to approximately 3 thousand million in 2002.

According to the institute which is responsible for the above mentioned percentages sensors are economically seen the most interesting product, mainly because of their use in the control of car exhaust fumes emissions.

11.4.2 Electrical properties of materials

Starting point for this paragraph is the electrical conduction of metals, a phenomenon with which everyone will be familiar. A simplified crystal structure of metals was already discussed in chapter 3, in the paragraph on “Chemical bonds”. In a metal, there is question of an electron cloud which moves between the metal ions. When the metal is connected

Table 11.4.1 The European market for sophisticated electroceramics: percentages and kinds of products in 2002

product	**percentage**
insulators	31
ferrites	18
capacitors	20
sensors	22
variable resistors	3
piezoceramics	6

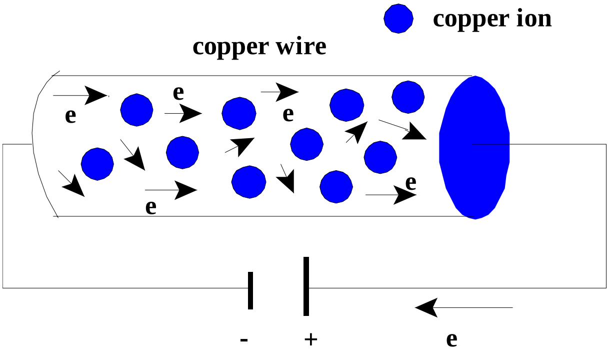


Fig. 11.4.1 The flow of electrons in a copper wire.

to a voltage supply, the movement of the electrons is converted into a flow of electrons (fig. 11.4.1)

In figure 11.4.1 some copper ions can be seen. They vibrate around their lattice positions and the intensity of these vibrations increases as the temperature rises. The vibrations are the reason why the flow of the electrons is inhibited. The electrons continuously collide with the copper ions and that is why we say that the electrons experience resistance. The size of the resistance of the copper wire can be calculated using Ohm's law.

Ohm's law $R = \rho \cdot \frac{l}{A}$

where R is resistance, unit ohm (Ω), l is the length of wire (m), A is the cross section of wire (m^2), ρ is specific resistance (Ωm)

Within the framework of the paragraph, however, the electrical conductivity is more interesting that a material's resistance.

Electrical conductivity $\sigma = \frac{1}{\rho} \Omega^{-1} m^{-1}$

Both specific resistance and electrical conductivity depend on temperature. Materials can differ considerably as far as electrical conductivity is concerned and this fact is used to subdivide them, as illustrated in table 11.4.2.

11.4.3 From insulator to superconductor

In the paragraph on fine ceramics, in the item on glazings, we saw that electrons in isolated atoms are bound to the nucleus and only appear in certain orbits. Every orbit is linked to one particular energy

Table 11.4.2 The electrical conductivity of some materials at room temperature: a classification based on conductivity

material	**σ ($\Omega^{-1}m^{-1}$)**	**classification based on conductivity**
silver	6.3×10^7	
copper	5.8×10^7	***conductors***
aluminium	3.4×10^7	
graphite	10^5	
germanium	2.2	***semiconductors***
silicon	4.3×10^{-4}	
polyethene	10^{-14}	***insulators***
diamond	10^{-14}	

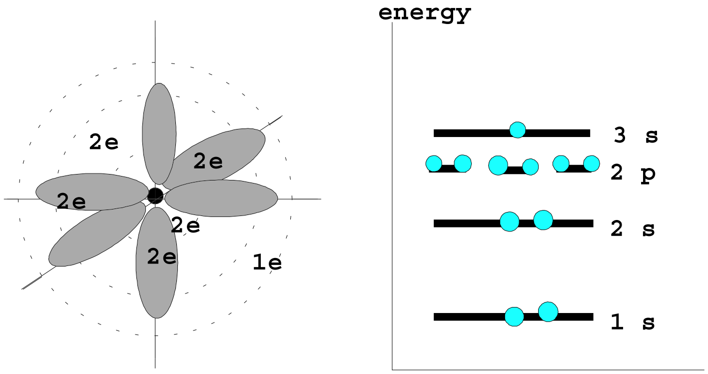


Fig.11.4.2 The orbital model of a sodium atom and the accompanying energy levels.

level. In figure 11.4.2 this is shown for a sodium atom with the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^1$.

In a sodium atom, the 3s valence electrons of the atoms will collide. Due to this the valence electrons of the individual atoms will not all possess the same energy, yet at the same time differ little in energy. As a result various, closely spaced 3s levels will occur in the energy diagram, which together form the so-called valence band (fig. 11.4.3)

Owing to the interaction between the valence electrons, there will constantly be electrons at the 3p energy level. These electrons contribute to the conduction. For the same reason as in the case of 3s, there

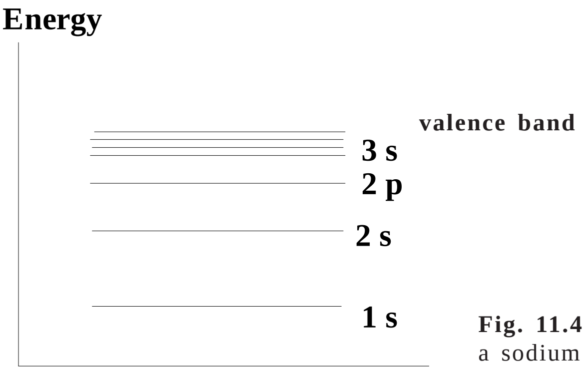


Fig. 11.4.3 The energy levels in a sodium crystal.

are also various, closely spaced 3p levels which together form the conduction band. In sodium and the other metals, the valence and conduction bands overlap or they lie closely together. In both cases very little energy is required for an electron to be sent from the valence band to the conduction band. Consequently metals are generally good conductors of electricity. However, because of their low melting points, sodium and the other metals of groups 1 and 2 of the periodic table do not qualify as useful conductors.

Insulator

In an insulator the electrons are closely bound to the atoms or ions. They can only be persuaded to move, i.e. they will only move from the valence band to the conduction band, when relatively much energy is provided. The energy diagram of these materials is represented in figure 11.4.4.

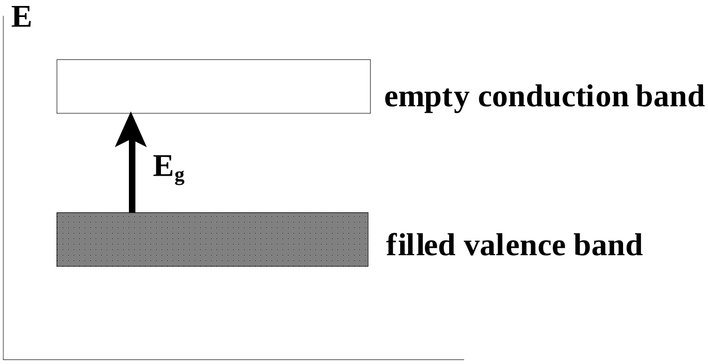


Fig. 11.4.4 The energy diagram of an insulator.

The energy which is required to send an electron from the valence band to the conduction band is indicated by Eg and is relatively large in an insulator. Some examples of insulators are porcelain (which contains approximately 50% clay, 25% silicon dioxide and 25% feldspar), forsterite (Mg_2SiO_4) and aluminium oxide.

Semiconductor

The electrical conductivity of a semiconductor lies between that of an insulator and a well conducting material. For a further examination of the conduction, our starting points are silicon and germanium. Both elements have the cubic shape of a diamond structure, as shown in figure 11.4.5.

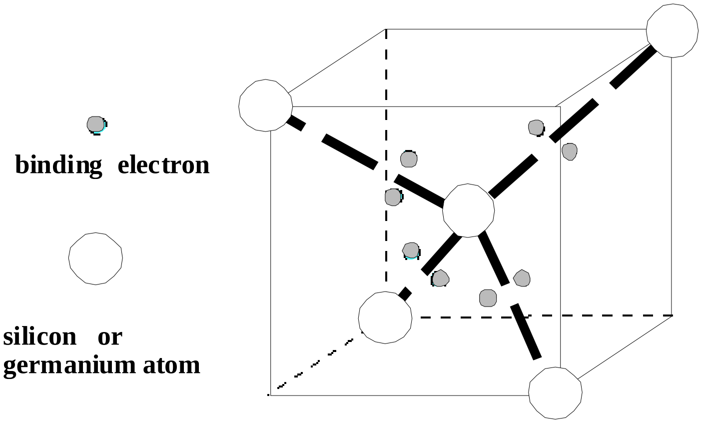


Fig. 11.4.5 The elementary cell in a silicon or germanium crystal.

In a silicon or germanium crystal, every atom is the centre of a cube of which four corners are also occupied. In addition, every atom is the vertex and the centre of a cube.

Semiconductors can be divided into two groups: intrinsic and extrinsic semiconductors.

Intrinsic semiconductors

Some examples of intrinsic semiconductors are silicon and germanium. These materials do not contain any impurities. The conduction mechanism can be represented in a simplified way by means of a projection diagram of a silicon or germanium crystal (fig. 11.4.6)

By supplying energy to the material, the electrons are torn free from their atoms and positively charged electron holes (+) arise. Placing the material in an electric field will result in the transport of “holes”

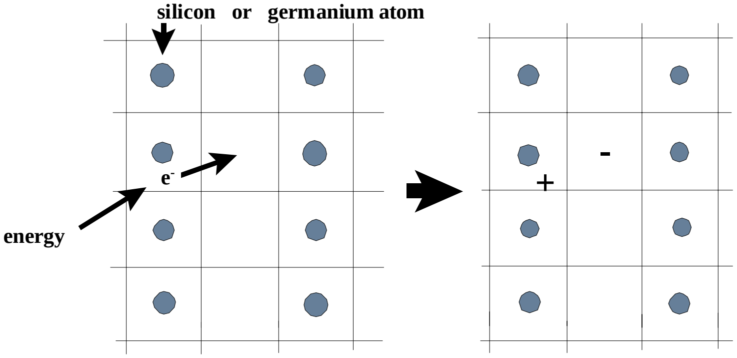


Fig. 11.4.6 Conduction in a silicon or germanium crystal.

and electrons in opposite directions. This transport of holes can be seen as the filling of holes by electrons. At a temperature of 300K, Eg (Si) = 1.1eV and Eg(Ge) = 6.7 eV; consequently germanium is a better conductor than silicon.

Extrinsic semiconductors

An extrinsic semiconductor is a material into which impurities have been incorporated, like raisins in a cake. This process is known as doping. The impurities can possess more or fewer valence electrons than the atoms of the "cake" or mother material and the classification into two types of semiconductors is based on this fact:

Extrinsic semiconductors of the n-type and p-type

A semiconductor of the **n-type** is formed, for example, when silicon is doped with arsenic atoms. The inbuilt arsenic atom uses four valence electrons to bind to the four surrounding silicon atoms (fig. 11.4.7) and the fifth valence electron is not needed for binding to

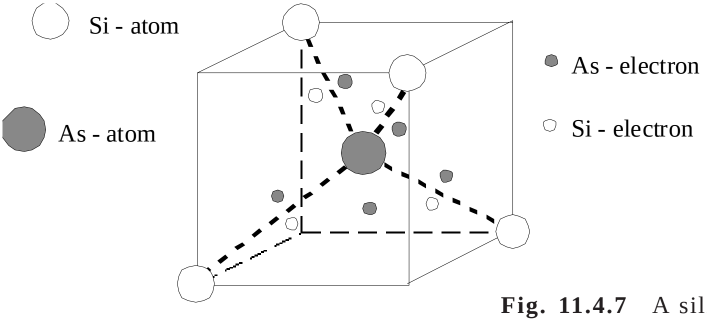


Fig. 11.4.7 A silicon crystal doped with arsenic atoms.

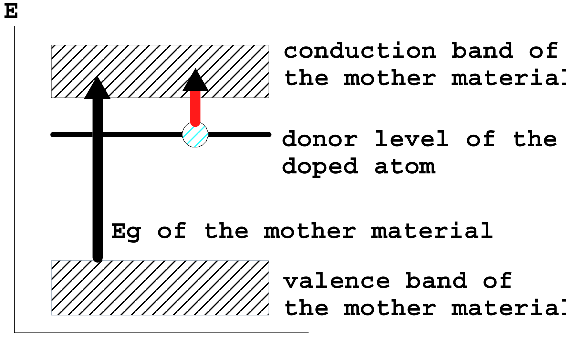


Fig. 11.4.8 Energy diagram of an *n*-type semiconductor.

adjacent atoms and is thus free to be used in the conduction.

In figure 11.4.8 the energy diagram of an n-type semiconductor is shown. The electron of the doped atom which is not used for binding has an energy which is close to that of the conduction band of the mother material. Consequently the transition to the conduction band will cost less energy than in the case of the pure mother material. The doped atom is called the electron donor.

So the conduction is caused by (negatively charged) electrons and that is why the material is called an n-type semiconductor, with the “n” of “negative”.

A semiconductor of the **p-type** is made by doping the mother material with atoms with fewer valence electrons than those of the mother material. When germanium is doped with boron, one in every four bonds will be one electron short (fig. 11.4.9).

The boron atom is one electron short and will consequently try to attract this electron from elsewhere in the crystal. For that reason the boron atom is called the electron acceptor. Figure 11.4.10 shows the accompanying energy diagram.

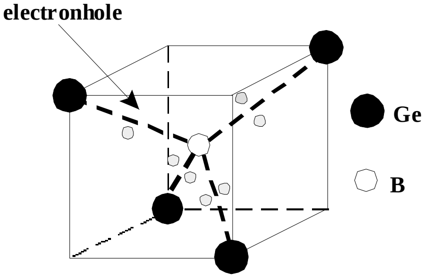


Fig. 11.4.9 Crystal lattice of germanium with doped boron atoms.

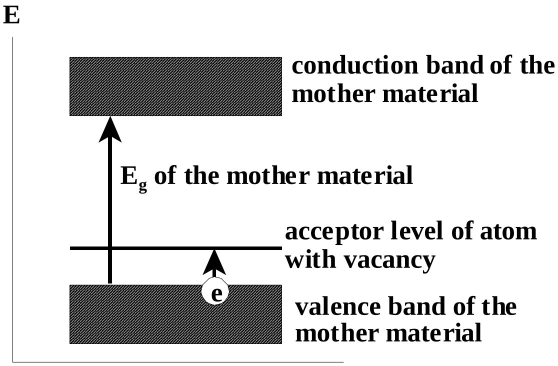


Fig. 11.4.10 Energy diagram of a *p*-type semiconductor.

The boron atom contains an electron hole or an electron vacancy. In order to fill this vacancy, the doped atom takes up an electron from the mother material (arrow). In this way a new vacancy is formed in the valence band, et cetera. The additional electrons in the energy level of the doped atoms enable conduction to take place. This conduction is the transport of vacancies. A vacancy has a shortage of one electron and is thus positively charged. That is why this semiconductor is of the *p*-type.

Some examples of ceramic semiconductors are magnetite (Fe_3O_4), doped barium titanate and doped zinc oxide. By for instance doping zinc oxide with bismuth, cobalt, manganese or antimony, you can vary the resistance of zinc oxide.

Semiconductor materials are applied in diodes, transistors, radiation detectors22, solar batteries and microprocessors.

Semiconductor circuits are often supplied with a cover made of 90–94% (m/m) aluminium oxide.

11.4.4 Superconductors

As mentioned earlier, electrical resistance is the property of a conducting material that an electric voltage is required to allow a current to flow through that material. This resistance is dependent on the motility of the particles and consequently on temperature. In metals, resistance and temperature are usually directly proportional; there are exceptions, however.

As can be seen in the graph 11.4.11, the resistance of mercury at 4.2 K suddenly drops to an immeasurably small value. At lower temperatures an electric current will flow through the mercury without generating any heat, so without any resistance. This phenomenon is

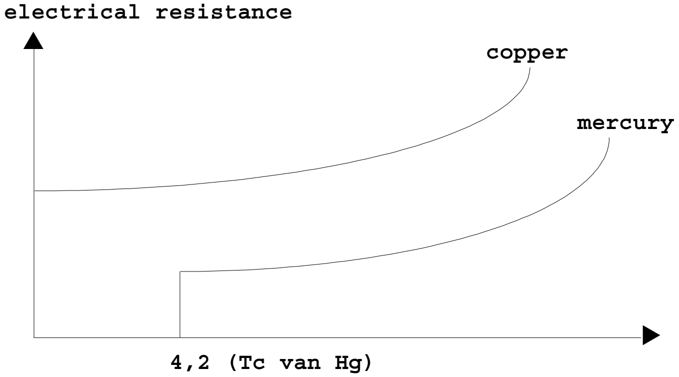


Fig. 11.4.11 Electrical resistance of copper and mercury as a function of temperature.

called **superconductivity**. Approximately 26 metals and hundreds of alloys and compounds are known to be superconductors. The temperature at which the resistance becomes too small to be measured is called the critical temperature T_c.

Until 1986 many experiments were carried out using metals and alloys. However, in 1986 Georg Bednorz and Alex Müller, two researchers of the IBM laboratory in Ruschlikon near Zürich, published an article in the "Zeitschrift fur Physik" in which they announced that they had made a superconducting ceramic material. It turned out to be a compound made of barium, copper, lanthanum and oxygen, which became superconducting at 35 K. They were awarded the Nobel prize for this discovery. After this, superconductors developed rapidly, at least as far as critical temperature is concerned.

I found the article "Introduction to High Temperature Superconductivity" on the Internet. It starts with the discovery of superconductivity in mercury by the Dutch physicist Heike Kamerlingh Onnes in 1911. In the 75 years which followed, many applications were developed, among which powerful magnets for a medical technique called Magnetic Resonance Imaging. However, liquid helium had to be used to reach the extremely low tmperature necessary for superconductivity. This made the technique expensive and limited the number of possible applications. In April 1986 Müller and Bednorz announced their promising results. At the end of the same year a revolutionary development was started. Paul C.W. Chu and colleagues at Houston University frequently observed superconductivity at temperatures over 77 K, but the samples they used were poorly characterized. Nevertheless, su-

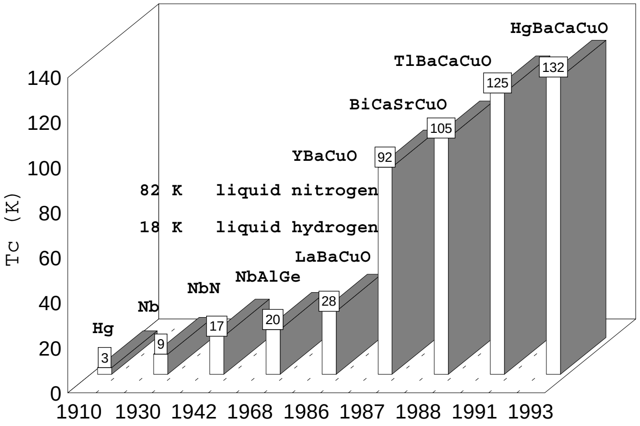


Fig. 11.4.12 The development of superconductors. Source: Material Research in the Czech Republic, Praha 1996.

perconductivity in liquid nitrogen was now considered to be possible. In January 1987 the Houston group was able to produce stable and reproducible superconductivity in $Y_1Ba_2Cu_3O_y$ at temperatures as high as 90 K and with a critical temperature of close to 100 K. It appears that the T_c-value is influenced by the oxygen content of the compound, which explains the value y. These developments continued until mercury compounds with transition temperatures of up to 164 K were discovered in 1993.

After this short historical survey, two questions on superconductivity still have to be answered: how can superconductivity be explained and how can it be demonstrated?

An explanation

These last few years superconductivity in metals and alloys has mainly been explained with the help of the so-called Cooper electron pairs. At the low temperatures at which super-conductivity occurs, the metal ions do not vibrate any more. In that case the movement of an electron through the lattice is enough to deform that lattice. The metal ions in the vicinity of the electron move towards that electron and thus provide a net positive charge, causing a second electron to be attracted, (fig. 11.4.13b). In the figure b and c, the metal ions have been reduced in size because the figure is more clear then.

Subsequently the metal ions move back in the direction of their lattice position and rush past in the other direction. This, in its turn,

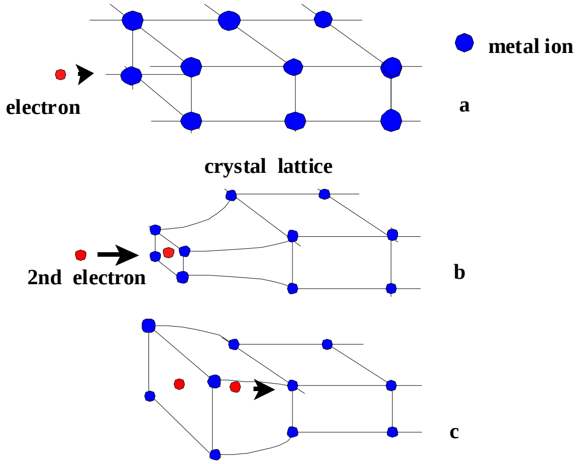


Fig. 11.4.13 Simplified model of the electron transport in a metallic superconductor.

results in a net negative charge at that site and the electron repel each other (fig. 11.4.13c). Owing to this process of alternately attraction and repulsion, the electrons seem to be interconnected: they form Cooper pairs, named after one of the scientists who developed this theory (fig. 11.4.13). The entire process is repeated in the next crystal plane.

Throughout the entire material there is question of a tangle of these pairs which moves through the matter with no resistance at all. Once this collection of pairs has been set in motion by an electrical field, the current will flow continuously.

Can this model also be applied to ceramic superconductors? After extensive correspondence and a literature search involving scanning tunneling electronmicroscopy and screw dislocations in crystals, I decided to drop this subject, mainly because it exceeds the level of this book. It can, however, be concluded that superconductivity in ceramic materials is based on a different mechanism.

Demonstrations

The best demonstration experiment is “the floating pill” experiment which was first conducted by the Russian physicist Arkadiev. Strong, permanent magnets, for example, $SmCo_5$ are alternately placed in the North/South and South/North directions. When a superconducting pill has been cooled in liquid nitrogen, it can float approximately 2 mm above the magnets for a few seconds. This information and a photograph of the pill experiment were sent to me by the Energy Cen-

Floating superconducting ceramic disk (by ECN, Petten, Netherlands).

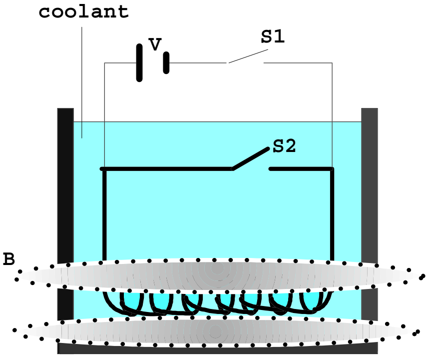


Fig. 11.4.14 Demonstration of superconductivity. Source: the Dutch magazine "Natuur & Techniek".

tre in Petten, The Netherlands.

When a current flows through a helical wire, a magnetic field is formed around that wire. This phenomenon is used to demonstrate superconductivity (fig. 11.4.14).

By closing switch S1, a current is sent through the superconducting coil. Next the coil is short-circuited by means of the superconducting switch S2 and the voltage source V is removed. The current will continue to flow through the coil, which can be demonstrated with the help of the generated magnetic field B.

A synthesis

Nowadays experiments in which ceramic superconductors are synthesized can be carried out in secondary schools. The required chemicals are relatively cheap and the equipment is quite easy to operate. In addition, liquid nitrogen is readily available. One of the firms which supply these materials is Leybold Didactic in Hürth, Germany. In the “Journal of the Chemical Education”, vol. 64, no 10, October 1987 you can find the article “Preparation, Iodometric Analysis and Classroom Demonstration of Superconductivity in $YBa_2Cu_3O_{8-x}$”.

At present, research mainly concentrates on ceramic superconductors which have been synthesized from the oxides of yttrium (III), barium and copper(II) and several substituents. These materials have a T_c value which is higher that 77 K, the boiling boint of liquid nitrogen, but they are relatively easy to make. Yttrium oxide, barium oxide and copper carbonate have to be mixed in the proper quantities and then heated to about 950 °C for several hours. During this heating the carbonate breaks down in barium oxide and carbon dioxide, the latter of which will evaporate. After the first heating cycle, the product is ground and reheated to the same temperature and subsequently cooled. During this cooling, the compound takes up oxygen and a superconductor is formed. The oxygen content depends on the partial oxygen pressure during cooling. The T_c-value is also dependent on the oxygen content. Figure 11.4.15 shows the ideal structure of such a superconductor.

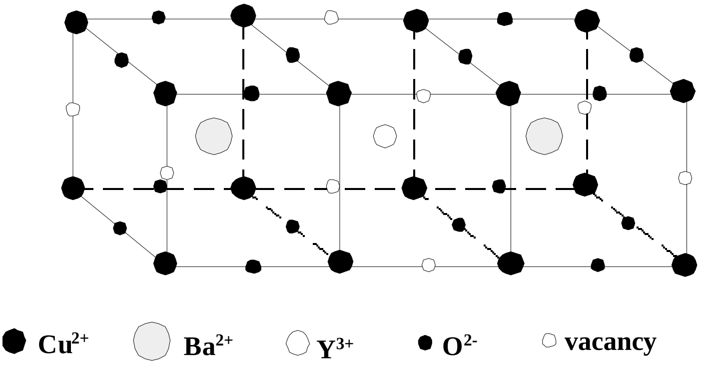


Fig. 11.4.15 Ideal structure of the Y-Ba-Cu-O superconductor. Source: Principles of Material Science and Engineering, page 837.

11.4.5 Capacitor

Starting point for the discussion of the capacitor is a metal sphere which is charged and then provided with a metal capsule (fig.11.4.16) When the distance d between the sphere and the capsule is relatively small, the electric field will be homogeneous.

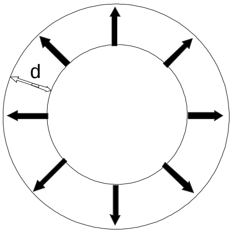


Fig. 11.4.16 Electric field in a “spherical capacitor”.

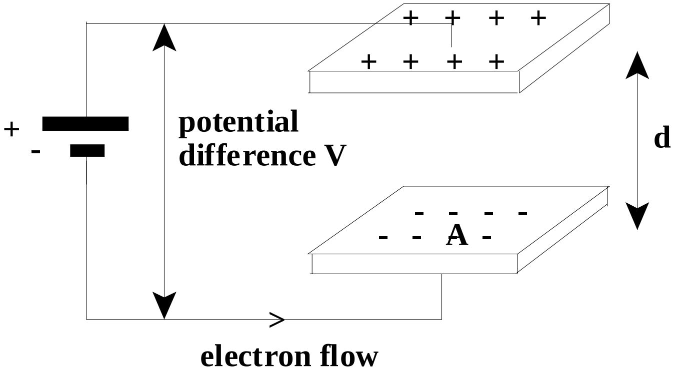


Fig. 11.4.17 Charging a capacitor.

Suppose that the radius of the sphere would increase to infinity, this would result in the parallel-plate capacitor as shown in figure 11.4.17. When this parallel-plate capacitor is connected to a voltage source, the source will send electrons to the capacitor which is thus charged.

The charge *Q* which a capacitor can store, the capacity *C*, depends on the area *A* of the plates, the distance *d* between the plates and the nature of the material between the plates, the so-called dielectric

$$\frac{Q}{V} = C = \frac{\varepsilon_0 \times A}{d} \text{ F(arad)}$$

The above-mentioned formula applies when there is a vacuum between the plates; ε_0 is the permittivity of the vacuum:

$$\varepsilon_o = 8.854 \times 10^{-12} \quad \text{F/m}$$

When another medium is placed between the plates, which in reality are not as widely spaced as they have been drawn in figure 11.4...., then the formula also changes.

$$C = \frac{\varepsilon_0 \times \varepsilon_r \times A}{d} = \frac{\varepsilon \times A}{d} F$$

ε_r is the relative permittivity of the medium, a number without a unit which indicates how many times the permittivity of the medium is compared with that of the vacuum. Table 11.4.3 lists a number of ε_r- and ε-values,

The insertion of a dielectric between the plates of a capacitor increases the capacitance of the capacitor. This is illustrated in figure 11.4.18.

By choosing the right dielectric it is possible to reduce the area A and distance d of the capacitor while retaining the capacitance.

Why can a capacitor with a dielectric take up a bigger charge than one without a dielectric? The positive and negative charges in the dielectric outside the plates are equally distributed throughout the material. When the material is placed in an electric field between the plates, the electric potentials shift position. The ends of the material which are in contact with the plates have to attract more charge on

Table 11.4.3 ε_r- and ε-values of dielectrics

dielectric	ε_r	$\varepsilon (\times 10^{12})$
bakelite	3.5	30.99
ebonite	2.8	24.79
polyethene	3.5	30.99
PVC	2.25	19.92
rubber	3	26.56
glass	7	61.98
air	1	8.854
paper	3.5	30.99
water	80	708.4
oil	3	26.56
paraffin	2	17.71
mica	7	31.87
steatite	3.6	31.87
porcelain	3.2	28.33
magnesium titanate	12×24	106.3–354.2
sodium titanate	12×700	106.3×61980

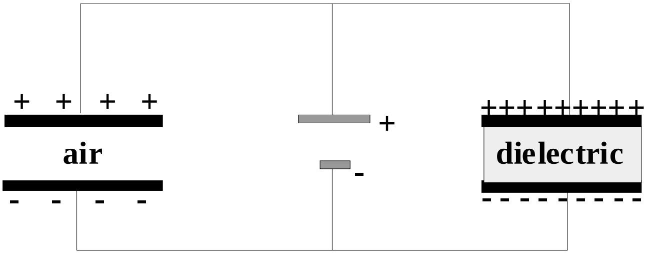


Fig. 11.4.18 Comparison of capacitors with and without dielectrics.

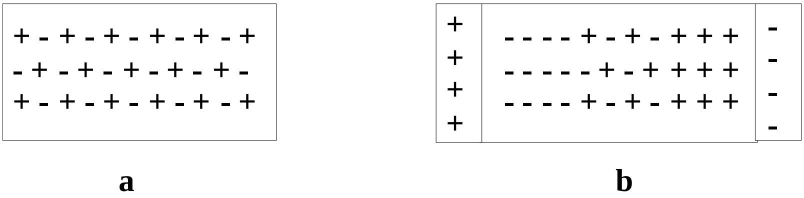


Fig. 11.4.19 Comparison of dielectrics outside (a) and between (b) the plates of a capacitor.

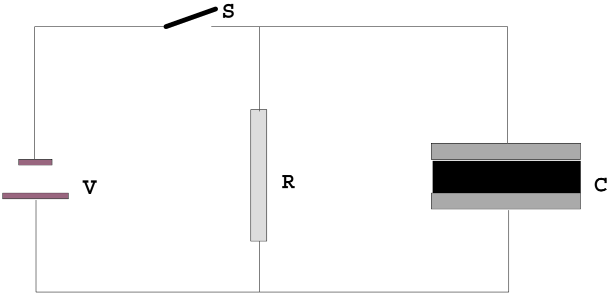


Fig. 11.4.20 Circuit for the discharge of a capacitor.

those plates to compensate for the charge in the materials (fig. 11.4.19).

A well-known application of the capacitor is its discharge in a flashlight. See figure 11.4.20 for the circuit in question.

The capacitor is charged by means of the switch S. When this switch is opened, the capacitor is discharged over the flashlight.

Finally some data on the construction of capacitors. Figure 11.4.21 shows the step by step construction of a common type of ceramic capacitor.

Figure A is the dielectric. In B two thin silver layers have been applied. In C you can see the conduction wires and in D the capacitor

Fig. 11.4.21 The construction of a ceramic capacitor.

has been wrapped in plastic. Figure 11.4.22 is a representation of a cylindrical capacitor with aluminium as metal and paper as dielectric.

A common type of capacitor is the so-called multi-layer capacitor (fig. 11.4.23). This type meets the modern requirements for small-sized capacitors which can store enormous amounts of charge. It is used in many devices commonly found on your desk or in your car, but is also found in domestic appliances, telecommunication and in measuring & control equipment.

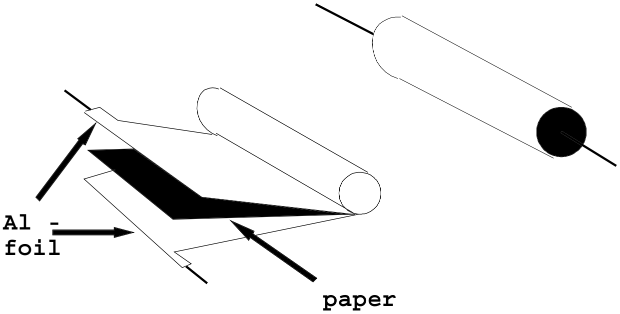


Fig. 11.4.22 The construction of a cylindrical capacitor.

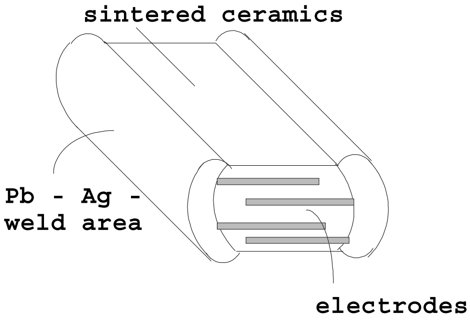


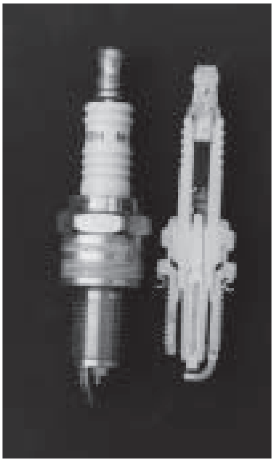
Fig. 11.4.23 A multi-layer capacitor.

11.4.6 Spark plugs

The use of spark plugs in internal combustion engines is well-known. There are many different types of spark plugs which are manufactured by several companies. The white part with on it the name of the manufacturer is made of ceramics. As you can see in the cross-section, the ceramic element functions as an insulator between both electrodes.

Manufacture

The spark plug casing is made of steel, the basic material of which is either an extrusion rod or a hexagonal steel bar. Other machines produce the steel ends for the cable lead. The central electrode is made of iron with a thin layer of copper onto which a special nickel alloy has been soldered in order to protect the electrode from heat and corrosion. Next the curved electrode, again a nickel alloy, is welded to the electrode body. The central electrode is passed through an insulator because the current which flows through it has to be completely isolated from the casing. The insulator is made of aluminium oxide powder. This is mixed with water and a binding agent and subsequently spray-dried. Next the powder is compressed into a mould, the profile is applied and the material is baked. Name and type number are added and finally the baked mass is covered with a vitreous layer. Different spark plugs have different assembly processes. Often the central electrode is cemented into the casing using so-called SILLMENT -powder under high pressure. This powder is protected by a patent.



Champion spark plug.

Quality control

Spark plugs are checked on their dimensions and on the density, porosity and breaking strength of the insulator. Their electrical behaviour is tested in a test engine.

Working

When a spark is formed between both electrodes, a mixture of petrol vapour and air (oxygen) is ignited according to the chemical equation:

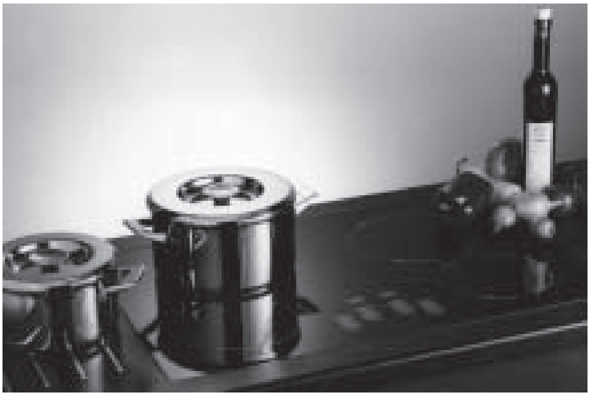
$$2\ C_4H_{10} + 13\ O_2 \rightarrow 8\ CO_2 + 10\ H_2O + \text{energy}$$

The released energy causes the gases to suddenly increase in volume, resulting in a movement of the piston

11.4.7 The ceramic heating plate

Approximately 6,000 years ago glass was accidently made for the first time in an Egyptian pottery. The extreme heat had caused a glass-like layer to form on the pots.At the time they did not yet understand what had happened. About 3500 years later, an Assyrian scientist wrote in a clay tablet: “*Take 60 parts of sand, 180 parts of ash from seaplants and 5 parts of chalk; heat this and glass will be formed*”. In 1879 Otto Schott discovered that the properties of ordinary glass could be changed by replacing and / or adding components (see the chapter on Fine Ceramics, glazes).

Electrolux and AEG, both manufacturers of ceramic heating plates, have more or less introduced me to a firm called Schott. This firm



Ceramic hot plate Electrolux AG, Zürich, Switzerland.

makes many kinds of glass. Schott used to be a German company but now has subsidiaries all over the world. They claim that they make glass-types for numerous applications:”*ranging from 7000 metres below sea level to 10^{12} metres above it*”: e.g. heat and cold resistant glass, windows for submarines and airplanes, glass fibres for e.g. medical equipment, laser glass, bulletproof glass, borosilicate glass for chemical reaction glassware, the telescope mirror of the weather satellite Meteostat and of course ceramic heating plates. It should, however, be born in mind that the material used for a ceramic heating plate stands midway between glass and ceramics and is called glass ceramics for precisely that reason. This means that the material is partly amorphous and partly crystalline.

Schott provided me with information on the production process of the “Ceran” heating plate. It is produced in two stages: the glass production and the ceramizing, i.e. changing glass into glass ceramics. The raw material for the glass production is a patented, and consequently secret, mixture of more than 15 components. Figure 11.4.24 shows the production of the glass plates for ceramic cookers.

After the glass plates have been cut to size, their edges are polished and provided with a decoration. This part of the process is not included in the figure. The decoration process involves ceramic dye which is applied under pressure and subsequently burned into the glass. After that the glass is ceramized, i.e. the crystal growth in the glass

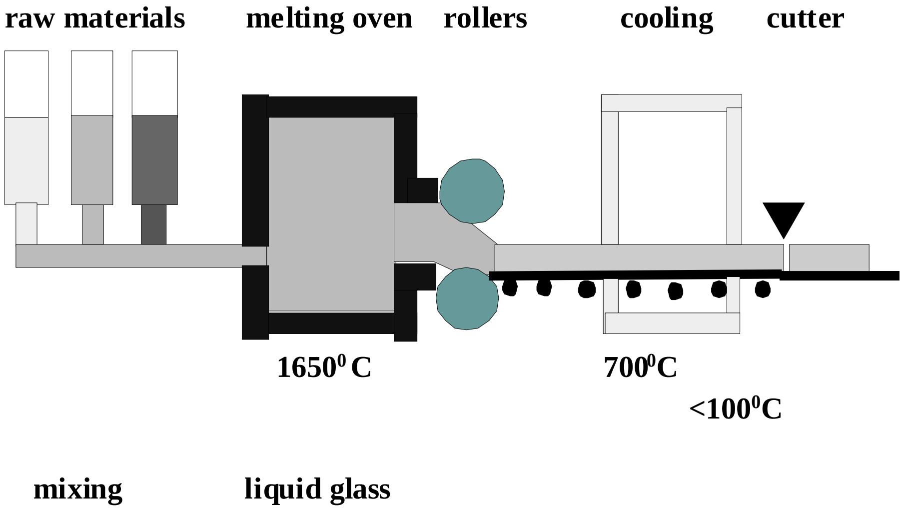


Fig. 11.4.24 The production of glass plates for the “Ceran” ceramic heating plate as made by Schott.

is initiated and also stopped in time by means of a special heat treatment. The result is a partly crystalline, partly amorphous material: a glass ceramic.

Finally the plate is tested on heat expansion coefficient, temperature shock resistance, temperature stress (6,000 hours at 650^0C), density, E-modulus (92×10^3 N/mm^2), flexural strength, impact resistance, Knoop hardness, acid and base resistance. The heating element is insulated with a compressed mixture of powder and fibre which contains aluminium oxide and silicon oxide. In the middle the element contains a so-called Stabausdehnungsbegrenzer (= expansion limiter), which automatically switches the element off in case the temperature exceeds a certain pre-set value.

11.4.8 Piezoceramics

Before the phenomenon piezoceramics can be discussed, some attention should be paid to **ferroelectric ceramics**.

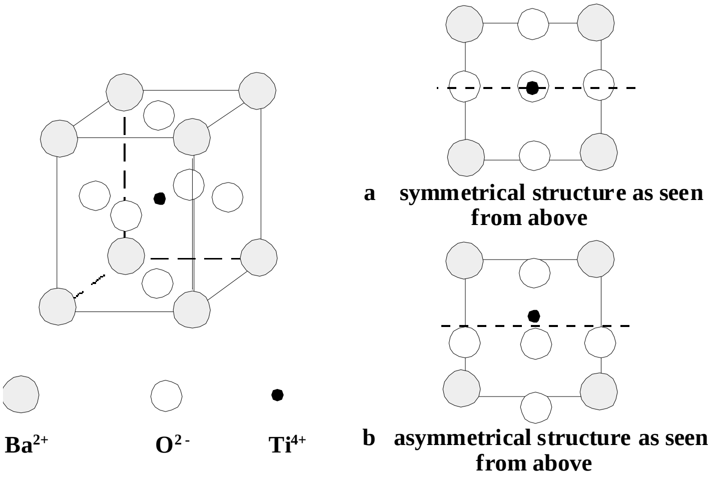
By placing a material in an external electric field, ionogenic compounds can be polarised. Without the electric field the centres of the positive and negative charges always coincide and the matter is not polarised. A compound like titanium (IV) oxide,TiO_2, is polarised in an electric field.When the field is switched off, the polarisation immediately disappears. Such a compound is called para-electric. A ferroelectric substance is also polarised in an electric field but retains part of its polarisation even after the field has been switched off. A well-known example is barium titanate, which belongs to the group of compounds commonly denoted by means of the ABO_3-formula. They have adopted the ideal perovskite crystal structure ($CaTiO_3$); A and B can be:

$$ABO_3 \qquad \begin{array}{l} A = Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+} \\ B = Ti^{4+}, Sn^{4+}, Zr^{4+} \end{array}$$

In perovskite the calcium and oxygen ions form a cubic and closely packed structure with

Ti^{4+} ions in 1/4 of the octahedral sites. The titanium ion is relatively small compared with the octahedral site which is formed by the six oxygen ions. In the perfect structure, i.e. when the titanium ion is precisely placed in the centre of the octahedral, the centre of the positive charges coincides with that of the negative ones. As a result the crystal structure is symmetrical. Under the influence of an external electric field, the titanium ion can easily shift, due to which the crystal lattice can be polarised. After the field has been switched off, a certain polarisation persists and this phenomenon is called “ferroelectric behaviour”. In figure 11.4.25 a barium titanate unit cell is shown with the symmetrical and asymmetrical crystal structure as seen from above.

At temperatures higher than 120^0C barium titanate possesses a symmetrical structure. Below that temperature the Ti^{4+}-ion and the surrounding O^{2-}-ions will have moved slightly in the opposite direction from the symmetrical structure. As a result the crystal will possess a small dipole moment because the centres of the positive and negative charges are slightly separated (the theory of the dipole was discussed in chapter 3, Chemistry).



a symmetrical structure as seen from above

b asymmetrical structure as seen from above

Fig. 11.4.25 Unit cell of barium titanate.

Let’s return for a moment to the dielectric of the capacitor. The ε_r - value of the dielectric is dependent on the ability to shift charges within that dielectric. This explains why barium titanate is a suitable dielectric and why the ε_r - value can be varied when you influence the mobility of the titanium ions by building in foreign ions. The latter is illustrated in Table 11.4.4.

The piezoelectric effect is an electromechanical effect in which mechanical evoke and reverse an electric reaction in a ferroelectric material and vice versa. The word “piezo” has been derived from the Greek “piezein” which means “press”. Compounds are composed of positive and negative ions and are electrically neutral as a whole. The fact that electrically charged particles are still present in the crystal can for example be demonstrated by means of the electric

Table 11.4.4 Some ε_r values of barium titanate dielectrics

ε_r – value	dielectric
325	$BaTiO_3$ = $CaTiO_3$ = low% $Bi_2Sn_3O_9$
6500	$BaTiO_3$ + low % $CaZrO_3$ or $CaTiO_3$ + $BaZrO_3$

conductivity of salt solutions.

In some crystals the presence of ions can be demonstrated without making use of destructive techniques. These crystals produce an electric effect when they are compressed. Due to this pressure, ions are displaced and this displacement of electrical charges is a voltage. The deformation in a crystal leads to movement of both negative and positive ions. When these both move equally far and in the same direction, the result is no net voltage. A crystal will only exhibit piezoelectricity when the positive and negative ions cover a different distance once subjected to pressure. What exactly take place in such a crystal is illustrated in figure 11.4.26

In the figure above three positive and three negative ions form a crystal unit. When there is no question of pressure, the centres of the negative and positive charges coincide. Should a pressure be exerted in the direction indicated by the arrow, then the negative ions move differently from the positive ones. As a result the centres slightly separate and a small voltage may be detected. When the crystal is no longer subjected to any pressure, the centres return to their original positions and a reverse voltage arises.

Piezoelectricity also has a converse: the production of a mechanical

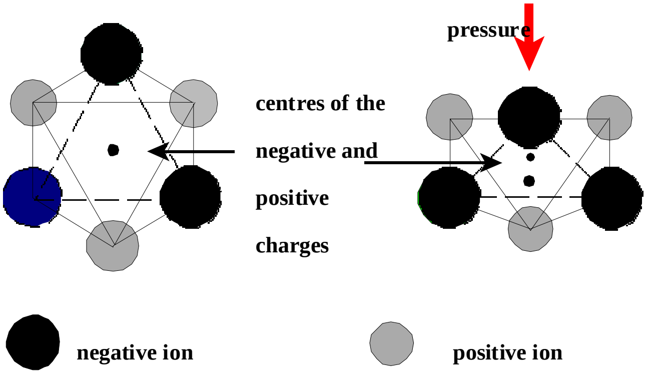


Fig. 11.4.26 Fictitious crystal unit of a piezocrystal, not subjected and subjected to pressure.

deformation in a crystal across which an electric field is applied. When the field is removed, the crystal resumes its original shape. This effect is often applied in high-frequency technology. Extremely thin piezoelectric slabs can be made to produce high-frequency vibrations by applying an electric field.

As mentioned earlier, only certain crystal exhibits piezoelectric behaviour. Only pressure on certain electrically neutral crystals - those not having a centre of structural symmetry - polarizes them by slightly separating the centre of the positive charge from that of the negative charge. Some examples of such crystals are:

Sodium chlorate	$NaClO_3$
sodium bromate	$NaBrO_3$
nickel sulphate	$NiSO_4.6H_20$
Rochelle salt (sodium potassium tartrate – tetrahydrate)	$KNaC_4H_4O_6.4H_2O$

Because many of these suitable substances are hygroscopic, quartz is used a lot nowadays.

It is quite easy to make the above-mentioned piezoelectric compounds (with the exception of quartz) and some other crystals from aqueous solutions. In the case of Rochelle salt the piezoeffect is so strong that it can be demonstrated with a simple experiment (fig. 11.4.27).

One hammer-blow on the crystal produces a sudden change in form which – in its turn – causes a small current surge. A split second

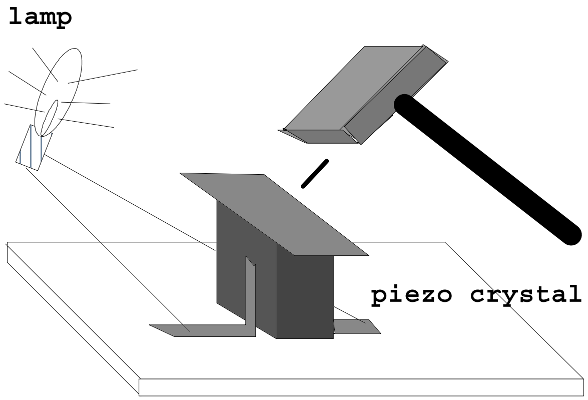


Fig. 11.4.27 Test rig for a demonstration of the piezoelectric effect. (Source: Crystals and Crystal Growing, Doubleday & Company).

later the crystal resumes its original shape which results in a surge in the reversed direction. Consequently, a succession of hammer-blows produces an alternating current.

Some applications of piezoelectric materials:

* quartz plates in transmitters
* in ultrasonic techniques form generating waves, e.g. in ultrasonic purification
* quartz watches
* crystal microphones: mechanical vibrations are converted into electrical impulses
* crystal elements in phonographic pickups
* musical greeting cards: they contain a chip, a battery and a minute piezoceramic loudspeaker
* scaling: the ceramic energy converter causes the top of the dentist's instrument to vibrate.

The instrument itself propels a cleaning liquid to the top and in this way the deposit is removed.

* gas lighters: mechanical energy is converted into a spark
* $Pb(Ti,Zr)O_3$-ceramic used as a sensor in a car engine to detect knocking noises and to adjust the ignition. This ceramic is also used in sonor equipment.

11.5
Magnetoceramics

Magnetic fields and forces are caused by the movement of the most elementary charge, the electron, around the nucleus of the atom.

In figure 11.5.1 you can see two of these electrons in the same shell. Because they circulate around the atomic nucleus and also spin on their own axes, electrons generate a small magnetic field or magnetic moment, also called magnetic dipole. In atoms with an even number of electrons (and consequently an even atomic number) these magnetic fields cancel out because the electrons spin in different directions on their axes. Consequently it would be logical for atoms with odd atomic numbers to exhibit magnetic behaviour, due to the unpaired electron. However, the unpaired electron is usually the valence electron and its magnetic field is cancelled out by the valence electron of a neighbouring atom.

There are, however, certain elements whose atoms possess shells with unpaired electrons other than valence shells, e.g. some so-called transition metals from groups 3 up to and including 12 of the Periodic Table.

In paragraph 11.1 in the item on glazes the filling of the orbits with electrons was represented schematically. When this same principle is applied to the elements 23 up to and including 29 you will find

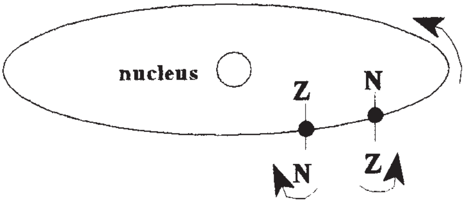


Fig. 11.5.1 An electron which moves around the nucleus of an atom generates a minute magnetic field NZ.

that some elements deviate from it, as can be seen in the electron distributions in table 11.5.

Table 11.5.1 Electron distributions of the elements 23 up to and including 29. An electron is represented by means of a vertical line

<table>
<tr><th>Atomic number</th><th>Element</th><th colspan="5">Electron distribution over five 3d-shells</th><th>Number of electrons in 4s-shell</th></tr>
<tr><td>23</td><td>V</td><td>|</td><td>|</td><td>|</td><td></td><td></td><td>||</td></tr>
<tr><td>24</td><td>Cr</td><td>|</td><td>|</td><td>|</td><td>|</td><td>|</td><td>|</td></tr>
<tr><td>25</td><td>Mn</td><td>|</td><td>|</td><td>|</td><td>|</td><td>|</td><td>||</td></tr>
<tr><td>26</td><td>Fe</td><td>||</td><td>|</td><td>|</td><td>|</td><td>|</td><td>||</td></tr>
<tr><td>27</td><td>Co</td><td>||</td><td>||</td><td>|</td><td>|</td><td>|</td><td>||</td></tr>
<tr><td>28</td><td>Ni</td><td>||</td><td>||</td><td>||</td><td>|</td><td>|</td><td>||</td></tr>
<tr><td>29</td><td>Cu</td><td>||</td><td>||</td><td>||</td><td>||</td><td>||</td><td>|</td></tr>
</table>

The magnetic moment of the 4*s*-valence electron of a chromium and a copper atom is cancelled out by the magnetic moment of a neighbouring atom’s valence electron. All atoms in the table, except for copper, have unpaired electrons in *d*-orbits due to which you would expect a magnetic moment. They exhibit this behaviour when they are placed in an external magnetic field. As soon as this external magnetic field is switched off, the magnetism in the metals disappears.

Of all well-known metals only **iron**, **cobalt** and **nickel** can be magnetized permanently. This means that the magnetic field will remain present even after the external field has been switched off.

Gadolinium (Gd) can also be magnetized permanently at temperatures $< 16\,^{o}$C, but the number of industrial applications is slight.

Other magnetic materials based on rare earth metals are NdFeB with neodymium Nd and SmCo with samarium Sm. These materials are characterized by huge magnetic forces at relatively small dimensions.

So the possession of unpaired electrons is a prerequisite for permanent magnetization. A second important condition appears to be that the ratio between the atomic distance and the diameter of the 3*d*-orbit should have a value that lies between 1.4 and 2.7, a condition which only Fe, Co and Ni appear to meet.

Magnetizability

A material can be magnetized by wrapping a copper wire around it and leading a current through that wire. Without any material in its centre, the coiled wire, also called coil, produces a magnetic field with a strength of *H* when current flows through it. In formula:

$$\text{magnetic field H in a coil:} \quad H = \frac{n \times I}{l} \ \text{A/m (Ampere/metre)}$$

where n is the number of turns, I the strength of current (A), l is the length of the coil (m).

The presence of the magnetic field can be demonstrated by means of iron powder. The iron particles are aligned and grouped and the magnetic lines of force become visible. The direction and the number of lines per given area are called the magnetic flux.

Another related term is:

flux density *B* in an empty coil = number of lines of force per area unit:

$$\mathrm{B} = \mu_0 \times H \ \text{Tesla [or Weber/m}^2\text{]}$$

$$[\mu_0 = \text{magnetic field constant} = 4\pi \times 10^{-7} \ \text{Weber/A.m.}]$$

When we fill the interior of a coil with a certain material, the value *B* will change because magnetic dipoles in the material turn into alignment.

$$\text{Flux density in a filled coil: } \mathrm{B} = \mu \times H \quad \text{with } \mu = \mu_r \times \mu_0$$

[μ = absolute permeability of the material inside the coil,
μ_r = relative permeability of the material inside the coil]

In literature, μ_r is used to describe the behaviour of a material within a coil because its value indicates whether or not a material is easily magnetized.

A calculation example: Which material can be used to insert into a coil when you consider the following requirements: the material must be able to withstand a flux density of 0.3 Tesla. A current of 12 mA flows through the coil and the coil consists of 10 windings per centimetre.

$$H = \frac{10 \times 0.012\ A}{0.01m} = 12\,\text{A/m}$$

$$B = \mu \times H \rightarrow 0.3 = \mu \times 12 \rightarrow \mu = 0.025\ \text{Tesla/A/m}$$

$$\mu_r = \frac{\mu}{\mu_0} = \frac{0.025}{4\pi \times 10^{-7}} = 2.0 \times 10^4$$

Based on the μ_r value, we can now choose the material.

The increase in flux density: $B = \mu \times H - \mu_0 \times H = \mu_0 \times M$ M is the magnetizability of the material inside the coil

Finally, the last formula in this chapter:

$$\chi = \text{magnetic susceptibility} = \frac{M}{H}$$

Magnetic susceptibility is a measure for the change in the magnetic field strength in the coil when a material is placed inside it.

Several kinds of magnetism will now be described on the basis of magnetic susceptibility.

Types of magnetism

In a magnetic field materials behave differently owing to different interactions between the magnetic dipoles in the material and the external field. When we introduce a material in a magnetic field, the field upsets the balance of the electrons inside this material.

The result may be that small magnetic dipoles are formed in the atoms or ions which are oppositely aligned to the external field. Consequently, a minute magnetic field is induced in the material, which is oppositely aligned to the external field. This phenomenon is called **diamagnetism, χ = appr 10^{-6}.**

The magnetization is negative and the materials have a μ_r-value of approximately 0.99995. Diamagnetism can only exist in an external field and among the materials which exhibit this phenomenon are Cd, Cu, Ag, Sn and Al_2O_3, as well as the minerals calcite $CaCO_3$ and fluorite CaF_2.

Other materials exhibit a minute positive magnetic susceptibility of appr. 10^{-6}–10^{-2}. This phenomenon is called **paramagnetism χ = appr. 10^{-6}–10^{-2}** and occurs because dipoles of atoms or molecules in a material align themselves in a magnetic field. Some examples are: Al, oxygen O_2, platinum, titanium. The magnetic dipoles in the material line up with the external field. Since no interaction occurs between the dipoles, a strong external field is needed for an optimal magnetization of the material.

The most important form of magnetic behaviour is **ferromagnetism** χ = appr. 10^6.

Once a ferromagnetic material is magnetized in an external field, the material will remain magnetic even when the field is removed. Ferromagnetic materials are fairly strongly magnetized in a relatively weak external field, because a strong interaction takes place between the magnetic moments of the neighbouring atoms or ions. The most important ferromagnetic materials are ***iron, cobalt and nickel.***

Once the magnetic dipoles have aligned, the orientation becomes so strong that it is hardly affected by vibrations of atoms or ions. This contrary to diamagnetism and paramagnetism in which cases the orientation is strongly disturbed by the vibrations of the building blocks of the materials, even at low temperatures.

By increasing the temperature of a ferromagnetic you can reach a point at which the ferromagnetic character disappears and the material becomes paramagnetic. This is called the *Curie temperature*. Curie temperatures of some ferromagnetic sustances are: iron: 770 °C, nickel: 358 °C and cobalt: 1123 °C.

Let us now have a closer look at a ferromagnetic material before it is magnetized. In that case a number of areas exist in the material which are called domains. Within these domains a certain orientation of magnetic moments is present, which can vary in the individual domains (see figure 11.5.2).

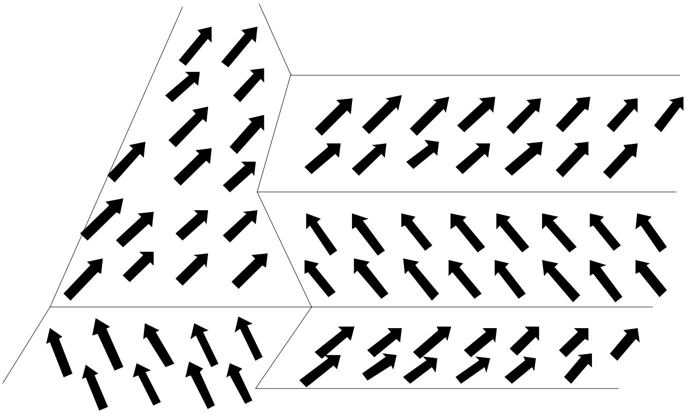


Fig. 11.5.2. Magnetic domains in a ferromagnetic material.

When the demagnetized material is inserted into an external magnetic field, the domains which are almost parallel to the external field will grow at the expense of the ones which are not parallel (see figure 11.5.3).

a. starting condition **b. domain growth**

c. more growth **d. rotation**

→

direction of external magnetic field

Fig. 11.5.3 Growth of magnetic domains in an external field.

Once the external field is removed, a ferromagnetic material will remain magnetized. Some loss will occur, however, due to which some domains will revert to their original alignment. In figure 11.5.4 the magnetic induction or flux density B has been plotted as a function of the strength of the external magnetic field H.

When a demagnetized ferromagnetic material is placed in an external field H of increasing strength, the magnetic induction B will follow the curve OA until it reaches a maximum value for B, which is indicated by point A. When the strength of H is subsequently, decreased the value of B will follow the curve AC. In order to decrease the magnetic induction to 0 a negative external field with a size of H_c is necessary, the *coercive force*.

As you can also see in figure 11.5.4, an amount of magnetization remains behind in the material when the external field is no longer present. On increasing the value of the negative external field, B falls to a value corresponding with point E in the curve. The total curve is called a *hysteresis loop*.

Based on figure 11.5.4 two kinds of magnetic materials can be defined, viz.

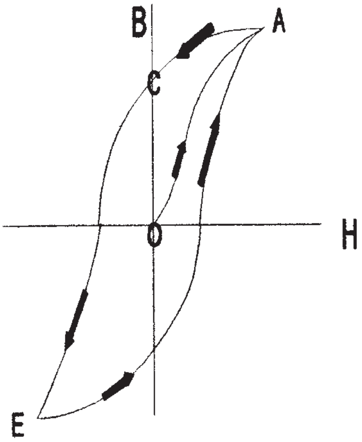


Fig. 11.5.4 Magnetic induction or flux density *B* as a function of the strength *H* of an external field.

Soft magnetic materials: such a material can easily be magnetized and demagnetized (fig. 11.5.5.a), i.e. a small external field suffices to realize the (de)magnetization. Examples of such materials are iron with 3–4% silicon and metallic glasses. The latter are relatively new materials. They are non-crystalline and mainly consist of combinations of ferromagnetic Fe, Co and Ni with the non-metals boron and silicon, e.g. $Fe_{67}Co_{18}B_{14}Si$. They are applied in transformers, magnetic sensors and recording heads.

Hard magnetic materials: these materials cannot be magnetized nor demagnetized easily (fig. 11.5.5b). Examples of such materials are Alnico alloys containing iron, alloys of rare earths and Fe–Cr–Co alloys.

In some ceramic compounds, the different kinds of ions possess different and strong magnetic dipoles. In addition, both kinds are partially oppositely aligned in an external field. Since the sizes of the magnetization are unequal, the result is a net magnetization which can considerably reinforce the external field. This is called **ferrimagnetism.**

This form of magnetism can be demonstrated by means of lodestone or magnetite (Fe_3O_4) which freely occurs in nature. A unit of this contains one Fe^{2+} ion, two Fe^{3+} ions and four O^{2-} ions. Its crystal structure is a cubic close packing of oxygen ions with an Fe^{3+} ion in 1/8 of the tetrahedral cavities, an Fe^{3+} ion in 1/4 of the octahedral cavities and an Fe^{2+} ions in 1/4 of the octahedral cavities. Magnetic dipoles at tetrahedral sites line up antiparallel to the external field and dipoles in the octahedral cavities line up parallel to the field.

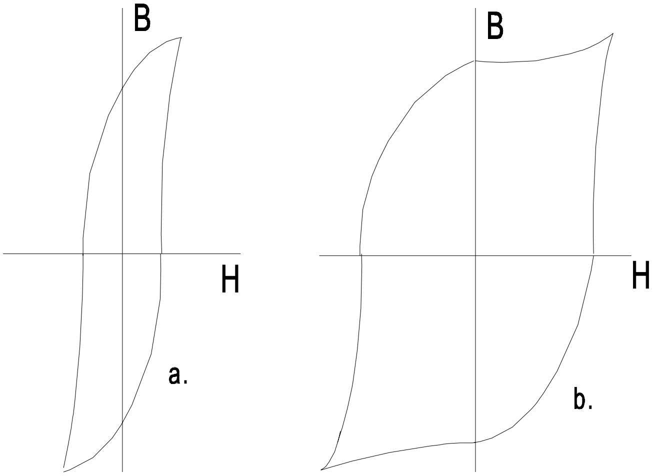


Fig.11.5.5 Hysteresis loop of a soft (a) and a hard (b) magnetic material.

The Fe $^{3+}$ ions consequently cancel out and the Fe $^{2+}$ ions reinforce the field.

Synthetic ferrites also exhibit ferrimagnetism. Ferrites are magnetic ceramic materials which are made by mixing iron (III) oxide with, for instance, powdered oxides and carbonates and subsequently compressing and sintering them. They are produced in large quantities and in many different shapes. We distinguish soft and hard ferrites.

Hard ferrites: in general have the formula $MO.6Fe_2O_3$, where M = Ba $^{2+}$, Sr $^{2+}$ or Pb $^{2+}$. They are mainly used as permanent magnets.

Soft ferrites: usually have the formula $MO.Fe_2O_3$, where M = Fe $^{2+}$, Mn $^{2+}$, Ni $^{2+}$ or Zn $^{2+}$.

11.6
Bioceramics

11.6.1 Introduction

On 20 May 1992, a Dutch periodical published an article in which they mentioned the possibility of healing fractures with mother-of-pearl and coral. With this method painful operations could be avoided. The article was illustrated with an ancient Maya skull which showed a hole filled with mother-of-pearl. The ancient Mayas were well ahead of their time.

By the end of the 1980s this method had surfaced again in medicine. A group of French scientists discovered that coral is very useful when healing fractures. The French firm Inoteb now obtains coral from seas all over the world, cleans it and prepares it for implantation into the body.

The main components of calcareous corals are calcium carbonate in the modification calcite, magnesium carbonate and proteins which act as binding agents. Coral from the southern seas appears to resemble human bone. It has the same bubble-like structure and, like bone, its chemical composition is based on calcium carbonate. Coral cells are not considered to be “intruders”, provided all organic material is carefully removed. Consequently coral is not rejected by the human body when implanted. As soon as a piece of coral has been introduced in the bone, the surrounding bone cells start to penetrate the bone completely, while simultaneously digesting everything they come across. Thus the coral is gradually replaced by human bone. The material is used in operations on the jaw, corrections of the spine and in case of broken limbs.

Yet another product of the sea is a huge oyster found south of the Philippine island Palawan. It is called Pinctada maxima and can weigh up to ten kilogrammes. This oyster produces a shell which is as strong as reinforced vibrated concrete. Like coral, this shell is made of calcium carbonate. The inside is covered with mother-of-pearl which cannot be “digested” by human bone cells. Mother-of-pearl consists for approximately 66% of calcium carbonate and for about 31% of water. The rest is conchioline, a though and horny product.

The surface of the mother-of-pearl is somewhat permeable for human cells and consequently these cells can form a strong bond between the mother-of-pearl and the bone. Mother-of-pearl is also used in the manufacture of artificial dental roots. These can be attached to the jaw much more firmly than any metal whatsoever. It is thought that mother-of-pearl contains certain natural substances which accelerate the production of human bone.

Thus it appears that nature teaches us how certain defects in the human body can be mended in a natural way.

Calcium carbonate, mother-of-pearl, magnesite, dolomite and other inorganic materials which nature uses to provide an organism with solidity, have been categorized under the name bioceramic materials. Later some synthetic materials were added to this group. This means that the definition of a ceramic material, as given at the beginning of this book, must somewhat be adjusted as the heat treatment of a ceramic material obviously does not apply in the animal world.

11.6.2 Implants

Definition

As mentioned in paragraph 11.6.1 bioceramics are used to repair defects in the human body. Thus a material from outside the body is brought into direct contact with body tissue without any intermediate layer like the skin. These materials are called implants or biomaterials and can be defined in several ways. Two of these definitions are:

A biomaterial is a synthetic material used to replace part of a living system or to function in direct contact with living tissue.

In 1987 La Revue published an elaborate definition of implants:

- materials for prolonged implantation in human tissue, e.g. artificial veins, teeth and joints
- products for prolonged contact with vessels and tissue, e.g. catheters and intravenous drips
- products for brief contact with tissue or bone, like probes or research instruments
- materials for obtaining and storing blood and blood plasma
- surgical instruments

Summarized: Solid, soluble or insoluble, degradable or non-degradable products for brief or prolonged contact with human tissue.

Although hearing aids and removable artificial limbs are made of synthetic material, they are not included in the definition. This is because the skin forms a barrier between the living organism and the outside world.

Applications

Since the beginning of the 19th century people have experimented with many different materials to manufacture implants. These materials can be subdivided into three main groups.

a. Plastics: e.g. polyesters and silicones

The mechanical properties of these materials are too weak to use them in places in the body where much pressure is exerted. It is virtually impossible to achieve 100% polymerisation during the production process. Consequently the material contains impurities which may lead to toxic, allergic or carcinogenic processes. In future so-called biodegradable plastics will be used in applications such as artificial skin, synthetic blood, bone plates and in the controlled release of medication.

b. Metals and alloys, e.g. titanium and cobalt chromium alloys

The main advantage of this group of materials is resistance to pressure. However, there are also disadvantages, such as a high rigidity in comparison to bone, local pitting corrosion due to the fact that there is no protective layer, metal fatigue and friction corrosion. The latter results in rejection which is caused by released ions.

c. Ceramics

There are countless applications possible. Nowadays, it is possible to replace human parts with synthetic materials virtually anywhere in the body. Table 11.6.1 lists a number of examples of plastic and metal implants. Ceramic implants are not mentioned here because they will be discussed elaborately in this chapter.

Table 11.6.1 Some examples of implants

Material	Application
plastic	transdermal plaster artificial skin blood vessel prosthesis eye lens voice prosthesis ear and nose
metals and alloys	hip joint bone plates and screws dental root implants

Requirements

A material is a biomaterial when it meets certain requirements: it has to have the right physical and chemical properties and, in addition, be biocompatible, which means that it must not be rejected by the body. The material may not release any substances which might activate the host's immune system. As indicated earlier, the first biomaterials were metals and these still play an important part. Of all metals and alloys, titanium appears to be accepted best by tissues. Actually this is rather peculiar, as titanium is relatively rare in vegetable and animal tissue but relatively abundant in the earth's crust (0.2% of the mass of the earth's crust is titanium; only six other metals are even more abundant). For some time now, titanium has been used in dental surgery and in attaching and replacing bones and joints.

11.6.3 History of implantology

In literature implants and transplants are often considered to be related. In table 11.6.1 some examples of both were given. Both similarities and differences exist between both groups.

A similarity is that in both cases a nonself object is brought into contact with body tissue which is not separated from this object by skin.

A difference is that an implant consists of synthetic material, whereas a transplant is usually made of material from another living organism.

Since implant materials are fairly recent, transplants might be considered to be the precursors of implants; a brief historical survey confirms this view.

The first successful transplants of teeth, noses and even entire legs date from the Middle Ages. At that time noses were sometimes lost in sword fights or as a result of an advanced stage of syphilis. Many accounts exist of requests to transplant one part of the body to another, e.g. skin or flesh from an arm to the nose. In 1596 Tagliacozzi described the first skin transplant. After the Middle Ages transplants of noses and teeth from slaves were reported.

At about 1860 the first sterile surgical techniques were introduced by Lister. About 100 years ago, the research into the field of implants, notably of the hip joint, was started. In 1891 Znamensky first described the use of ceramic materials in the manufacture of implants.

Around 1900 bone plates to secure broken bones were introduced. Many of these plates broke due to design flaws, i.e. they were too thin and / or had angles with tension concentrations. Scientists also experimented with vanadium steel, this material has good mechanical properties, but corrodes fast in the body. At about 1930 stainless steel and Co/Cr alloys were also applied.

In 1931 Brill published the article: “Über die Implantation von Porzellan Wurzeln” (On the transplanting of procelain dental roots) and which was followed in 1934 by Abel’s “Die Befestigung implantierten Porzellanzahnersatzes mittel Wiplakieferschrauben” (Attaching porcelain teeth by means of Wipla jaw screws).

In 1993 Rock patented the use of aluminium oxide ceramics as implant materials: “Patent-erteiling über Aluminiumoxidekeramik für das Innere und Außere des menschlichen und tierischen Körpers”.

During World War II pilots were sometimes injured by PMMA fragments from the roof of their airplanes. However, these fragments did not appear to have detrimental effects on their bodies.

This discovery soon led to the use of PMMA in cornea transplants and in the replacement of damaged skull bones.

The first synthetic blood vessels date from the 1950s.

In 1952 professor PerIngvan Brånemark in Lund, Sweden accidentally discovered the tissue-friendly properties of titanium. He was microscopically investigating living bone tissue on a titanium surface. After some time the titanium appeared to be irreversibly attached to the tissue.

In the 1960s the first heart valve was replaced. At approximately the same time the Englishman Sir John Charnley developed a bone cement on the basis of PMMA. Nowadays an improved version of this cement is still used, e.g. to secure an artificial hip joint to the upper leg.

Because the shafts of artificial hips joints fractured quite often, much research was aimed at improving the solidity of the materials in the 1970s. Nowadays much better materials are available, notably titanium alloys.

These last few decades many ceramic materials have been used as implants. This development will be discussed in the next paragraphs. As far as the present state of affairs is concerned, nature is still the best engineer. The ideal implant has not yet been found. Pure titanium is best tolerated by living tissue. However, increasingly often a porous surface layer is applied to the metal. In this way it is easier for the bone cells to attach themselves to the metal. In addition we now use materials which were thought to be unsuitable in the past. Improved surgical techniques and the development of antibiotics have been of vital importance here.

Table 11.6.2 The most commonly used ceramic implant materials

Name	Chemical formula
aluminium oxide	Al_2O_3
zirconium oxide	ZrO_2
hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$
barium titanate	$BaTiO_3$
glass ceramics (collective name)	e.g. mixtures of SiO_2, Na_2O, CaO and P_2O_5 $Ca_3(PO_4)_2$
tricalcium phosphate	$Ca_3(PO_4)_2$
calcium aluminate	$CaAl_2O_4$
composite materials (collective name)	e.g. Al_2O_3, reinforced with ZrO_2

11.6.4 Ceramic implant materials

Materials

Recently mainly synthetic materials have been used as ceramic implantation materials. Table 11.6.2 lists the most commonly used materials.

The materials can be divided into bio-inert, bio-tolerant and bio-active materials. The difference depends on the kind of contact the tissue makes with the introduced material.

With a bio-inert material, like aluminium oxide, the tissue makes direct contact with the implant material after some time. When a bio-tolerant material like bone cement is introduced, new bone tissue is formed at some distance from the implant. A layer of connective tissue separates the implant from the bone tissue. In the case of a bio-active material, like for instance hydroxyapaptite, new tissue penetrates the implant. In due course the original separation between the implant and tissue disappears. In this way the implant is as it were integrated into the tissue.

There exists an inverse relationship between the biological and mechanical properties of bio-materials: the better the tissue tolerates the implant material, the worse the mechanical properties of the material are (figure 11.6.3).

Bio-inert materials

The most common bio-inert materials are aluminium oxide and zirconium oxide.

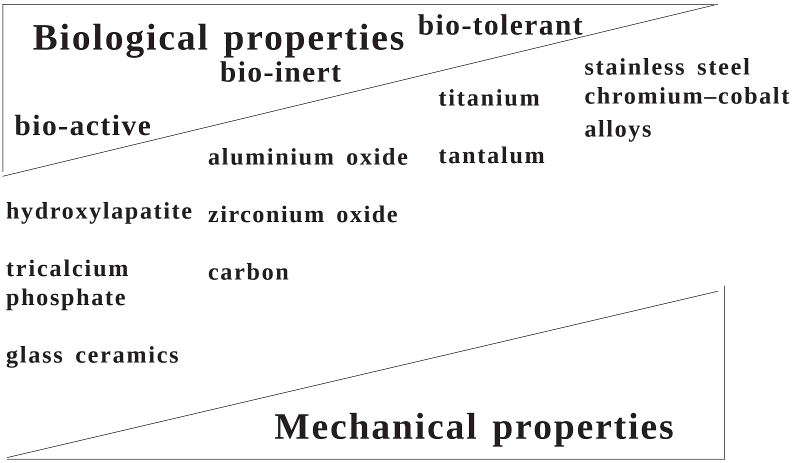
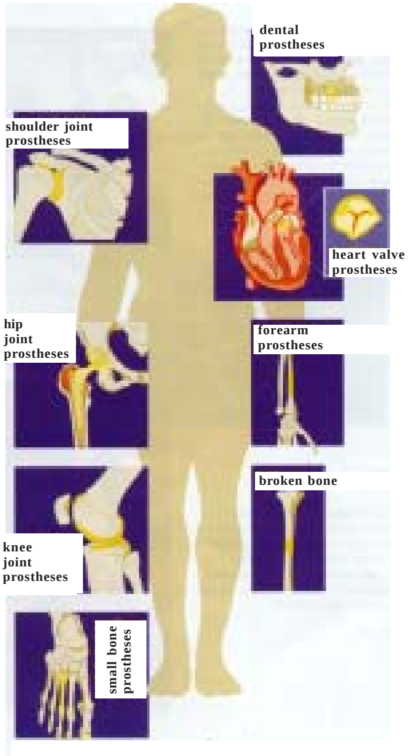


Fig. 11.6.1 The relationship between the biological and mechanical properties of bio-materials.



Ceramics in the human body (source: the Dutch magazine *Natuur y Techniek*),

The raw material

Aluminium oxide is the oldest ceramic material used in medicine. Bauxite and corundum are the main natural sources of aluminium oxide. Bauxite is a mixture of diaspore, gibbsite, iron hydroxides, clay minerals and quartz. It is formed by the tropical weathering of silicate rocks during which quartz and the elements sodium, calcium, magnesium and potassium are largely washed away. This is the reason why the remaining material becomes richer in the resistant elements titanium, iron and aluminium. The latter is extracted from this mixture in the form of aluminium hydroxide. In its turn this compound is converted into aluminium oxide by heating the mixture to 1200–1300 °C, this is called calcination. The hydroxide is thus made anhydrous.

Several crystal structures of the oxide are known. The most common one is α-Al_2O_3 which is made by the calcination of $Al_2O_5.3H_2O$. Natural corundum is found as semi-translucent masses with a white or greyish colour. It resembles quartz. Chemically seen, corundum is related to the much more beautiful sapphire and ruby. These have the same formula, Al_2O_3, but in their cases impurities result in the colour.

Aluminium oxide as implant material

Al_2O_3 is absolutely bio-inert. It is also called bio-stable. Consequently the material became very popular in orthopedics and dentistry in the mid-seventies. Earlier industry had already put much effort in making the oxide resistant to wear and corrosion. By far the most important application in medicine is as the femur head ball in the ball-and-socket joint of the hip.

In comparison with metals, aluminium oxide releases very few ions. This is measured in several ways, one of which is by inserting the implant material in artificial saliva for 6 months. After this period the number of released metal ions is measured by means of special trace analysis techniques.

Aluminium oxide ceramics contain elements with an atom mass which is virtually identical to the atom mass of the elements in bone. The crystal lattice contains Al^{3+} and O^{2-} ions. The aluminium oxide is not stable in the air as it wants to combine with components in the air. That is why the surface of a crystal only contains O^{2-} ions. These attract substances with a large dipole from the environment, like for instance water molecules and protein-containing body substances. Since the aluminium oxide implant in the body is covered by a layer of protein molecules, the body does not recognize the implant as nonself, and consequently the defence mechanism is not activated.

The bio-compatibility of the oxide, which is also called bio-tolerance, was tested in vitro (in tissue culture) and in vivo (in animals and humans). In addition bio-mechanical experiments were carried out on animals, some were spread over a short period of time (approximately 9 weeks) and others over a longer one (up to approximately 104 weeks). Implants in human beings are checked at intervals of 6 weeks, 3, 6 and 12 months and annually.

The corrosion speed (even in concentrated HCl, HF and H_3PO_4) is not even 10^{-4} g/cm/day, which equals 1 mm/10 years. In blood serum (which is a saline solution rich in proteins) with a pH of almost 7, the corrosion speed is even less.

The material which is released because of the wearing of the aluminium oxide, must be assimilated at once and should not cause any rejection symptoms.

In table 11.6.3 some chemical properties of an aluminium oxide (trade name Biolox) are compared with those of some other metals.

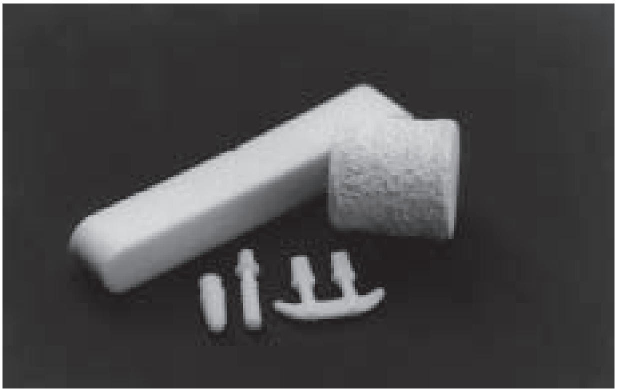
From the table above, it appears that aluminium oxide is extremely hard. That is why the material has to be processed with diamond. The compression, bending and tensile strengths of metals are dependent on the heat treatment. The modulus of elasticity of aluminium oxide is almost double that of stainless steel; this means that twice the strength is needed for the same elastic deformation. Single crystals of aluminium oxide have been successfully used as implant material. They are made by adding the oxide powder to the surface of a seed crystal which is slowly withdrawn from an electric arc flame or oxygen/

Table 11.6.3 Comparison of some properties of Biolox aluminium oxide with those some other metals

	stainless steel	**titanium**	**tantalum**	**biolox**
density (g/cm^3)	7.8	4.5	16.6	3.9
hardness (Vickers)	150	90	100	2300
compression strength (N/mm^2)	appr. 800	appr. 600	appr. 1000	5000
bending strength (N/mm^2)	appr. 800	appr. 600	appr. 1000	500
tensile strength (N/mm^2)	appr. 800	appr. 600	appr. 1000	300
modulus of elasticity (kN/mm^2)	200	200	190	380
corrosion resistance in the body	good	good	good	excellent

hydrogen flame. At present this is for instance carried out in an improved version of Verneuil's oven (see else-where in this book).

Some examples of implants of aluminium oxide are teeth, teeth anchorings, the head of the hip joint, phalanges of the foot, knee, finger joints, shoulder joints, coating promoting tissue ingrowths and heart valves.



Dense ceramics (bar), porous ceramics (cylinder), teeth anchorings (by : J.Aarsen)

Zirconium oxide ZrO_2

Zirconium oxide is considered to be the second most important ceramic material for orthopaedic implants, both for implants which have to be able to endure loads and for those which do not. At room temperature the stable crystal structure is the monoclinic form. However, this is unsuitable for mechanical applications, since the volume changes after the sintering takes place in the cool down period. This problem can be solved by adding calcium, magnesium or the rare earth metals like yttrium to the tetragonal and cubic crystal structure of the zirconium oxides. In this way these materials also become stable at room temperature. The most advanced zirconium oxide nowadays is ZrO_2-TZP. This zirconium oxide has been stabilized with tetragonal polycrystals to make the ceramic tougher.

Compared with aluminium oxide, zirconium oxide - the alternative ceramic material for hip heads - has both advantages and disadvantages. The advantages are: higher bending strength, higher breaking strength, less surface roughness and a more favourable friction behaviour with regard to polyethylene. Obviously, the latter is highly desirable for a hip head, which must rotate in a polyethelene socket. The biocampatibility of zirconium oxide is equal to or slightly better than that of aluminium oxide.

The disadvantages are: reduced hardness (HV = 1250) and the fact that it is impossible to remove traces of thorium from the raw material. Due to this impurity the surroundings of the implant are exposed to radiation.

Thus the only, but extremely widespread, application of zirconium oxide is in the head of the hip joint prosthesis.

Bio-tolerant materials

Bone cement is used to attach joint prostheses to hip and knee joints. The material mainly consists of PMMA powder and the monomer liquid methyl methacrylate. In addition another substance is added to prevent premature polymerisation, e.g. under the influence of light.

Bio-active materials

The most important bio-active materials are calcium phosphate, hydroxyapatite and glass ceramics.

Calcium phosphate $Ca_3(PO_4)_2$

Calcium phosphate, also called tricalcium phosphate (TCP), serves as a model for a whole group of calcium phosphates which end with hydroxyapatite (HA). Another name for these materials, which resemble the mineral part of the bone chemically seen, is resorbable ceramics.

Bone mainly consists of HA, but during the various development stages of bone other calcium phosphates are also found. They occur in the following series, the chemical formula of the calcium –phosphorus ratio Ca/P of which varies from 1.00 to 1.67; not all values between the extremeties are mentioned:

$CaHPO_4.2H_2O$ .... $Ca_8H_2(PO_4)_6.5H_2O$..... $Ca_3(PO_4)_2$ .....$Ca_{10}(PO_4)_6(OH)_2$
Ca/P = 1.00 Ca/P = 1.33 Ca/P = 1.5 Ca/P = 1.67
hydroxyapatite

Of this series the salts with Ca/P values between 1.00 and 1.33 dissolve too well to be useful physiologically. When TCP is used to fill bone cavities, it is reabsorbed by the bone tissue during the period of recovery and convalescence.

The bone tissue grows into the pore structure of the phosphate material, which, in its turn, slowly dissolves. At the same time mineralised bone is formed.

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$

Ideally, hydroxyapatite has the formula mentioned above. The synthetic material usually contains fewer than 10 Ca-ions and more than 2 OH-ions per crystal unit. Important differences in crystal structure, composition and specific surface exist between synthetic and biologic apatite. These differences result from the processing method of the raw materials and the synthetic method used.

Hard bone tissue contains Ca, PO_4, OH, small amounts of carbonate, magnesium and sodium and trace elements of fluorine, chlorine and sulphur. That is why the Ca/P value in bone is not 1.67. Substitution of strange ions results in a change in the crystal structure. Consequently it is impossible to imitate the mineral part of bone exactly.

Many attempts have been made to produce biological HA with all its properties. One starting point in the production of Ca-phosphate ceramics is a powder which is obtained from an aqueous environment. Solutions of calcium nitrate [$Ca(NO_3)_2$] and diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] are brought to a pH of 11–12 with a concentrated ammonia solution. Subsequently the phosphate solution is added to the calcium solution drop by drop while stirring. Ideally a precipitate of one phosphate will result from this. Many factors influ-ence the nature of the product in a synthesis like this, among which the addition speed of the reagents and the pH during the formation of the phosphate precipitate. When the precipitate has dried, it is condensed, usually under pressure. Subsequently another condensation follows by sintering at 1100–1300 °C. Under the right circumstances both dense and porous ceramics are made. Here we distinguish between microporosity and macroporosity.

A microporous material has obtained pores of a few micrometres due to insufficient sintering. Macroporosity is desirable to increase tissue growth. One method of making macroporous material is by drilling holes in the sintered product. Another method is mixing calcium phosphate powder with an organic substance, e.g. cellulose. During the heat treatment this substance will evaporate and at higher temperatures it will disintegrate, thus causing macropores.

Implants made of TCP and, to some extent, also of HA are partly resorbed after the implanta-tion. This may take place cellularly, in which case the material will be incorporated into the normal physiological process of making and breaking down bone. This phenomenon promotes the formation of new bone material and the strong connection between the rest of the implant and the living tissue. By immersing the bio-material into the patient's osteoblasts (= self bone cells) which have been cultivated in vitro, we can stimulate these processes.

Hydroxyapatite is extremely bio-compatible and is integrated in the bone. According to literature, the dimensions and volume of the pores in HA are of importance for the ingrowing of the bone. The material is used in many shapes:as a solid body with little porosity, as grains, as a porous mass and as a coating on metal implants. Solid, pre-shaped HA implants seem to be fairly insuccessful due to the fact that dimensional problems frequently occur. Grains of 20 - 60 µm are frequently injected into cavities resulting from the extraction of teeth. In this way the ridge of the socket can be reinforced.

By means of plasma syringes a coating is applied, mainly on tooth implants or hip joints made of titanium. Because the hip joint turns longitudinally in the HA jet, the coating obtains a layered structure. The surface is rough and porous, which guarantees a proper attachment of the human bone.

In The Netherlands the firm Cam Implants in Leiden manufactures a series of implants on the basis of HA, among which bio-active coatings on orthopaedic and dental implants, implants for the small bones of the middle ear, which are made of dense ceramics, porous ceramics for the middle ear and jaw and facial implants. The latter are e.g. small blocks to fill holes resulting from the removal of cysts and tumours.

Glass ceramics

As explained earlier in the chapter on Electroceramics, glass ceramics are made by the controlled crystallisation of glass. Since 1967 research has been carried out into special glass formulas for bioceramic applications. This has resulted in a material which forms a bond on the line between the implant and the host tissue, the so-called bio-glass with the following composition, expressed in mass percentages:

45% (m/m) SiO_2	24.5% (m/m) Na_2O
24.5% (m/m) CaO	6% (m/m) P_2O_5

Note that this material also contains calcium and phosphorous. After some time, this mass exhibited a stable bond with bone after implantation in a rat’s femur. This property was also observed with 6% (m/m) P_2O_5 and subsequent alteration of the other percentages.

In view of the bio-compatibility the composition of glass cannot be altered in such a way that its mechanical strength becomes equally good as that of the glass ceramics of, e.g., a ceramic cooking plate. Consequently, the material is unsuited for important load-bearing implants like joint implants. It is, however, suitable as a filler in bone cement, in composites for tooth repair, as a replacement for part of the skull and a coating material.

An “exotic”material

Barium titanate with a prepared surface is used in experiments to bring about the fixation of implants in bone. The material is piezoelectric, a property which was discussed in the chapter on Electroceramics. The electric signals which are generated by the mechanical load are thought to be capable of stimulating the ingrowing and healing of bone. Another possibility to achieve this is by exposing the implant to ultrasonic sound waves. The biological effects of this material are being researched at this moment and are consequently very speculative.

11.6.5 Artificial hip joint

Structure of the joint

Many kinds of artificial hip joints are available commercially, but they all consist of the same parts, i.e. a metal stem or shaft, usually made of a titanium alloy and a ceramic head of aluminium or zirconium oxide. The production of the ceramic head starts with a powder and ends with the sintering process. The heat treatment will cause the head to shrink. After production, the head is thoroughly tested, e.g. on its spherical shape and surface roughness.

The head turns in a so-called socket of polyethylene (PE), because the material combination Al_2O_3/ZrO_2–PE has excellent tribological properties. This plastic socket is mounted in a metal socket which, in its turn, is mounted in the hip. The stem and the socket can be provided with a HA-layer to promote bone tissue growth.

At the beginning of the 1960s, the great breakthrough in hip prosthesis surgery took place when Charnley introduced the combination stainless steel and polyethylene. Before that time hemi-prostheses were mainly implanted, which meant that the socket of the hip joint was not replaced. Many parts of the original joint as designed by Charnley have been improved since then. A prosthesis used to be made out of one piece of steel. Nowadays many prostheses are modular, e.g. the head is clipped onto the hip stem. More and more arguments are being heard in favour of returning to the prosthesis made of one piece, as corrosion and wear can take place on the connecting lines. Another point of discussion is whether or not a hip should be cemented. In addition, opinions vary on the efficiency of an HA-coating. When it is decided to apply such a coating, it must be extremely thin because, according to literature, thicker layers can come loose and the resulting material might lead to premature polyethylene wear.

Medical aspects

The anamnesis of a hip implant starts with pain due to which the patient is limited in his or her movements. The causes are usually arthrosis, rheumatoid arthritis, a trauma or deviations in form like dysplasia.

Once the decision to operate has been made and the kind of implant has been decided on, a computer can calculate the shape of the prosthesis with the help of X-ray pictures. Next a computer-operated cutting machine produces the model which is made of a titanium alloy. In case of difficult operations, the computer can also be used to make a plastic model of the hip; this will enable the surgeon to prepare for the operation at his or her desk.

A routine operation usually proceeds as follows. First the head of the femur is sawn off. The socket in the pelvis (the acetabulum) is then made deeper with a cutting machine and subsequently the metal socket is stamped into the hip. This metal is then lined with plastic to facilitate sliding movements. The femur is scooped out with a rasp and filled with cement. This cement is a mixture of plastics which automatically polymerizes in the femur. Since 1997 it has been becoming customary to grind up old hip heads and use the bone shreds together with the cement as a filler for the shaft of the prosthesis. The stem of the prosthesis is hammered into the femur, the spherical head is attached to it and inserted into the plastic socket.

After the operation rejection symptoms may occur. These may be caused either by products resulting from wear or by an infection. Wear can be reduced by not operating on very yound patients, prescribing a certain mode of life and making certain that the polyethylene layer in the socket of the pelvis is thick enough. By operating in special theatres with overpressure and ventilation, by using antibiotics and adding antibiotics to the bone cement it is possible to fight infections.

Some days after the operation, the patient is allowed to walk on crutches; he has to continue to do so for about 6 weeks.

The life span of a prosthesis strongly depends on the patient’s life style. Normal walking alone, for instance, can increase the temperature to approximately 40 °C and three times the body weight will rest on the prosthesis. The patient should consequently avoid obesity.

The October 1996 issue of the Dutch magazine “Natuur & Techniek” makes mention of a research of the University of Bristol, Great Britain into the effects of implanting artificial hip joints and knees into the body. This research showed that metal particles and pieces of plastic, cement and polymers are gradually released from the artificial joints. Such particles were found in the neighbourhood of joints and lymph nodes. However, they were also present in the bone marrow, the spleen and the liver. The more artificial limbs are exposed to loads, the more particles will be released. So far there are no indications of health hazards, but it is not possible to predict long term effects.

11.6.6 Bone paste

A group of materials technologists and surgeons led by Brent Constanz of the Norian Corporation in Cupertino, California, USA developed a bone paste to be injected into bone fractures. The paste, trade name Norian SRS, hardens in minutes and thus braces broken bones. In 12 hours the material has a compression strength which equals that of natural bone. So far the material has been tested in fractures of the hip, knee, shoulder and wrist. The operations proceed faster than their traditional equivalents; fewer plates and screws are necessary and the patients are able to resume their normal activities much more quickly.

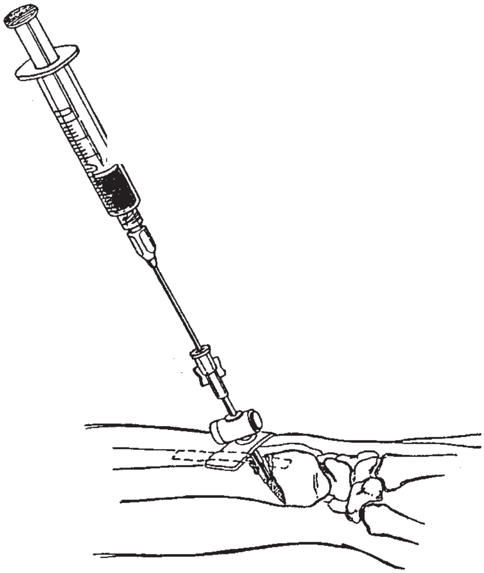
Constantz got the idea for the paste in 1985, when he was attending the University of California, Santa Cruz. He was studying corals which shape their skeletons differently from man. In vertebrates sphere-formation is regulated by proteins which control mineralisation of the bone. During this process a porous, slightly disorientated crystalline structure is formed. Coral, on the other hand, produces a skeleton without the help of proteins. Since nobody had been able to imitate protein-controlled bone formation in order to manufacture bone parts, the alternative was to copy coral growth. Constantz set up the Norian Corporation for Research. He soon discovered that he had to combine a dry calcium source with a crystalline form of phosphoric acid and mix this with a sodium phosphate solution. The result is a paste which crystallizes into a bone-like material and hardens in minutes, while forming dahlite with the formula $3Ca_3[PO_4]_2{\cdot}2CaCO_3{\cdot}H_2O$. Dahlite formation is complete after 12 hours. The composition and crystal morphology are analogue to those of bone.

11.6.7 The future

With regard to the future of bioceramics and implants in general, two questions arise: “Which direction will research take?” and “Will the demand for implants in future be such that expensive research is justified?”. The medical world will have to use its experience and provide research facilities with information, thus guiding their research. However, in practice this takes a very long time (by way of illustration: the ten year survival of hip prostheses is approximately 95%).

Many articles have been written on the demand for implants. It is difficult to estimate the market. The most popular implants are likely to be: hip, knee, finger, dental root, heart valve, pacemakers and jaw reinforcement. Worldwide the demand is: 100,000 heart valves, 220,000 pacemakers, 400,000 hip prostheses and 1,500,000 blood vessel prostheses.

It is believed that in future the use of bio-materials as far as composites and ceramics are concerned will grow and exceed the application of metal and plastics.



Norian SRS bone mineral substitute is injected directly into osteoporotic and other traumatic fracture sites, filling the bone void. Hardening in minutes, Norian SRS is a patented formulation that forms carbonaated apatite – the main contituent of natural bone – in the patient's body (Illustration courtesy of Norian Corporation, Cupertino, USA).

11. 7

Chemical and Structural Ceramics

11.7.1 MATERIALS, STRUCTURES AND PROPERTIES

In this branch of ceramics substances are used with many different properties. Of all these properties, high melting points and high hardnesses stand out. Table 11.7.1 lists nine sub-stances with high melting points, among which some ceramic materials.

Table 11.7.1 Materials with high melting points

name	examples	melting points (K)
- borides	CaB_6 V_3B_4 YB_6 HfB_2 Mo_3B_2	2250 - 3500
- carbides	ZrC B_4C WC CaC_2 U_2C_3	2200 - 4100
- elements	Cr B Hf Mo graphite	2090 - 4200
- intermetallic compounds	Al_2Mo ReW Zr_2Ge $HfMo_2$ WPt	2250 - 3300
- nitrides	Ta_2N Be_3N_2 AlN ThN HfN	2300 - 3600
- oxides	Al_2BaO_4 Cr_2O_3 $BaZrO_3$ ThO_2	2000 - 3500
- silicates	Mg_2SiO_4 $ZrSiO_3$ $ZrSiO_4$	2350 - 2850
- silicides	$MoSi_2$ WSi_2 $HfSi_2$	2300 - 2800
- sulphides and phosphides	SrS La_3S_4 BaS HfS Tl_2P_3	2300 - 2750

According to literature sources mainly oxides, nitrides, borides and carbides are used as ceramic raw materials of chemical and structural applications and the most common elements in these compounds are: Be, Mg, Ca, Ti, V, Cr, Y, Zr, La, Hf, W, B, Al, Si and Sn. These elements can be found in rather small area of the periodic table, i.e. in the groups 2 up to and including 6, 13 and 14. So apparently relatively few ingredients are used in this branch of ceramics to produce a wide range of products. The tricks of the trade are in the preparation. The properties are determined by a number of factors, such as the nature of the building blocks, the kind of bonds, the strength of the bonds, the crystal structure and the reactivity of the material.

In the chapter ‘Chemisty’ we have seen that every bond is partly ionic and partly covalent. As a general rule materials which are mainly ionic do not possess any directed bonds and exhibit low conductivity at low temperatures. Moreover their crystal structures result from ion packings. In the case of covalent materials the crystal structure is not the result of a close packing, but of a spatial expansion of the local structure with directed covalent bonds. The crystal structure is specific and relatively open, a three-dimensional network with holes and channels. The materials are extremely hard and heat-proof. They also exhibit high strengths and low heat expansion coefficients. By way of illustration:

Al_2O_3	60% ionic	composed of Al^{3+} and O^{2-}	melting point 2050 °C
ZrO_2	60% ionic	composed of Zr^{4+} and O^{2-}	melting point 2500 °C
TiC	20% ionic	directed covalent bonds	melting point 3100 °C

Let us now have a closer look at the four most used materials and some of their applications.

OXIDES

zirconium(IV) oxide – ZrO_2, high toughness, and for that reason suitable for cutting ceramics and tensile tools

aluminium titanate – Al_2TiO_5, for large and speedy temperature fluctuations, e.g. valves to dose liquid metals in foundries, especially aluminium

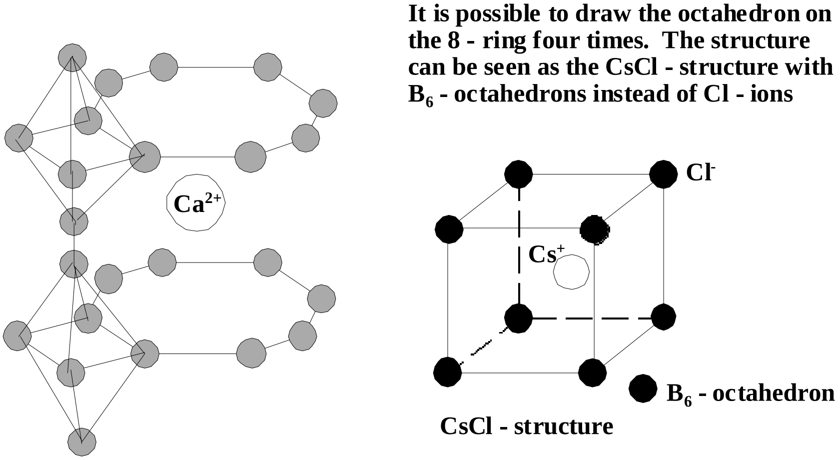
NITRIDES

We distinguish three kinds of nitrides, i.e. ionic nitrides (e.g. Th_3N_2), covalent nitrides (e.g. BN) and intermediate forms (e.g. VN). These intermediate forms are extremely inert, very hard and they have high melting points. VN has a Mohs hardness of 9–10 and a melting point of 2570 °C. Furthermore, the intermediate form conducts electricity since the electronic band structure of the metal is maintained when N atoms are placed in the cavities of the crystal lattice

Si_3N_4 silicon nitride has a low density, is resistant to speedy temperature fluctuations and mechanical loads. This compound is not affected by most acids, smelts, salts, liquid metals and gases. When it is heated in an oxidizing environment for a long time at a temperature of 900–1100 °C, a thin layer of SiO_2 forms on its surface which subsequently prevents any further corrosion. BN boron nitride is a white, fatty powder with a layered graphite-like structure containing alternately B and N atoms. At a suitably high pressure and temperature it is converted into a cubic form ‘borazon’ which is even harder than diamond. It is extremely stable, both chemically and thermally.

BORIDES

Borides stand out because some of them have special structures, e.g. CaB_6 (figure 11.7.1). This compound is synthesized according to the following reaction: $CaO + B_4C + 2\ B \rightarrow CaB_6 + CO$. It has a melting point of 2250 °C and is characterized by a high hardness due to which it is for example applied as an abrasive. The effects of boration have been known for more than 100 years. By diffusion of boron at the surface of a metal, a layer is formed in which boron reacts with the metal in question. For instance: in a reaction with iron, FeB_2 is formed. Borated objects exhibit a higher resistance to wear.



It is possible to draw the octahedron on the 8 - ring four times. The structure can be seen as the CsCl - structure with B_6 - octahedrons instead of Cl - ions

Each B_6 - octahedron belongs to 8 cubes; consequently the formula is $CaB_{48/8} = CaB_6$

Fig. 11.7.1 Structure of calcium hexaboride.

CARBIDES

In carbides, carbon is bound to elements with lower or similar EN-values. We distinguish three types of carbides. The salt-like carbides with elements from groups 1, 2 and 3 are decomposed by water: $Al_4C_3 + 12\ H_2O \rightarrow 4\ Al(OH)_3 + 3\ CH_4$. In addition, there are the covalent carbides like SiC and B_4C and a intermediate group with most transition metals. In the intermediate group C atoms are located in the octahedral cavities of metal close packings. The melting points vary from 3000 to some extreme values of about 4800 °C and their hardness lies between 7 and 10 on the Mohs’ scale. Furthermore, the compounds have an electric conductivity which is similar to that of metals. The free electron structure and other characteristics of pure metals are hardly affected by placing C atoms in the crystal lattice. The C atoms stabilize the lattice which results in an increased hardness and melting point.

B_4C boron carbide has a melting point of 2450 °C and a hardness somewhere between those of SiC and diamond. This makes the material a suitable abrasive. It is used in heads of sand blasting equipment, in mortars and in armour plating. For the latter application a B_4C plate is provided on both sides with a plastic which has been reinforced with glass fibre. This is done to reduce the risk of splintering. Boron carbide is also used as the raw material for many other boron compounds:

$$B_4C + 2\,N_2 \rightarrow 4\,BN + C \quad (1800\text{–}1900\ °C)$$
$$B_4C + 2\,TiC \rightarrow 2\,TiB_2 + 3C$$

B_4C has a NaCl-like crystal structure, built up of groups of three C atoms and groups of twelve boron atoms.

SiC, like boron carbide, silicon carbide is nearly completely covalent and is e.g. used as grinding powder, in the manufacture of ball bearings, balls, outlet casings and jet nozzles, as well as in packing rings of pumps used to transport materials which are likely to cause wear.

SiSiC is a special form of this compound, which consists of SiC which is fully infiltrated by silicon. It is a composite which retains its shape at temperatures up to 1350 °C and which is for instance applied in oven rollers.

A comparison

A comparison of the hardness reveals that the values of the various kinds of compounds overlap each other.

The highest electrical and thermal conductivity are found in the most simple structures, i.e. structures built up of only one element, of elements with similar atomic masses and / or dimensions or structures without impurities. Graphite solely consists of carbon atoms and has a high conductivity, but only in the direction of the parallel layers. Perpendicular to the layers this conductivity is much less. SiC and B_4C consist of atoms of roughly similar size and mass. For that reasons vibrations in the crystal lattice are transmitted freely which results in a high thermal conductivity.

A comparison within one group also shows large differences (table 11.7.2)

Table 11.7.2 A comparison of some borides

formula	melting point °C	Vickers hardness (kg/mm^2)	density (g/cm^3)
CrB_2	1950	1800	5.2
CaB_6	2230	2750	2.4
HfB_2	3250	2900	11.2

11.7. 2 Applications

The number of applications within the sector of structural and technical ceramics is so large that a classification of applications and some examples will have to suffice here. In the other sections of this chapter some applications will be discussed further.

A commonly used classification is:

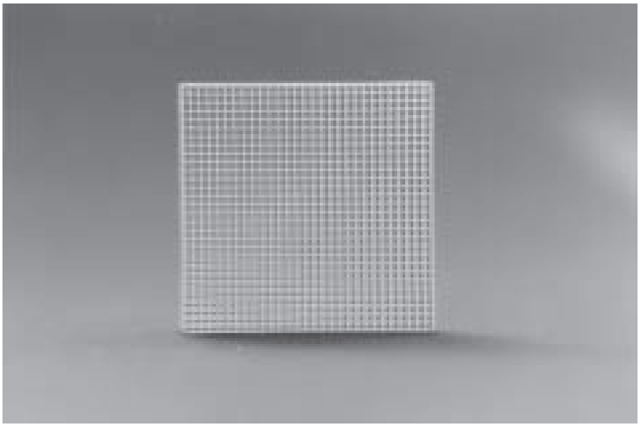
Processing/Machining
Chemical / process technology
Construction of machinery
Engines

Grinding and cutting ceramics as well as the use of ceramic grinding balls and ball mill pots all fall in the category processing. Sillimanite, corundum, carbides of non-metals and nitrides are used for grinding. Cutting tools on the other hand are made of aluminium oxides, nitrides of metals and non-metals, carbides of metals and composites containing fibres and particles.

The number of application grows in the chemical / process technology. Quite often we only speak of ‘chemical technology’ and subdivide this into ‘active technical ceramics (e.g. sensors, see elsewhere in this chapter) and ‘passive technical ceramics’ (e.g. vessels, pumps, filters and catalytic agent carriers). When ceramic parts are exposed to corrosion caused by a metallic or non-metallic smelt, they are provided with a coating (see elsewhere in this chapter).

Some applications:

- *catalytic agent carriers*	a catalytic agent is a metal which is coated onto an inert (ceramic) carrier material. This carrier material can be aluminium silicate, magnesium silicate, aluminium oxide or silicon carbide. Catalytic agents are for instance applied in the oxidation



Catalytic agent carrier.

	or reduction of waste gases of the chemical process industry and in cars.
- *vessel inlets*	are for instance made of aluminium oxide
- *filters and membranes*	are applied in waste water purification, distributions of gases in liquids, filtration of gases and in metal foundries. They are made of quartz, chamotte, corundum, silicon carbide or carbon.
- *lab technology*	In a laboratory so-called lab porcelain is used: tiles, dishes, mortars and crucibles. These have to meet certain requirements: mechanically strong, resistant to chemicals and thermally stable. Glazed porcelain can be used at temperatures up to 1000 oC. For higher temperatures other ceramics are used: e.g. aluminium oxide.

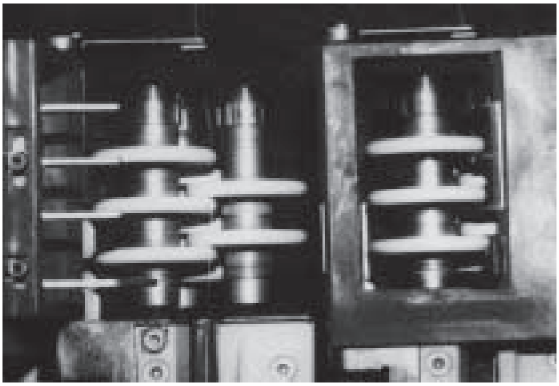
With the construction of machinery we mean moving or stationary machinery components which are not part of an engine and are liable to wear. They are made of hard porcelain, lithium aluminium silicate, aluminium oxide, titanium (IV) oxide, zirconium (IV) ox-

Laboratory crucible

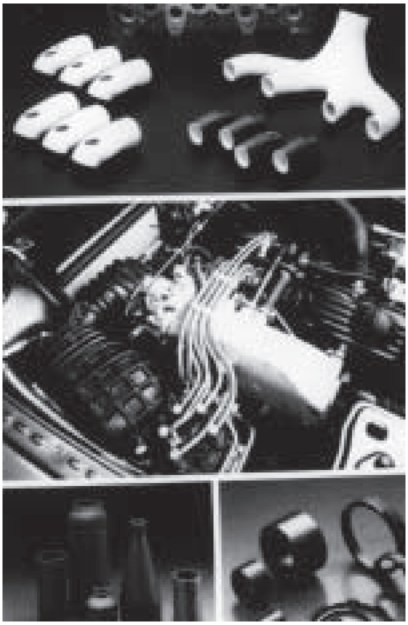
ide, carbon, certain carbides and nitrides and fibre-reinforced composites. Some applications are:

- rollers for roller ovens
- sand blasting heads
- tubes for heating elements
- insulation rods for thermo-elements
- packings (e.g. Al_2O_3 in modern domestic taps)
- valves
- wire guides in the textile industry (Al_2O_3, TiO_2, ZrO_2)
- spray heads (lime milk or lime powder in flue gas desulphurization, sand blasting, water jet cutting equipment)

Parts from high-frequency tubes (Feldmühle, Germany).



Ceramic friction discs in textile industry (Feldmühle, Germany)



Engine parts (Hoechst, Germany).

Washer (Ceradisc).

In the manufacture of engines turbine blades, bearings and plungers are made of ceramics. The materials used here are cordierite, Li–Al silicate, mullite, titanate, SiC, Al_2O_3 , ZrO_2, certain nitrides as well as particles- and fibre-reinforced composites and layered composites.

11.7.3 Bonding techniques

Why a section on bonding techniques? The main reason is that, at this moment the bonding of materials is a live topic in both materials science and research. We want to combine ceramics with identical or different ceramics, but also with metals and plastic. Moreover ceramicists are also interested in joining materials from an artistic point of view. Certain developments in technology require not only identical, but mostly different materials to be linked. When an object or component is too big or too complex to make it entirely of ceramics, part of it is made of metals and consequently the metals and the ceramics have to be joined. Since ceramics are quite often brittle, is may be desirable to make the ceramic part of the object as little as possible and to manufacture the remaning part of metal. This section will make clear that materials can be joined in many different ways, depending on the combination of materials and the circumstances under which they must be joined.

We shall not discuss the scientific backgrounds of bonding materials. Any interested reader wishing to study this will come across a combination of factors, like chemical bonds, physical bonding, electrical forces and mechanical adhesion. Many joining techniques are still under heated discussion. In this section we shall review some bonding methods in order to give the reader some idea of the vast variety of possibilities and to demonstrate that an extensive study always proceeds the bonding of materials.

Bonding techniques can be divided in four groups: glueing, soldering, mechanical bonding and solid- solid bonding. Let us have a closer look at some of these techniques.

Glueing

Glues which are used at low temperatures have an organically based composition and consist of two or more components. In the case of ceramics-ceramics bonds a selection can be made from phenol resin, polyurethane, epoxy resin or silicons and the maximum temperature at which these can be used varies from appr. 115 to 200 °C. In the case of higher temperatures of use ceramic glues are advised for joining ceramics and metals, glass, ceramics or graphite. A ceramic glue contains oxides as the ceramics basic material, a wetting agent and a binding agent.

When glue bonds will have to be able to withstand high temperatures, attention should be paid to the following:

– the area of contact. Increase the area of contact when an object is subject to tensile or shear stresses after glueing. This

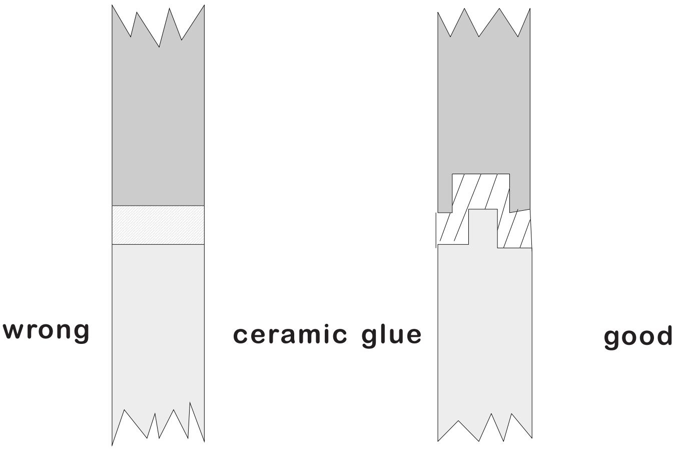


Fig. 11.7.2 Increasing the area of contact for applications at high temperatures.

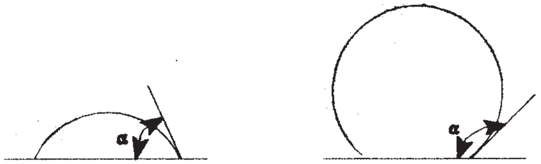
will reduce the stress (figure 11.7.2).

- a bond in vacuum must be leakproof
- should the bond be able to absorb thermal or mechanical shocks?
- when a metal is glued to ceramics, a problem occurs because of the large difference in the expansion coefficient. Realise the bond in such a way that the resulting stress is released as a compressive stress on the glue layer.
- is the hardened glue porous or should the bond be able to withstand a moist environment?

What are the consequences for the bond when it absorbs water?

Soldering

In order for soldering to be successful many requirements have to be met. One of these is that the surface has to be wetted by the solder (figure 11.7.3)



angle of contact α < 90°
wetted

angle of contact > 90°
not wetted

Fig. 11.7.3 Wetting a surface.

The problem with soldering ceramics is that a ceramic object is generally not wetted by the molten metal. In order to solve this problem the ceramics are often provided with a metal coating, mostly made of nickel. However, it is not possible to simply apply this coating. For example: nickel must be applied galvanically onto aluminum oxide, but aluminium oxide is an insulator! Consequently, the ceramic object must first be given a metallized layer by means of a metallizing paste. This paste contains a solvent to which molybdenum, manganese or manganese (IV) oxide and a binding agents are added. The object and the paste are heated until a temperature of at most ~1500 °C and this is done under a certain atmosphere. During this process, some reactions occur and the final result is that the ceramic surface is covered with a partly amorphous mixture with on it a crystalline metal layer. The nickel layer is applied onto the metal layer and then soldering can take place.

In another procedure the ceramic surface is covered with titanium hydride TiH_2. When it is heated to 500 °C, the hydride decomposes mainly into titanium which is bound to the ceramic layer by means of the also formed titanium (IV) oxide. Another metal can now be soldered onto the titanium layer.

In the case of so-called active soldering an active solder is used: a metallic solder containing interface active additives which make certain that the molten solder wets the ceramics. An example of such a solder is a silver / copper alloy with a titanium or titanium / indium additive which can be used when soldering zirconium (IV) oxide to certain steels, aluminium oxide to nickel / cobalt or iron / nickel alloys and aluminium oxide to a iron / nickel / cobalt alloy.

Shrinking

Shrinking is a so-called mechanical bonding technique. Two hot objects are fitted together. When they cool the outer part attaches itself to the inner one. For this to be possible the outer part must have a bigger thermal expansion coefficient than the inner one. In this way ceramics and metals can be joined.

Common sintering

Green components of the same material can be joined by means of common sintering. First the joints are covered with a slip of the same composition and then they are compressed and sintered at the same time. In this way a handle is attached to a porcelain tea pot.

Bonding by means of ceramic foil

A flexible ceramic foil with 15–20 mass % organic binding agents is placed between two ceramic objects. Next all of this is sintered and at the same time compressed. The foil must share properties with the ceramic material with which it is to be sintered and it should be possible to sinter it at considerably lower temperatures than the components which are joined. The method can for instance be applied when the ceramic object must be composed of more than one piece.

Sophisticated techniques

Radiofrequency welding, also called high frequency welding (HF-welding), pulsed high current discharge, electron beam fusion welding, thermo compression bonding and ultrasonic bonding are some examples of sophisticated bonding techniques. These techniques will not be discussed here.

11.7.4 Sensors

A sensor is a part of or an element in a measuring chain which converts an environmental parameter (variable) into a signal. Environmental parameters are temperature, pressure and the concentration of gases.

In this section we will have a closer look at the sensors which are used for measuring substances, the so-called chemical sensors. A very well-known example of such a sensor in a chemical laboratory is the pH-meter used to measure the acidity of solutions. In particular the so-called Lambda-probe, abbreviated λ-probe, which is used in cars to optimize the combustion process will be discussed in more detail.

The working of a chemical sensor is based on the interaction between free particles (e.g. gas molecules) and the surface of a solid. This interaction might be a physical absorption and in that case the sensor can be used at low temperatures because the absorption forces will not be great. However, the absorption might also be chemical and then there is question of a strong chemical bond to the surface of the sensor. This can lead to very specific changes in the electrical sensor properties.

A surface sensor works even differently. Here the electrical conductivity of the sensor material is affected by catalytic reactions between the sensor and the atmosphere. This book deals with ceramics and the λ-probe contains an O_2-surface sensor which in its turn contains ceramics. This sensor is used to measure the oxygen content of exhaust fumes. Nowadays many cars are equipped with so-called 3-way converters

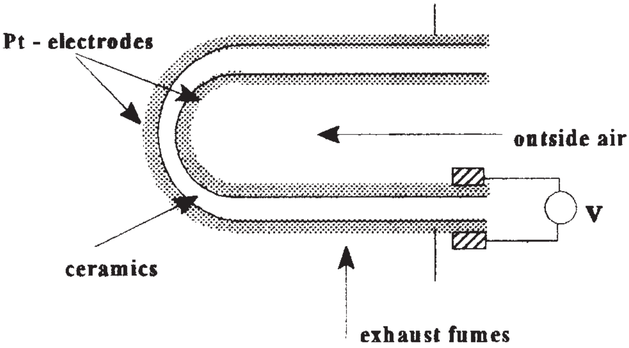


Fig. 11.7.4 Extremely schematic representation of the labda-probe.

which can become polluted due to an incorrect composition of the exhaust fumes.

In figure 11.7.4 you can see an extremely schematic representation of an λ-probe.

Measuring the oxygen content of the exhaust fumes gives a clear indication of whether or not the combustion of the air - fuel mixture in the cylinder was complete. The purpose of this measurement is to check the air–fuel ratio and, if necessary, adjust it.

In formula:

$$V = k \times \ln \frac{\sqrt{P(\mathrm{O}_2)} - \text{outside air}}{\sqrt{P(\mathrm{O}_2)} - \text{exhaust fume}}$$

When the ratio between both partial vapour pressures changes, the value *V* changes. The electronics in the car react to this by adjusting the air:fuel ratio.

Let us now take a closer look at the function of ceramics in the labda-probe, e.g. titanium (IV) oxide, TiO_2. In the perfect crystal structure of this oxide each Ti^{4+} ion is surrounded octahedrally by six O^{2-} ions. Figure 11.7.5 shows a cross-section of the crystal lattice.

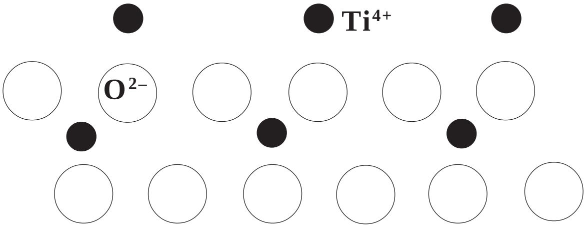


Fig. 11.7.5 The ideal crystal structure of a titanium (IV) oxide, TiO_2.

In titanium (IV) oxide, the ratio $Ti^{4+} : O^{2-} = 1 : 2$. The compound can also be made with an insufficient amount of oxygen. In that case the formula is TiO_{2-x}. There is not enough oxygen present to oxidize all Ti^{2+} ions to Ti^{4+}. The result is a crystal structure with Ti^{2+} in some places instead of Ti^{4+}. For every Ti^{2+} ion there is one O^{2-} ion short, a so-called O^{2-} vacancy (figure 11.7.6).

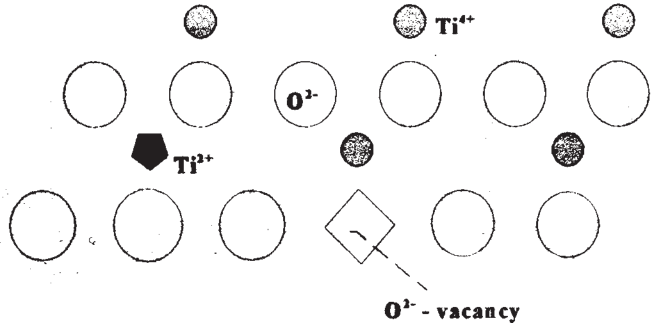


Fig. 11.7.6 A TiO_2 crystal with O^{2-} vacancies.

Now the conduction in the material proceeds as follows. The O^{2-} ions diffuse through the crystal lattice via the vacancies. Therefore the titanium ions constantly change charge form 4+ to 2+ and vice versa:

$$O^{2-} \rightleftarrows \frac{1}{2} O_{2(g)} + 2e^{-}$$

This equation indicates that electrons are withdrawn from the material and oxygen ions are formed as the partial pressure of the surrounding oxygen increases. A reduction in the number of electrons results in a decrease in conductivity. Because the outside air and the exhaust fumes have different $P(O_2)$ values there are different amounts of electrons per volume unit present in the parts of the ceramic material which are adjacent to these gases and that causes the difference in voltage.

A similar story applies to ZrO_2, zirconium (IV) oxide. This crystal lattice is often doped (polluted on purpose) with yttrium (III) oxide, Y_2O_3. This means that two parts of ZrO_2 (i.e. two Zr^{4+} and four O^{2-} ions) are replaced by one part of Y_2O_3 (i.e. two Y^{3+} and three O^{2-} ions). The result is one O^{2-} vacancy per doped Y_2O_3 part. The conduction proceeds similar to that in TiO_{2-x}.

11.7.5 Microspheres

(with thanks to Dr E. Brandau of the firm BRACE GmbH, Alzenau, Germany)

Ceramic powders and granulates have several disadvantages. They cause dust clouds when they are being used, they have a considerable range in grain size and the grains have different shapes and are not spherical, which can lead to material loss due to wear. All of these disadvantages can result in extra work, since the required grain size fraction has to be isolated. In addition, separation of grains with different diameters, and consequently with different masses, will occur in the bulk.

The German firm BRACE recognized these disadvantages and now makes little spheres with the following properties: near-perfect round form, extremely small grain size distribution, diameters of 50 µm to 5 mm, hardly any dust or wear, extremely dense or porous, soft or hard and the spheres are capable of incorporating specific substances, e.g. bacteria or enzymes (catalysts in living organisms). The products can be divided into four groups, depending on their starting mass:

- from a sol you can make little spheres of Al_2O_3, ZrO_2, HfO_2, CeO_4, SiO_2 and mixed oxides which can be used in high-tech ceramic products like catalytic converter carriers and filter material. Very effective and wear-proof grinding spheres are made by sintering Al-, Zr- or Hf-oxide spheres.
- from a smelt of inorganic or organic compounds, metal alloys and polymers you can make little spheres which can be used as additives for plastics. After incorporating certain active compounds, they can be used in pharmaceutical and cosmetic industries.
- from soluble chemical compounds spheres are made by means of precipitation reactions for agricultural chemistry, food industries and for pharmaceutical and cosmetic industries.
- from a suspension you can make enzyme- and bacterium-containing spheres.

Sometimes the spheres are chemically and/or physically further processed after production. This involves washing, drying, colouring or sorting.

The production of the spheres

The starting mass is a smelt, solution, dispersion, emulsion or sol. With relatively little pressure, this mass is pressed into a spray head, which is then vibrated. This causes the liquid jet from the head to be interrupted and little segments to be formed. During their fall these assume a spherical shape because of the surface tension. The spheres can be made stronger in suitable gaseous and/or liquid reaction media (figure 11.7.7).

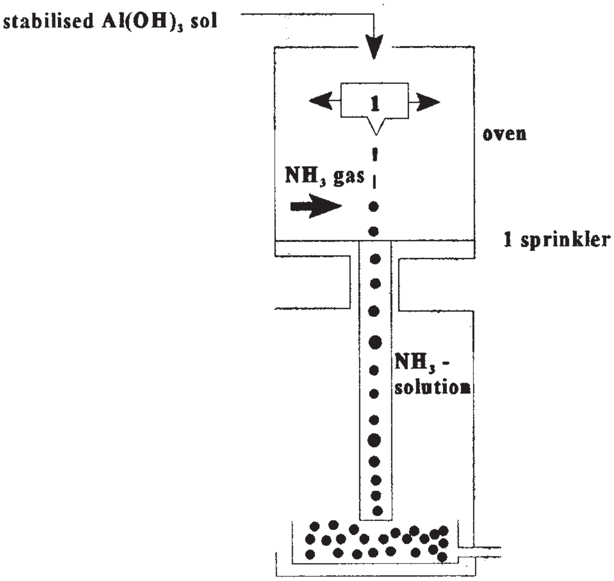
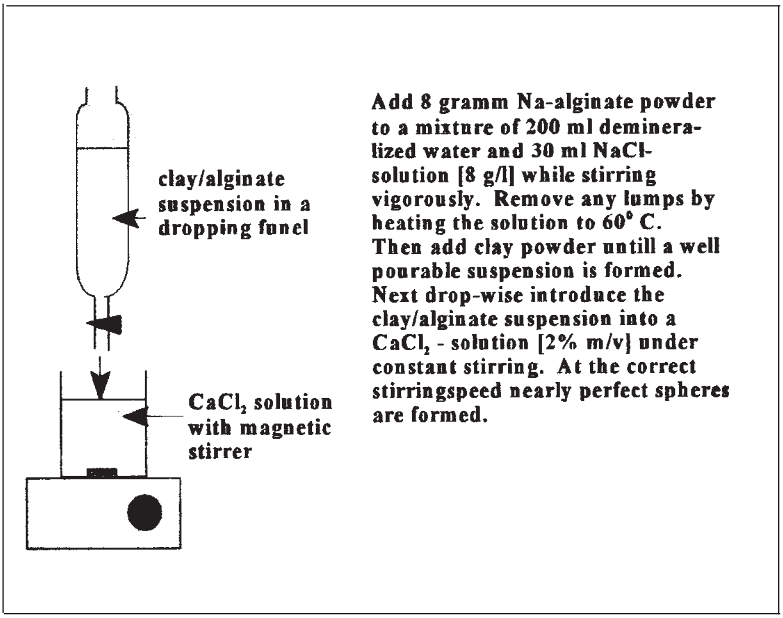


Fig. 11.7.7 Production of microspheres according to the BRACE-method.

Let’s take a closer look at the production of Al_2O_3 spheres from an $Al(OH)_3$ sol. The sol must have a low viscosity and is stabilized using a polyalcohol, e.g. PVA (polyvinyl alcohol).

Sometimes urea is added to create pores. The drops which fall from the spray head are gelatized by ammonia gas. Gelation is the first step in the solidification of matter.The solidification process can be continued by dropping the little spheres in an ammonia solution. The concentration of the ammonia and the duration of the reaction both influence the properties of the spheres. Any further treatment depends on the application of the spheres.

Experiment: It will be clear that manufacturing ceramic microspheres in the manner described above is not possible within a classroom situation and it is also not advisable. However, it is possible to carry out a simple analogous synthesis which offer many possibilities for expansion. The idea was suggested to me by one of my colleagues, a teacher of biology, who immobilizes enzymes as part of his practical trainings, i.e. he traps enzymes in a polymer network. I have adjusted the technique to a clay suspension. Theory: The clay suspension is mixed with sodium alginate, which is the sodium salt of alginic acid, an acid polysaccharide. Alginic acid is produced in the alkaline extraction of brown seaweed. The acid is not stable and for that reason it is preferably marketed as the sodium salt. When droplets of a clay/alginate solution are introduced into a $CaCl_2$ solution, a calcium alginate network arises with a trapped clay suspension. In the next box you can see the test rig and recipe. The recipe offers many possibilities for experiments with the parameters: solid content of the clay suspension and other contents, trickling speed (in case of a continuous flow you can make trails), other metal ions instead of calcium ones, stirring speed, etc. Figure 11.7.8 is an illustration of the test rig.



Add 8 gramm Na-alginate powder to a mixture of 200 ml demineralized water and 30 ml NaCl-solution [8 g/l] while stirring vigorously. Remove any lumps by heating the solution to 60° C. Then add clay powder untill a well pourable suspension is formed. Next drop-wise introduce the clay/alginate suspension into a $CaCl_2$ - solution [2% m/v] under constant stirring. At the correct stirringspeed nearly perfect spheres are formed.

Fig. 11.7.8 Manufacturing clay microspheres.

11.7.6 Coatings

The progress made by technology calls for increasingly complex demands as far as machine components and the materials they are made of are concerned. When the material is not satisfactory, a coating is applied. The purpose of this coating is to resist wear, heat, oxidation, atmospheric corrosion and corrosion on immersion or acquiring of electrical conductivity, resistance or a better adhesiveness. Examples of applications can be found in the chemical and oil industries, electronics, the car industry, medical equipment, the navy, aviation and space travel, as well as in every day life in electric irons, biros and frying pans.

There are two ways in which coatings can be applied: thermomechanical processes (e.g. detonation gun, flame spraying and plasma spraying) and vapour phase deposition processes. The latter category can be subdivided into CVD (chemical vapour deposition) and PVD (physical vapour deposition). In the case of a CVD process, a chemical reaction takes place in an oven and as a result the coating material is formed and deposited on the object. Figures 11.7.9 and 11.7.10 are representations of two methods to apply coatings.

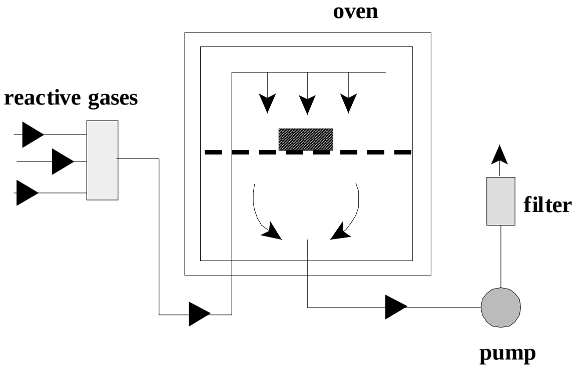


Fig. 11.7.9 Schematic representation of a CVD unit.

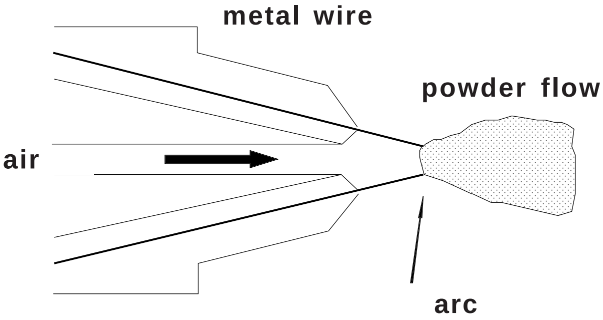


Fig. 11.7.10 Arc spraying.

In the oven, the ceramic material for the coating is formed from the reactive gases and then deposited on the object. Two examples:

1. $TiCl_4 + CH_4 \rightarrow TiC + 4\ HCl$
2. $2\ AlCl_3 + 3\ CO_2 + 3\ H_2 \rightarrow Al_2O_3 + 3\ CO + 6\ HCl$

Arc spraying

The wire-shaped coating material is electrically charged and when two wires are joined together an arc is created. The air flow ‘shoots’ the molten material onto the object.

Finally, some examples of coatings:

- chromium nitride CrN is applied by means of a PVD technique and forms a relatively dense, silver-grey layer with a high corrosion resistance. Is applied to tools for the plastic industry, to shaping tools for non-ferrous metals and in metal-removing machining operations of titanium and nickel alloys.
- titanium aluminium nitride TiAlN is resistant to high temperatures, is extremely hard and for instance suitable for high cutting metal removal in relatively tough material. With a coated drill bit five times as many drill holes can be made than with a non-coated one.

12

A Collection of Short Articles on Various Ceramic items

In writing this book I made ample use of the Internet. In the beginning my searching activities were less efficient and I came across items of which I wondered whether or not to include them in my book. Very often they were too brief to devote an entire chapter to them and sometimes they had no relationship to ceramics whatsoever, although the titles implied that they did. This chapter is a collection of a number of items, some which (*) have been worked out because sufficient material was available. The articles all revolve around ceramics in unexpected applications or they have been incorporated on a "interesting to know" basis.

I came across the following items:

(*) Westerwald, an area in Germany with lots of ceramics
(*) Ceramic screwdriver
(*) Musical instruments made of clay
Ceramic chalk
(*) Ceramics in living organisms
Cold porcelain
(*) Paper clay
(*) Polymer clay and stone clay
Quick clay
3D ceramic pictures
Ceramic photographs
Crystal glazes
(*) Virtual ceramics
Synthetic clay
Clay magic
Ceramic marker
Mystic ceramics
Ceramic sharpener
(*) Healing clay

Bio-ceramic soap
Coiled ceramics
(*) Densifying ceramics explosively
(*) Pitfired ceramics
(*) Ceramics derived from metals and wood Clay balls (found in Turkey, but archeologists have no clue as to what their purpose is)
(*) Ceramics without firing

12.1 THE WESTERWALD IN GERMANY

The Westerwald is the oldest and largest area in Germany where clay is won and where a ceramic industry has developed over the centuries. Archaeological discoveries indicate that pottery was already made there in prehistoric times. Since the Middle Ages there has been a continuous production of ceramics and the area is known all over the world as a centre of ceramic activities. I visited the South-West of the Westerwald, the so-called “Kannenbäckerland” surrounding the towns Höhr-Grenzhausen (H-G), Ransback-Baumback and Wirges. I toured the area for several days, using H-G (a centre of ceramic education and research) as a base. The name “Kannenbäckerland” dates from the end of the 18th century and is related to the area’s main products: jars (German: Kannen) and jugs (especially for beer) made of salt-glazed white, bluish grey or brown stoneware (German: Steingut). For a long time there was question of a so-called “beer culture”. Beer was (and perhaps still is?) the main beverage during important events, such as the closing of contracts. A journey to the area can start at home with the help of the Internet address

www.keramik.de

where you cannot only find information on education and research, but also on the ceramics production, tourism and culture. If you look into the matter a little more deeply, you will notice a close cooperation between these three ceramic branches which is aimed at boosting the image of the area as a ceramic centre. Participants in this collaboration are: several technical and artistic training institutes which offer courses at various levels, a research institute, the “Keramik Museum” and a so-called “KeraTech-Center” which is to be set up somewhere in the future; all of which are situated in H-G.

One of the schools in the area is the “Fachhochschule Rheinland-Pfalz / Koblenz / Fachbereich Keramik”, which is a polytechnic. Here future engineers are trained in the materials technology and process engineering of ceramics. The “Keramischen Zentrum” incorporates a few schools for ceramic education at different technical and artistic levels, among which the “Staatliche Fachschule für Keramikgestaltung”.

The reseach centre “Forschungsinstitut für Anorganische Werkstoffe - Glass / Keramik - GmbH” not only carries out research but also offers services to companies. Here anyone wishing to do research and possibly set up a company in the area can rent accommodations.

In the near future a now disused ceramic factory site will accommodate the “KeraTechCenter”. This building will offer similar accommodation facilities to starting entrepreneurs.

The “Keramik Museum” with its lovely inner architecture displays the history of ceramics in the Westerwald. In addition there are varying exhibitions with the Westerwaldpreis and, thirdly, they offer a corner with technical ceramics. Here I saw exhibits I had never seen before, e.g. a nail file made of corundum, an orange peeler and veget. able grater with ceramic blades, child’s cooker with a ceramic heating plate and a pepper mill with a grinding mechanism made of zirconium oxide. In the restaurant I noticed a several metre long window-sill on which hundred of coffeepots were placed. The museum subdivided ceramics used for appliances and for art into the following groups:

Terracotta clinker porcelain majolica/faience stoneware (German: Steingut and Steinzeug) and pottery. During one of my conversations with a lecturer of the “Fachhochschule” I told him that I did not know how to translate the German “Steinzeug”. He answered with a phrase: “Steinzeug is gut und Steingut is Zeug” (Steinzeug is good, but Steingut is junk). So far I have not been able to understand the relevance of this phrase to my remark. The English language does not make a distinction between “Steinzeug” and “Steingut”, both are called pottery. Any collector of ceramics doing some research will soon discover that the differences in the kinds of ceramics are mainly based on the porosity, the firing temperature and the used glazing.

In the leaflet “Keramik auf der Spur” of the Tourist Information Centre in Höhr-Grenzhausen you can find four circular walks from the “Keramik Museum”. All walks lead past ceramic workshops and companies which produce various products, both functional as well as artistic. With the help of the book “Keramik, ein Leitfaden durch das Kannenbäckerland” you can find clay pits or producers of heat-resistant systems and ceramic machines

12.2 The ceramic screwdriver

(Source: Dutch magazine "RB Electronica", September 1997)

In the Far East and in the USA hardly any electronic piece of equipment leaves its factory without first having been adjusted with a ceramic screwdriver. However, this tool is only rarely used in European companies. In the electronics branch ceramic screwdrivers are important tools both for producing and repairing. Metal screwdrivers can for example affect equipment in which frequencies need to be adjusted. They can cause short-circuits and transfer static electricity form a person to the device. In order to prevent these problems the use of a ceramic screwdriver is recommended.

Despite the fact that a ceramic screwdrivers have been reasonably priced for some time now, they are not used on a large scale. Few electrical engineers are aware of their unique properties. They are non-magnetic, non-inductive and consequently indispensable when adjusting sensitive electronic equipment. Adjustment mistakes can be considered a thing of the past.

When a regular screwdriver is taken off the adjustment component, there is a considerable chance that the painstakingly acquired value changes again. This is for example a common problem in the case of circuits which must amplify smally currents (e.g. in meas-

Ceramic screwdriver (JAMA) (by: E.Bormans).

uring equipment). It is caused by the inductance of ordinary screwdrivers which can affect small currents near a potentiometer. Plastic screwdrivers can also be highly static, which again causes the value to change.

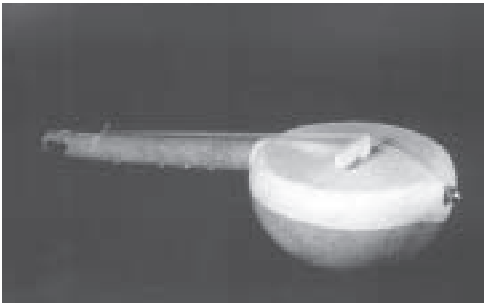
The inductance of adjustable coils with a ferrite core and the capacity of trim capacitors are strongly influenced by metal screwdrivers. It is important for trim capacitors and coils in oscillator circuits to be adjusted in the precise centre of the resonance area. Should this occur at the side, then oscillators sometimes fail to REACT when there is question of a change in temperature or ageing of components. Thus more situations can be mentioned in which you can benefit from the advantages of ceramic screwdrivers.

The manufacturer of ceramic screwdrivers – JAWA – has developed a high-quality, reasonably priced screwdriver. It is made of zirconia (zirconium oxide) ceramics, which is harder and more durable than ordinary ceramics.

12.3 Musical instruments made of clay (by Barry Hall)

Clay is a fascinating material from which to make musical instruments because it can produce a multitude of sounds. Different types of clay and various firing techniques can be employed to create musical instruments that sound quite dissimilar to each other. And the plasticity of clay, before firing, makes it possible to create a variety of unusually shaped air chambers and resonators for wind and percussion instruments.

As a builder of musical instruments, I am constantly challenged by the endless musical opportunities presented by the many instrument families (e.g., wind, string, percussion) and the myriad types of clay available. I enjoy making all types of ceramic musical in-



Barry Hall and his musical instruments made of clay.

struments, including drums, flutes, ocarinas, horns, didjeridus, fiddles, chimes, shakers, and musical pots and bowls. However, "hybrid" instruments – creations that are synergistic combinations of several different instrument families – especially fascinate me. The following hybrid inventions, the *didjibodhrán* and the *stone fiddle*, are two of my favourites.

The Didjibodhrán

The didjibodhrán is an original hybrid instrument, a combination of two traditional instruments from different cultures. It is constructed as an Irish frame drum, called a *bodhrán*, which has a stretched goatskin drum head. Additionally, the ceramic drum frame is a circular *didjeridu*, an ancient wind instrument developed by aboriginal people of Australia. When blowing into the didjibodhrán as a didjeridu, the drum head vibrates sympathetically, creating resonances and pseudo-reverberation effects. The didjibodhrán can also be played with the fingers like a Middle-Eastern or North African tar (frame drum) while blowing into it as a didjeridu, or just as a bodhrán in the traditional Irish style using a stick or your hand.

Clay makes an excellent material for didjeridus. Although fired clay is rigid, and even brittle, compared to other materials like wood it is also very resonant and has some unique acoustical properties that work well-suited to didjeridu playing. I use stoneware clay that is best suited to sculpting large forms and fire it to “cone 10”, about 2400 degrees Fahrenheit. This produces a vitrified, hard, dense and durable instrument with exceptional resonant qualities.

Didjeridus can be made from clay using several techniques. One technique is to roll out a big slab of clay and then form it into a cone or wrap it around a stick to form a tube. You can also roll out a thin snake of clay and gradually build up a long tube of any shape by coiling it around and around. I manufacture the didjibodhrán using an *extruder*, a mechanical device that helps me form hollow tubes of clay by forcing the clay through a set of metal dies.

Once a hollow segment is extruded, it can’t be bent nor its shape changed,so I have to coax the clay out of the extruder with exactly the curve I want it to have in its final form. The didjibodhrán is extruded in four separate segments, which are attached once they have dried to a leather-hard state. The goatskin drum head is then attached using water-soluble glue.

The Stone Fiddle

The *Stone Fiddle* is an original stoneware instrument that is a hybrid of three instruments from different musical families. It is created as a two-stringed bowed instrument, similar to the violin and the Egyptian *rebabba*, while the neck of the fiddle serves as a flute. In the photograph you can see the flute’s blow hole and finger holes on the side of the fiddle’s neck.

The goatskin soundboard or resonator of the fiddle can be played as a drum, and the fiddle’s bridge can be plucked. As a player, it is interesting to explore how the three systems (string, wind and percussion) interact. For example, when playing the instrument as a flute or drum, the strings sympathetically vibrate and produce their own sound. Additionally, when playing it as a flute, the drum chamber of the instrument amplifies the flute’s notes while the goatskin membrane creates a reverberation effect.

The stone fiddle is built by hand, using a combination of extrusion and coiling.The neck of the instrument is extruded, like the didjibodhrán. The body is formed of rows of clay coils, or snakes, which are stacked one upon the other and then smoothed by hand into a bowl shape. A goatskin membrane is glued to the face of the instrument to form the sound board.Gut strings are stretched from a wooden end pin and tensioned by wooden pegs that are fitted in holes in the neck. A wooden bridge transmits the sound of the bowed vibrating strings to the goatskin membrane. The instrument's sound is amplified and coloured by the instrument's main body cavity, which is open in the back.

I call my ceramic musical enterprise "Burnt Earth" with reverence for the earth, air, fire and water that are intimately involved in the production of each of my instruments. Clay is one of the oldest materials for making musical instruments know to humans. It's exciting to realise that the clay instruments we create today could last for thousands of years. Let's make some good ones!

Barry Hall, *Burnt Earth Ceramic Musical Instruments, PO Box 4674, Walnut Creek, California 94596, USA*
Telephone & Fax (925) 947 - 5537
Email : burntearth@ninestones.com; Web site : http://www.ninestones.com/burntearth.shtml

12.4 Ceramics in living organisms

In this chapter we discuss some examples of natural occuring ceramics in living organisms.

When we analyse skeletons of living organisms, we mainly come across carbonates as inorganic material. This compound was already discussed in the chapter "Bioceramics", but then mostly in the form of hydroxylapatite. However, there are also organisms which have skeletons which mainly consist of silicon dioxide. In most "constructions" inorganic material is interwoven with organic compounds (e.g. proteins) to form the composite material specific for the organism in which it is found. This results in a unique combination of properties. A genetically controlled production process ensures the formation of composite materials.

As you can see in the table, most skeletons of living organisms contain calcium ions. This is because calcium can easily be found in nature. Especially the sea water of tropical beaches is saturated with calcium. That is why more calcium than silicon compounds are found in skeletons.

Two important calcium salts are present in skeletons: carbonates and phosphates. Together with organic compounds they form composite materials: phosphates mainly with collagen in for instance the disagreement. According to Driessens 1980 the mineral composition is as follows:

Table 12.1 Common ceramic materials in living organisms

name	formula	occurs in
calcite	$CaCO_3$	bird eggs, skeletons of echinoderms (*e.g. sea daisies, sea urchins, sea cucumbers), teeth, crustaceans (e.g. lobsters, crabs), mollusks (e.g. squid, mussels), sponge spicules (**)
aragonite	$CaCO_3$	reptile eggs, mollusks
dolomite	$CaMg(CO_3)_2$	teeth of echinoderms
magnesite	$MgCO_3$	sponge spicules
hydroxyl-apatite	$Ca_{10}[(PO_4)_6/(OH)_2]$	bone, teeth
amorphous hydrated silica	$SiO_2.(H_2O)_n$	sponge spicules, radiolaria, teeth

* Echinoderms (Latin: Echnodermata) are often found as fossils. The calicite skeletons of their skin fossilizes quite easily. In certain geological layers certain fossils are found which are characteristic for the period during which the layer was formed. That is why these fossils are also called guide or index fossils.

** Spicules sponges are minute needles made of calcium carbonate which support the essentially jelly-like sponge in such a way that it retains its shape.

vertebrates (organisms which have a spinal column, so this includes man) and brachiopods (certain crustaceans) and carbonate with other proteins and polysaccarides in most other vertebrates.

So let us have a closer look at human bone material. You might say that bone is *mineralised tissue with a complex compostion.* Another description of bone is “*a fibre-like matrix (mother matrix) in which inorganic salts are imbedded*”. The fibre-like matrix consists for 90–95% of the protein collagen and for about 5% of other proteins.

In literature opinions differ on the mineral compostition. This composition is determined with the help of X-ray diffraction, but this cannot be used for the amorphous part and there lies the origin of

The Stone Crab.

15% mangesium whitlockite	$Ca_9Mg(HPO_4)(PO_4)_6$
25% sodium carbonate with inbuilt apatite	$Ca_{8-5}Na_{1-5}[(PO_4)_{4-5}(CO_3)_{1-5}]CO_3$
60% carbonate-containing calcium phosphate	$Ca_8(PO_4)_4(CO_3)(OH)_2$

Scientists agree that the main components of bone are calcium (Ca^{2+}), phosphate (PO_4^{3-}) and hydroxyl (OH^-) ions. For that reason the mineral phase is usually denoted as hyroxyl apatite (HA) with the formula $Ca_{10}[(PO_4)_6/(OH)_2]$. However, some literature sources claim that most HA is actually dahlite 3 $Ca_3[PO_4]_2.2Ca[CO_3].H_2O$ or francolite $Ca_5[F/(PO_4,CO_3,OH)_3]$.

Bone is a so-called composite material, i.e. it combines two properties which are rarely present in one material: namely it is extremely strong and light in weight. For example: bone is 4 times as strong as cement and the skeleton of a person of 66 kg only weighs about 9 kg, which is merely 14% of the total body weight.

Apparently collagen initiates the formation of crystals. With the help of X-ray diffraction and electron microscopy you can see that the mineral crystals in an adult bone resemble thin sheets which are

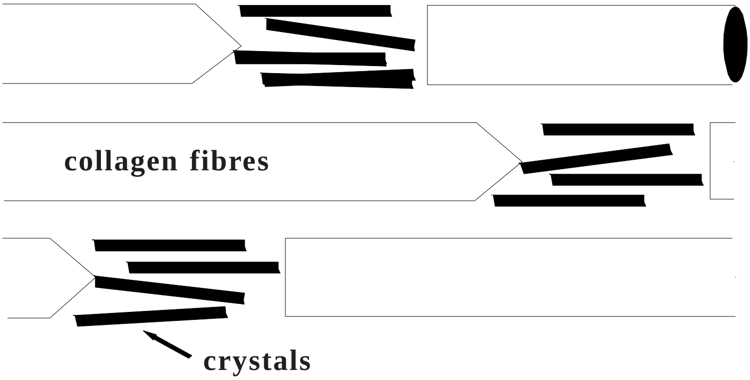


Fig. 12.1. The structure of solid bone from collagen fibres and crystals.

about 5.0 nm thick and 35 nm long in the direction of the longitudinal axis of the collagen fibre (fig. 12.1). Figure 12.1 is a simplified representation since the collagen fibres are in fact intertwined. Without collagen bones would be so brittle that the weight of the body would be sufficient to break them. Without minerals ‘bones’ would be flexible like rubber.

As you can see in the figure above, bone is porous. This porosity appears to increase its strength, consequently without porosity bones would not only be heavier, but they would also break more easily. Figure 12.2. illustrates how the collagen fibres and crystals are joined together to form larger units and finally bone.

Collagen fibres (a) and hydroxyl apatite crystals (b) together form larger units, the so-called micro-fibrils (c). It should be pointed out here that the collagen fibres are helically intertwined and consequently

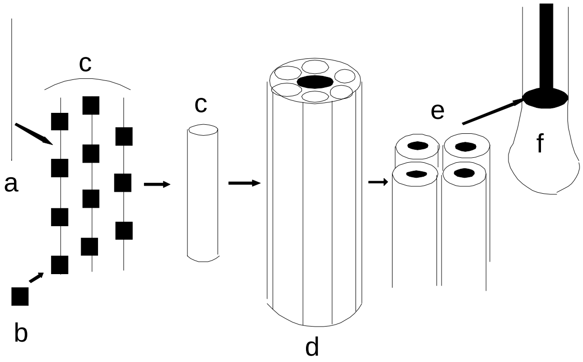


Fig. 12.2 Crystals and fibers in a bone.

not parallelly aligned as shown in figure c. These micro-fibrils in their turn are joined together to form a larger unit, the osteon (d). In the centre of an osteon there is a canal (the haversian canal) for bloodvessels. As shown in figure f, a collection of osteons together form the compact bone. This compact bone surrounds a hexagonal mass of spongy bone filled with marrow, the tissue which produces erythrocytes, i.e. the red blood cells which take care of the body's oxygen transport.

12.5 Paper clay

By mixing clay with cellulose fibres from paper you can make paper clay. This clay mass can be moulded and shaped into rollers. During moulding the behaviour of this clay type is totally different from that of clay without fibres, according to experts. These unique properties are partially attributable to the fact that the fibres are hollow and can be filled with minute clay particles and in this way a kind of composite is made. Most literature sources report a composition of appr. 30 % (v/v) paper pulp slurry and appr. 70 % clay slurry. Paper clay does not crack, can be moistened when bone-dry by immersing it in water, hardly warps during drying, can be glue together by means of clay silt and has an extremele high strength in the green product owing to which lighter and thinner objects can be manufactured. However, apparently it cannot be processed very well on a potter's wheel.

Anyone working with paper clay will find that a lot of experimenting will be necessary before the desired results can be obtained. It is quite interesting to use a microscope to verify that that the minute clay particles have indeed ended up in the paper fibres. Furthermore the nature of the fibres appears to be important. Paper can be broken down by tearing it into strips and subsequently soaking these in a tenfold volume of hot water. Paper which does not contain any lignin provides the best results, since lignin is water-resistant. Paper containing glue or kaolin does not break down easily in water. Paper clay very quickly has an unpleasantly smell and for that reason a little chlorine-containing bleach is added to the paper slurry. And finally, the organic fibres have to burn during the baking process and the gases must not be prevented from escaping. That is why the temperature is slowly increased to 300–500°C. Due to the production of smoke it is vital that the work place is well ventilated.

12.6 Polymer clay and stone clay

On the one hand the words ‘polymer clay’ and ‘Stone clay’ are misleading, and yet they are also correctly chosen. Misleading because we are not dealing with clay and correctly chosen because the materials exhibit polymer and clay properties and by adding certain substances to the polymer clay it can resemble a certain type of stone.

Polymer clay is a mixture of minute polyvinyl chloride particles and e.g. resins, gel, colourants, and various fillers and its properties are such that you can process it as a clay. It is possible to mix masses with different colours in order to obtain new colours but the individual colours can also be preserved. Techniques have been developed to give the polymer clay a granite, coral or jade-look and it that case we speak of stone clay. This material has a multicolour texture. A well-known trade name here is Granitex of Polyform Products Co. which is available in the colours pink, light blue, dark blue, violet, grey, brown, orange, and green. Stone clay consists of a mother material in a base colour which is mixed with minute fibres of contrasting colours. The fibres give the product its granular look. To give me a better idea of this stone clay, Polyform Products sent me a sample of Granitex (green), a baked product of the same material and a brochure which was titled: “Looks like stone.... soft and pliable... mix with Sculpey III colors to add texture .... knead it .... shape it..... twist it.... roll it..... excellent for rubber stamping projects”. The baked object produces a stone- (ceramic-) like sound when you tap it on a hard surface. When I showed my students the unbaked sample and the baked object and asked them what they thought these were made of, they all thought that it was real clay!

Polymer clay must be fired at temperatures between 210–300 °F, which amount to 100–150 °C (conversion formula: x°F = 5/9 (x – 32) °C). These temperatures are kept low in order not to affect the colours and dimensions of the particles. The firing time depends on the thickness of the object and can be as much as several hours.

At temperatures over 150 °C the ‘clay’ will burn, thus releasing harmful substances.

The oven does not need to be pre-heated. However, by baking the object in a preheated oven you can control the temperature better. When another object is covered with clay, it is advisable to gradually heat the covered object and consequently start the process in a cold oven. After firing allow the object to cool in the oven.

Components of polymer clay can leach out (even after firing). This makes the material unsuitable for any direct contact with food products.

Finally three addresses where you can obtain more information on Granitex:

1. **Polyform Products Co**. *1901 Estes Avenue, Elk Grove Village, IL 60007, USA*
2. **Polyform Products Co**. *PO Box 2119, Schiller Pk., IL 60176, USA*
3. **Blackwells of Hawkwell,** *The Old Maltings, 5 Weir Pond Rd., Rochford Essex, SS4 1AH, Great Britain*

12.7 Virtual Ceramics

Hello World

Visual Culture, the Object and the Virtual, by Steven Goldate

Today it is difficult to talk about the ‘object’, without talking about images. Our experience of the object relies heavily on the images we see in magazines and other media. You, at this very moment are part of that culture, learning about numerous ceramic projects and individual works, by viewing images in this book. In doing this, we form a learned opinion about the works we have seen, although in most cases we haven’t actually seen them ‘in the flesh’. This has become quite normal to us in an age of mass media and mass information distribution, based on economic principles. Thus western societies have become societies that are pervaded by the image. The image is omnipresent. This was not always so. Before the invention of the Gutenberg press in the 15th century, images were created by an elite, only to be seen by an elite. An example of this is manuscript illumination, a craft which was doomed once the printing press became popular. The object, which in earlier times was usually utilitarian, and not a showpiece, could be seen as another example. Our museum and gallery culture, where we put the object – even the utilitarian one – on display, is fairly recent.

The dissemination of the image was increased rapidly in the 19th century with the invention of high-speed printing presses and then photography. The dominance of the image was then further increased with the invention of motion pictures around the turn of the century, and finally television in the 20th century. Finally television? No, not quite - we now also have an ever-growing computer culture. The computer takes photography one step further. Through the use of the digital camera and photo-realistic inkjet printing technology, we can bypass the photo lab altogether, not to mention other ramifications of creating and storing images digitally.

What has all this got to do with the object? A lot. We, in the 20th C live in a gallery and museum culture, where we will place the object in the 'white cube' for the public to see. An exhibition of, let's say, contemporary ceramics, will be seen by perhaps hundreds, possibly thousands of people, depending on its importance. The show is then dismantled, perhaps to be toured, perhaps never to be seen in that form again. It is more than likely, that most visitors will never see the majority of works in that show ever again. At least not in the flesh. This is where the image steps in and 'takes possession' of the object in the form of the catalogue or the magazine. The catalogue becomes in Susan Sontag's words 'the reality of the event', which is there to refresh our memories forever more. She says that "ultimately, having an experience becomes identical with taking a photograph of it, and participating in a public event comes more and more to be equivalent to looking at it in a photographed form." [1] Of course in most cases we do not even get to see an exhibition at all, but rather know of it and the works displayed through a catalogue. Similarly we have never seen the majority of art and craft works that are familiar to us, but experience them through images. We may 'know' what a 17th C Thomas Toft plate looks like but how many of us have actually *seen* one? (I'm sure a few readers will have.) Similarly, our experience of the world is derived largely from images. Most of us will be familiar with the world famous image of the Taj Mahal mausoleum in Central India, but how many of us have actually been there? This surrogate experience is now even extended into space: we are familiar with images of the dark side of the Moon, Mars and other planets - places we are not likely to go. Our visual knowledge now also extends into the microcosm of the microscopic world of bacteria, viruses and even molecular structures.

Today we live in an information age. In comparison to only a few years ago, computers have become very accessible to the people of the first world. While there is still some apprehension amongst some of us about the amount of time and energy it might take to learn how to handle one, more and more craftspeople are comfortable working with them. It is inevitable that this technology will somehow influence our craft practice. The first major impact of the computer on traditional craft areas came in the form of CAD/CAM. Computer Aided

Design/Computer Aided Manufacturing is a process where an artist, craftsperson or designer creates an object using 3D modeling programs for eventual industrial production. Many an industrial teapot or vase have been designed in this way. CAD/CAM has also become particularly useful, even indispensable in architectural design.

What seems to be more interesting for the fine art application of ceramics, is the computer modeled ceramic object, which is designed as a craft artifact in itself - the virtual object, inhabiting the virtual space of the computer screen (perhaps a new type of ‘white cube’?), the Internet or other conceivable virtual spaces. Of course many will argue that a virtual object is not an object at all, and that Virtual Reality is not actually any form of reality. Or is it? Some will argue that surface and touch are essential to our experience of craft objects, but this experience is already denied us in the gallery and museum environment, and even more so when looking at catalogues or magazine articles. And yet in conjunction with our previous tactile experiences, this type of ‘viewing’ is seen as a valid method of learning. These questions lead me back to my previous thoughts on how we have become a society that experiences the world through images and how we rely on images to relay information to us (“a picture is worth a thousand words...”). Now we have reached a stage where we are able to digitally generate imagery practically indistinguishable from the ‘real thing’. Some virtual ceramic images have been mistaken by quite experienced people for physical ceramic objects, although trompe l’oeil is not necessarily the artistic intent. So we now have a situation where virtual objects are taking on the role of relaying valid information to the viewer. The extent of ‘correct’ interpretation of the ‘object’ (or the image thereof) will rely on the viewer’s knowledge and experience, but of course to varying degrees this has always been the case in any analysis of art and craft objects. I believe that much of the resistance to a Virtual Craft stems from the fact that a system of codification or symbolism for virtual craft imagery and objects has not yet been fully established. There is perhaps a tendency to blur the definitions of signifier and the signified.

I would like to posit that a Virtual Craft has already been established. It is concept based. It relies largely on Photoshop image manipulation and 3D modeling. The practice and techniques of Virtual Craft enable us to move our concepts into a virtual realm where they can be visualised, studied, manipulated and just as easily discarded. The craftsperson, with the help of computer technology, can explore concepts, regions and realities that would be difficult to tread in our physical world. A good example is the work of Dutch porcelain artist Jeroen Bechtold, whose virtual work often takes advantage of the fact that virtual spaces know no gravity.

While this Virtual Craft is strongly based in imagery, there is nothing stopping craftspeople transforming their ideas into a craft material if they wish. Translating the Virtual Object into a craft material can be quite an exciting undertaking. But a virtual craft limited to some 2D or 3D imaging, maybe a bit of animation, and translations of these into a physical, traditional craft material or other high-tech materials (using methods such as stereolithography) is not the end of the road in the transformation of the object. In the future, the craft object will boldly be going places where no object has gone before.

One of the next steps in this transformation of the object is the creation of a fully immersible 3D virtual reality environment. This environment could be an exhibition of computer generated ceramics in a 'white cube'. A Head Mounted Display (HMD) would project two separate images in front of the eyes, creating the stereoscopic effect. You would be able to move around in the gallery space. With the help of data gloves you would be able to pick up an object, look inside it, maybe even feel its surface. This particular exhibition could be sent overseas on a disk or transmitted via the Internet. The opening could be a global one, with people "jacked in" from around the world. Thus a few more of the physical limitations of the object will be dispensed with. Another path the object might take is that of holography. In that case objects, or holographic renderings of them, will appear in mid air, with the help of laser technology. It is already possible to generate beams of light that just stop at a given point. Using this kind of technology it should be possible to create 3 dimensional virtual objects indistinguishable from the real thing, such as the Holodeck on the Starship Enterprise. Perhaps one day in the not too distant future we will be able to buy the holographic equivalent of a desirable but otherwise unobtainable ceramic object.

Another option is the replication of an object using techniques of molecular manipulation. It is not unimaginable that at some time in the not too distant future machines will be able to rearrange the molecular structure of a cheap material, e.g. air or water, and materialise a pre-programmed craft object. The industrial processes of stereolithography, rapid prototyping and selective laser sintering already transform 3D computer models into solid objects. With the help of a computer file, a 3D object is 'rendered' in bonded paper, resin or nylon. Nanotechnology and self-replicating machines are a further step in this direction.

Will all this spell the death knell for the craft object and the craft practitioner? Are the traditional crafts doomed to become a nostalgic thing of the past? Maybe, maybe not, but I do think that some of the above described developments will happen in our life times, and craftspeople should be prepared for what might be coming.

Steven Goldate is based in Melbourne. His porcelain work is represented in Melbourne by Distelfink Gallery and in Sydney by Quadrivium Gallery. He has been involved in promoting the use of computer technology in the crafts and curated the exhibition **Craft is Dead, Long Live Craft**. He is also the founder of Intersect, The International Society for Electronic Craft Transformation (**http://www.helloworld.com.au/intersect**)

12.8 Healing clay

The Medical Annals of the District of Columbia, volume 10, no. 16, June 1961 contain an article which is titled ‘The value of Bentonite for Diarrhoea’. Diarrhoea may be caused by a virus infection, food allergy, food poisoning or by spastic colitis. A suspension of bentonite has been known to bring relief in 97 % of all cases. The conclusion of this article is: ‘By virtue of its physical action bentonite serves as an adsorbent aid in the detoxification of the intestinal canal’.

In the USA bentonite is a rather common name for a strongly polluted clay which is rich in montmorillonite and was formed in the erosion of volcanic ash with a high percentage of glass. In it 25 -35 trace elements can be found. This bentonite has to be purified before it is used. It is able to absorb more than 5 times its own mass of water and as a result the volume of the clay increases up to 15 times. Apart from being applied in medicine, bentonite is also used in foundries as a binding agent in moulding sand, to improve the plasticity of ceramic clay masses and as a component of face packs and cattle fodder. Large amounts are found in Russia, Czechoslovakia, Hungary, the USA and China. The clay particles are negatively charged and as a result they attract toxic substances present in the body as their particles are mostly positively charged. The large absorbing capacity is the result of the particles’ large surface / volume proportion. In a watery suspension the clay mineral layers trap bacteria on their surface.

The use of clay as a medicine has been known for quite a long time, however. In 1712 the missionary Father Deutrecolle described the use of clay in the fight against diarrhoea and cholera in China.

During the Balkan war in 1910 the use of hydrated aluminium silicate in combination with other drugs reduced the number of casualties among soldiers as a result of cholera from 60 % to 3 %. Research has shown that primitive tribes in the Andes, Central Africa and Australia used several types of clay to cure poisonings. Apparently these people were sometimes in the possession of small lumbs of clay. A little amount of this was suspended in water and subsequently food was soaked in this clay liquid before consumption. They explained their behaviour by saying that it "prevents a sick stomach".

Another literary source mentions the following: 'From Nature's own laboratory in Wyoming's Big Horn Mountains comes a wonderful healing clay called Pascalite'. Test and experiments demonstrated unbelievable healings. For instance: a scratch on a boy's leg had become infected and gangrenous. The doctor wanted to amputate, but the boy's father covered the leg with a thick Pascalite paste after it healed completely. Moreover there is mention of the healing or relieving of eczema, burns, psoriasis and cataract.

12.9 Densifying ceramics explosively

The densification of a ceramic material starts with moulding (e.g. pressing) and ends with a sintering process. It is, however, difficult to densify materials with strong, covalent bonds. In addition there are materials which decompose under the influence of the high sintering temperatures. An experimental technique which might present a solution to this problem is the "explosive densification": with the help of an explosive a shock wave is generated which can have a pressure as high as several hundreds of thousands atmospheres (1 atm. = 101.3 kPa). As a result the surface of the ceramic grains becomes extremely hot and melts. In this way the grains "stick together". It is also possible to densify in such a way that a porous structure is formed. You might use these pores to introduce another material with the help of capillary forces and thus form a composite. Figure 12.3 is a representation of a simplified trial set-up.

12.10 Pitfired ceramics

Pitfired pottery (by: Oliver Loveday)

Pitfired pottery is a part of my heritage as a Cherokee (Native American). It is the oldest method of transforming raw clay to a container that can be used for cooking or as a container. It is the only form of pottery

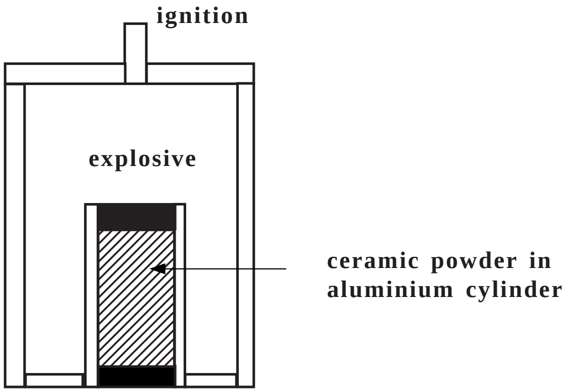


Fig.12.3 Simplified trial set-up for the explosive densification of a ceramic powder.

that can be used to cook with over a open fire. There are many variations for doing pit-fired pottery. One example comes from the Southwest tribes of the United States and Mexico where the pottery is covered with dried animal feces.The material is then covered with metal tin, or prior to such materials, a layer of dry clay, to help control the burning. The result is a dark black surface with designs that have been inscribed or painted on with pigmentation. This is best known as Pueblo pottery. Another example comes from a tribe in Africa that stacks the pots and then piles dry grass upon the pots until the pile is the size of a house. The grass pile will burn for a few hours and the intense heat will cause up to 80 per cent of the pots to break or crack. That is one of the drawbacks of pit-fired pottery, the high rate of breakage in the firing process. Today potters with access to kilns may bisque fire their pots first, to reduce the breakage. I fire my pots in a fire pit, similar to the fire one might make while camping in a wilderness. I build a fire and place the dried pots around it for several hours, turning them so they heat up evenly. This reduces the thermal shock and reduces the breakage. To give an example of how hot the pots should be at this point, one could put a piece of paper in a pot and it would burn. Then the pots are placed into the fire a few at a time and covered with wood. They remain in the fire until they are cherry red. (Remembering to continue to turn the unfired pots that remain around the fire.) Then they are removed and the process continues until all the pots are fired. One can seldom fire more than twenty pots in one day with this process. While I am continuing this process to preserve my heritage, I also enjoy the unique results that can only come from pit-fired pottery. Pit-fired pottery can be sculptural, designs can be inscribed in clay walls after the pot has been “buffed” with a smooth rock or metal spoon, and clay slips can be used as well.

Oliver Loveday

A few months after this contribution I received from Oliver additional information on the subject ‘pit firing’ and two pictures. In his letter he is sometimes talking to me. However I copied his letter here as I received it :

Pit firing is a method that has grown out of utilizing the materials available locally. The clay required has to be able to withstand thermal shock more so than clays used in more controlled firing environments. It must vitrify at a low temperature, and contain no harmful oxides, such as lead, if it is to be used for cooking, food storage, or eating purposes. These were some of the needs addressed when making pit fired pottery in pre-industrial settings, and the issues are still relevant today.

In areas such as the desert areas of Southwestern United States and Northern Mexico, there is a lack of trees for fuel, so animal feces are used as a fuel. Actually, this works better than wood, since it contains methane gas which is released in the firing process and produces a hotter flame than wood does. Given the low humidity in the desert regions, animal feces dries very fast and has similar characteristics as cooked bread when dry. There are considerations to observe when using this fuel, as with all fuels.

As the fuel is consumed, one places a metal container over the fire to produce a “reduction atmosphere”. This is one way to insure that the high black luster will occur on the surface of the pot. While the clay body can contain a high amount of iron oxide, like the clay body used in low-fire earthenware, covering the pots during the firing will cause some coloration irregardless of the amount of iron oxide in the clay body. Potters tend to use whatever metal container is easily available. Salvaged car hoods or metal wash tubs are common. Prior to the introduction of manufactured materials like this, one would cover the fire with a layer of dry dirt or soil.

While the clay body can contain iron, the reference to “cherry red “ is a reference to temperature. I am giving references that are relevant no matter what the unit of measurement would be otherwise. 1500 ^{0}F or Cone 06 would work in the United States, but not everywhere else. I am not sure who your intended readers are, so you can include the relevant temperature in (parenthesis) if you like. Porcelain clay bodies get cherry red as well, so iron isn't a factor when heating up a clay body.

One buffs a pot by rubbing the walls when it has dried to the point of being leather hard, using a smooth object, such as a river rock or metal spoon. This produces a very glossy surface that will take on a sheen when the pot is fired. Pit firing is the only process where buffing the pot will influence the final outcome. Pit fired pottery is found all over the world, as is shown in the time - line of the development of pottery through the ages. It is a trial and error at best, but with some experience, can produce some very satisfying results. One can use commercial clay, generally a low-fire earthenware clay body, to do pit fired pottery, but local hand dug clay is also practical. One needs to find a source that has a minimal amount of particles in it, such as pebbles, or else they will need to screen the clay before using it. Pit fired pottery is best learned from someone that is already doing it. It is difficult to learn the process from books or other media unless one has some experience to start with.

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12.11 Ceramics derived from metals and wood

Metals and ceramics

By infiltrating molten metals and alloys into porous ceramics you can make materials with a higher fracture toughness than that of the ceramic material itself. In addition these materials possess the conducting properties of metals. A combination of certain materials which results in a set of properties which the individual materials do not possess is called a *composite*. The entire chapter 14 is devoted to these materials. During and after the mentioned infiltration an exchange reaction can take place, e.g.

$$Ti_2O_{3\,(s)} + 8\ Al_{(l)} \rightarrow Al_2O_{3\,(s)} + 2\ Al_3Ti_{(s)}$$

In this example, the porous titanium (III) oxide is infiltrated by liquid aluminium. Depending on the reaction circumstances, the formed composite can be composed of titanium(III) oxide and aluminium, but also of aluminium oxide and aluminium titanide. In addition, intermediate compositions are also possible, for example all four components from the equation.

There is an increasing interest in these kinds of composites for the development of durable components of, for example, high-quality braking systems for vehicles which are exposed to high temperatures and extreme mechanical strains.

Wood and ceramics

At this moment a lot of research effort is invested in trying to make materials based on biological models, the so-called biomorphic materials material synthesis. Biological materials have evolved genetically and have thus attained excellent properties for special applications. Wood is a naturally formed composite whose main components are cellulose, hemicellulose and lignin. The latter, lignin, is a complex, highly polymeric resin which resembles polyphenols and therefore belongs to the polyaromates. As secondary components wood contains macromolecular compounds from many organic materials (fats, oils, resins, sugars, alkaloids and minerals). The total mass consists for about 50% of carbon.

Wood is built up of parallel columns of cells. Around these cells, cellulose embedded in lignin is wrapped. If wood is heated to temperatures above 600 °C (the exact temperature depends on the type of wood) in an inert atmosphere, then the polyaromatic biopolymers are broken down and what remains is a carbon skeleton with the anatomy of wood, both at a microscopic and macroscopic level. This skeleton facilitates the infiltration of, for instance, silicon and the reaction to silicon carbide.

Like wood, wood-derived composites also have anisotropic properties. For instance, the bending strength of a certain SiC ceramic with a density of 2.5 g/cm^3 varies from 2000 to 120 MPa, depending on the direction of the load in relation to the growth rings of the wood.

12.12 Ceramics without firing

ARCILLA RESEARCH is a small, Dutch-based, technology enterprise which has developed a special body of techniques and materials based on a mineral binder system, whereby products with ceramic-like properties are cured rather than fired. In partnership with industry, university and government institutions, ‘Arcilla’ is developing innovative products and systems to meet high technical specifications and which impact upon the environment, physical resources and mass needs. The mineral binder system and range of new materials are neither cements nor ceramics yet offer many of the advantages of both. Three units have been set up by Arcilla Research to develop its family of new materials into useful products:

ARCILLA Ceramic Technology has centred on the utilisation of coal fly ash to create products for building and construction. New techniques have been developed to make use of many other secondary materials. A brief listing of products and systems ripe for commercialisation or poised to enter the market includes:

APACA CERAFOAM Pellets
Harbour Sludge Utilisation
CERASTRAW Particle Board
Pellets from Contaminated Earth
Waste Gypsum Utilisation
Municipal Incineration Ash Utililisation
RUBBERAMIC road repair and flooring
Utilisation of Coal Mine Tailings

PYRAMIC Advanced Ceramic Materials is translating the work of Arcilla Research into high-performance materials and products, all made by simple means and *without* firing. Based on special versions of the inorganic binder, formulations have been devised for making high-density materials of exceptional strength and resistance to corrosion and low-density cellular materials as rigid insulation. Compositions have also been created for surface treatments, particularly coatings and adhesives.A brief listing of products and systems ready to enter the marketplace includes:

CERATREAT as Epoxy Replacement
CERAFOAM as Polyurethane Replacement Versions
CERAFABRIC and FIBERAMIC Systems
CERAGLAZE Anti-bacteria ‘Clean Rooms’
CERAMETAL SOLARAMIC Systems
ULTRA-DENSE Fibre-Reinforced
ULTRA-DENSE Electrical Insulators
ULTRA-DENSE in Castable Versions

RUBACON - Resource Utilisation for Building and Construction has developed a body of technology aimed at achieving maximum utilisation of secondary resources and agricultural by-products, grasses and plants. The Rubacon process makes use of renewable resources as mineral binder component, reinforcement fibre, wood alternative and - as a bonus - safely generates energy for the production process. This technology is called ‘RENEW’. Implementation will mean creation of a range of cost-effective building and construction materials in tune with the needs of people and the environment. RUBACON has developed water-resistant dense and cellular materials from loam clay; this technology could have significant consequences for housing and road building in many of the non-industrial countries.

The following is a brief listing of recent and current RUBACON activities:

In cooperation with partners in five Central European countries, work was carried out under the European Union ‘Copernicus’ programme. The project was aimed at recycling fly ash to produce building and construction materials based on the Arcilla-developed mineral binder system. A proposal to carry out product development work in Sumatra is currently awaiting approval by the Dutch Ministry of Economic Affairs; the project is to employ the RENEW technology for waste rice straw and husk utilisation. A broadly-based proposal to create building materials from agricultural residues is being submitted under the EU FAIR/CRAFT programme. An outline proposal has been approved under the international I M S programme to develop the RUBACON on-site manufacturing system of affordable housing. Projects planned for execution in Zimbabwe and Cuba are to employ a new binder for fibrous materials such as bagasse, straw and thatching grass. The phased lightweight system of building will proceed from ‘Shelter to House to Home’. Under development by Rubacon are two exciting architectural systems, CERAPANEL and AIRFORMED CERASHELL. The former is a sandwich composed of cellular insulation between two fibre-reinforced high-strength dense panels. The outer panel is a ceramic coated, non-woven, fibre matte, which provides at once a low-cost shelter in the first stage of construction. The special non-boxlike design system allows for placement in later stages of the insulative and structural components, creating extremely safe buildings of remarkable wind, earthquake, and fire-resistance. Fluid harmonious building forms, in a range of attractive colours, can be created using locally-available resources to reflect the aesthetic and cultural diversity of the inhabitants. The on-site production system, circumventing factory manufacture, avoids the economic and design constraints imposed byconventional materials which have condemned us to living in boxes.

AIRFORMED CERASHELL is based on the concept of air-supported forming, used successfully for the past 25 years with steel reinforced concrete structures. An airform, or balloon, is designed to inflate to a specific size and shape. Polyurethane foam is sprayed onto the inside surface of the balloon, with concrete as the interior coating. Steel reinforcing bars are pinned to the foam, prior to spraying the concrete. An extremely strong, column-free, energy efficient shell stands, without requiring any interior walls or columns for support. Airformed structures have been completed for schools, municipal buildings, residences, and used for grain, chemical and water storage.

The use of inorganic CERASHELL, a sandwich composed of cellular or foamed straw insulation between two fibre-reinforced high-strength dense materials, surpasses the characteristics of the foam/concrete composite. Pneumatic placement of a non-woven fibre matte as the outer shell results in a low-cost shelter in the first stage prior to placement in later stages of the insulative and structural components. The costs of steel reinforcement and urethane are eliminated, whilst extremely safe buildings of remarkable wind, earthquake, and fire-resistance are produced.

Ceramic materials, bonded by a mineral binder system which cures at ambient temperature, have been formulated to be sprayed on the outside of an air-inflated form or mold. The combination of chemically-bonded ceramics and pneumatic technologies heralds a dramatic breakthrough in construction cost, efficiency, strength and design flexibility.

The RUBACON programme slated for execution in developing countries consists of the following projects:

– Chemically bonded high-density straw, grass or bagasse fibrous products for use as thin-section shelter and roofing panelling, storage containers and light-weight ‘gender-sensitive’ pipe;

– The Rubacon ‘RENEW’ programme based on locally-available renewable resources such as straws, grasses, banana, tobacco processing waste and water hyacinth;

– Chemically bonded dense products for building and construction based on fly ash from coal-burning power stations and various aggregate types such as quartz sand, furnace slag and straws or grasses. Applications include flooring, wall, floor and terrace tiling, interior panelling and road repair and construction;

– Chemically bonded foamed cellular products based on fine powders such as fly ash, mine tailings and silica from the Rubacon ‘RENEW’ programme. Chopped fibrous material such as straw, grass or bagasse may possibly be incorporated;

– Chemically bonded materials of medium density based on straw, grass or bagasse for interior building applications such as wall and ceiling panelling;

– Chemically bonded dense and cellular materials based on waste gypsum for interior building applications such as acoustic ceiling tiles;

– Chemically bonded advanced ceramic materials with high wear and corrosion resistance for agricultural and industrial applications from steel and other industry waste.

During its twenty year existence, Arcillahas gathered together an international, multi-discipline team of some thirty specialist consultants to provide technical know-how and project management skills for realising the potential of its technology – ceramics without firing. In partnership with future-minded firms, institutions and universities, the three ARCILLA units are developing innovative products and systems to meet demanding technical specifications and market needs. Nearly two decades of laboratory research and in-depth testing has demonstrated the excellent properties of ARCILLA materials, particularly superior strength, wear, heat and corrosion resistance.

Additional information:

RUBACON RENEW

At the heart of the RUBACON programme is a body of technology aimed at achieving maximum utilisation of agricultural by-products, grasses and plants. The technology would use renewable resources as mineral binder component, fibre, organic additive, wood alternative, soil food and energy source. Implementation would mean creation of a range of new, cost-effective building and construction materials, in tune with the needs of people and the environment. Arcilla has chosen to call its technology ‘RENEW’.

RENEW BINDER

Bonding of renewable resources such as wood chips, sawdust, bark, chopped straw, thatch grass, bagasse and other cellulosic materials presents special problems: water absorption and resistance to heat. Arcilla Research created the RENEW binder to cope specifically with these problems - a new generation of particle boards is the outcome. The family of materials includes: high density panel and curvilinear shell, lightweight cellular insulation and fibre-reinforced versions. In combination with the mineral binder as coating and adhesive, the possibilities of ecology and people-friendly materials for building and construction are now within reach. Saving in energy and costs, compared to cement and synthetic resins, the RENEW materials family is also technically advanced.

OXIDOREDUCTASE PROCESS

Mineral powders may be extracted by the RENEW Oxidoreductase process, which advantageously results in simultaneous production of natural fertliizer and methane gas.The powders will find use as component in pellet adhesive, coating for panels and in products such as flooring and wall tiles.

THE MATERIALS

A short list of renewable resources includes:

Tobacco Waste
Bagasse
Sawmill Waste
Wheat Straw
Horsetail Grass
Banana By-product
Cotton Ginning Stems
Rice Husk and Straw
Maize Foilage
Soya Bean Stems

RENEW DENSE

The properties of the dense version of a fine powder composition are as follows:

	Water absorption
Immersion in H_2O One Side	± 9% by cured weight
Immersion in H_2O Complete	± 23% by cured weight
Water Repellancy	Excellent – Water forms droplets on surface
Surface Coating	To enhance strength properties and reduce H_2O penetration

RENEW CELLULAR

The properties of the cellular version of a fine powder composition are as follows:

Specific Gravity	270 Kilos / m^3
Target S.G.	250 Kilos / m^3
Water Absorption	N A Surface treatment by Coating / Adhesive
Water Repellancy	Excellent – water forms droplets on surface
Surface Coating	to enhance properties or Panel and reduce H_2O penetration
Suggested Form	Pellets to form sheet with superior strength
Insulation Value	Anticipated to provide excellent insulation in Walls / Roofing and Animal Stalls

INSTANT SHELTER

Based on the Renew materials, a system of instant shelter – *From Shelter to House to Home* – for the homeless everywhere is currently being designed by the RUBACON architectural design team. Two styles of construction are being designed, both with high resistance to storm and earthquake.

GENDER-SENSITIVE PIPE

In many countries, women and children often play an important part in agriculture. Irrigation is a most difficult task inasmuch as conventional pipe is quite heavy. Lightweight irrigation pipe of bagasse or straw will find a ready market due to the fact that it is gender-sensitive.

ARCILLA RESEARCH

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13

Analytical Methods

In the world of ceramics, analyses are carried out throughout the entire route from raw material to final product. The analyses performed on the raw materials are mainly chemical ones. As the final product comes within reach, physical-analytical methods gain the upper hand. For a long time these physical methods were always destructive, i.e. the object would be destroyed during the analysis. These last ten years, however, have been characterized by a strong development of non-destructive methods. This chapter deals with a selection of analytical methods applied throughout the route from raw materials to final product. The principle of each method will be described and the analytical results will give information about the ceramic materials and objects. In additions some suggestions for experiments are included (#).

1. WET CHEMICAL ANALYSIS OF RAW MATERIALS

These analyses are mainly performed on natural raw materials, notably on clay. The user of this clay is always interested in the mass percentage Fe, Ca and humus and in the mass percentage loam, fine sand and coarse sand. The contents of iron and calcium affect the baking colour and other contents are of influence on the properties of the mass as far as moulding and drying and firing behaviours are concerned. Furthermore we have learnt from the chapter on clay that this material may contain many more components which sometimes also need to be determined, for instance for environmental reasons.

Natural ceramic raw materials have the disadvantage that they are not soluble in water and consequently unsuitable for wet chemical analysis. That is why they are first destructed in the laboratory. Destruction means that a substance or a mixture of substances is heated together with a substance or a mixture of substances and as a result the component to be destructed is largely separated into ions and consequently dissolves in water. The destruction method and the substances are specific for the substance undergoing the destruction. Different methods applied to the same substance lead to different results.

Examples of destructive agents are: a solution of HF (for most silicates), molten sodium carbonate (Na_2CO_3) and molten potassium disulphate ($K_2S_2O_7$).

2. SPECTROPHOTOMETRY

After destruction the ions present in solution can be analysed. The contents of most transition metals (Periodic Table, groups 3 up to and including 12) and of some other metals can be determined spectrophotometrically. This method is based on the principle that a coloured compound is made of the metal ion and that the colour intensity is measured.

This colour intensity is a measure for the concentration of the metal. The coloured components are so-called complexes. We already came across these complexes in the item on glazes in the section on fine ceramics. Usually the structure of the coloured compound is an octahedron with a metal ion in its centre and at the corners the binding atoms of the ligand particles, the particles surrounding the metal ion. Six places are available for binding atoms in an octahedron, but the number of ligands can vary from 1 to 6. The nature and charge of the central ion, the number and the kind of ligands and the structure of the complex, all determine the colour.

Experiment: Dissolve some copper sulphate pentahydrate $CuSO_4.5H_2O$ in a little water. The solution is light blue, a colour caused by Cu^{2+} ions with four water molecules serving as ligands. Now add some drops of concentrated ammonia. The colour will change to a dark blue shade because the NH_3 molecules take up the places of the water molecules in the Cu^{2+} complex. Note: An ammonia solution is toxic. Make certain you work in a well ventilated place.

In figure 13.1 you can see the general structure of an octahedral complex and that of a red-coloured iron ion.

The complex contains three cyclic molecules serving as ligand particles and for every molecule two binding nitrogen atoms, so all six places around the iron ion are occupied.

The solution of the coloured compound is poured into a cuvette and placed in a spectrophotometer. Next it is radiated with the entire visible spectrum. The intensity of the absorbed radia-tion is measured as a function of the wavelength. Usually the result is a curve with a maximum (figure 13.2).

The wavelength λ_{max} belonging to the top of the curve, is the measuring wavelength. At this measuring wavelength the intensity of the absorption of a number of standard solutions with known concentrations is measured. In this way a calibration line is made. Next the concentration of the solution (sample) to be measured is determined (figure 13.3).

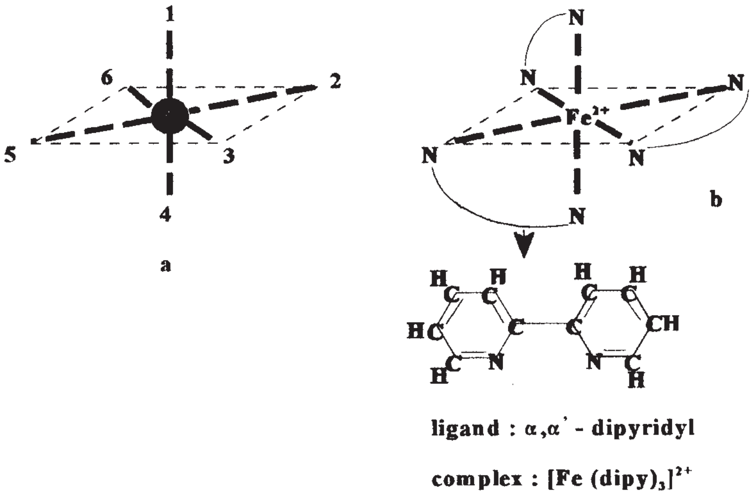

Fig. 13.1 The general structure of an octahedral complex (a) and the structure of a red-coloured iron complex (b).

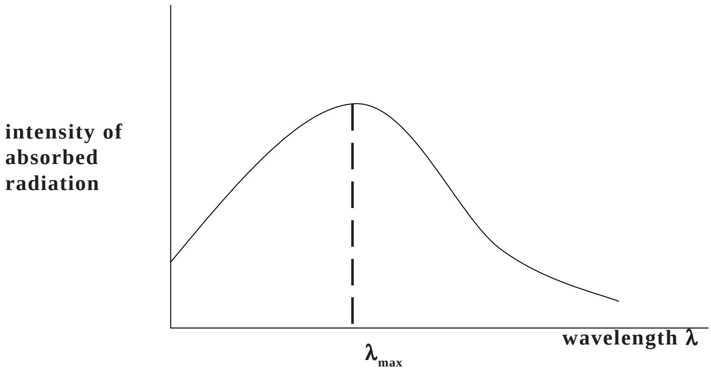

Fig. 13.2 Intensity of the absorbed radiation as a function of the wavelength of a solution of a coloured compound.

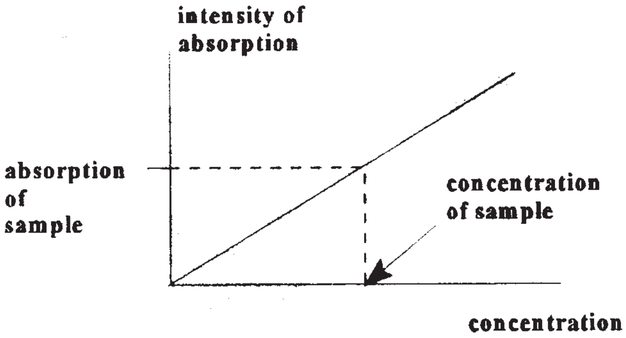

Fig. 13.3 Calibration line of a spectrophotometric analysis.

Demonstrate that clay can absorb substances, e.g. the dyes methylene blue and fuchsine.

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3. WATER ABSORPTION

In order to measure the water absorption of a clay, a glass crucible with a glass-filter bottom is connected to a pipette, a glass tube calibrated in volumes. The connection consists of a number of glass tubes. In this way the water can be absorbed by the clay. This system is the principle of Ensling's device. By measuring the absorbed volume of water over a period of time you can gather information on the speed of absorption and release, the quantity absorbed per gramme of clay, etc. In this way clay is tested to see if it is a suitable wall for a landfill. You can find out whether rainwater containing dissolved pollutions will easily percolate through such a clay wall and end up in the ground water.

Water absorption is good and illustrative experiment, just like a comparison of the water permeabilities of clay and sand.

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4. COLOUR OF THE RAW MATERIAL

5. PHYSICALLY AND CHEMICALLY BOUND WATER

The physically bound water in the raw material clay is determined by drying the sample at 105 °C until it has a constant mass. In order to determine the chemically bound water it is necessary to heat the sample to 1100 °C. Remember that between the clay sheets water molecules are bound to the ions of the sheets: an ionic dipole bond. In addition some molecules are interconnected by means of H-bridges, which are weaker bonds than the former ones. The stronger the bond, the higher the temperature will need to be to break it.

The required temperature for water release in a clay object to be dried is mainly determined by the size of the pores in which the water is located and the depth of the pores in the material.

The DTA technique is used to precisely determine the temperature at which the water is released.

6. GRAIN SIZE DISTRIBUTION

The grain size distribution for instance affects the adsorption capacity of clay, the viscosity of a casting slip, the plasticity of the raw material mixture and the reaction speed of the sintering process. Some methods to determine the grain size distribution are the simple sieving analysis which was elaborately discussed in chapter 9 and the more sophisticated methods:

Sieving analysis is a simple experiment.

Absorption of X-rays

A well-known device here is the Sedigraph in which a cuvette containing a suspension moves in relation to an X-ray beam (figure 13.4).

The Sedigraph is connected to a plotter which can represent the grain size distribution in several ways, for example as in figure 13.5.

As far as figure 13.5 is concerned, it should be noted that the percentage along the y axis only applies to the cumulative curve.

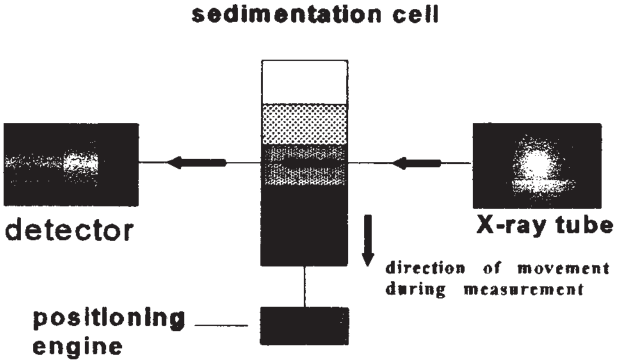

Fig.13.4 The principle of a Sedigraph.

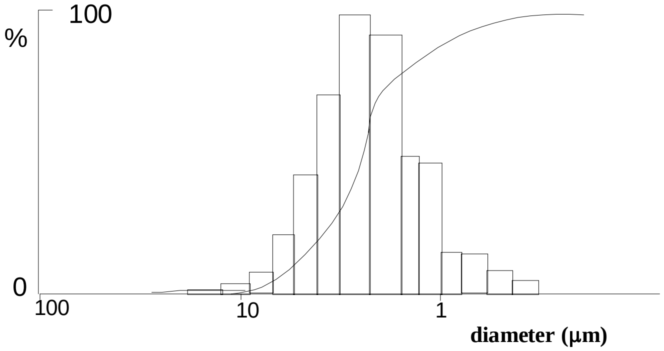

Fig. 13.5 Histogram of the mass percentage of particles as a function of the particle diameter and the accompanying cumulative curve.

Coulter Counter

The Coulter Counter contains a capillary through which a suspension is pumped. The electrical resistance of the liquid column is measured and depends on the resistance of the liquid medium, the resistance of the solid phase and the proportion of solid material in the suspension. From the size of the change in electrical resistance, certain conclusion can be drawn about the dimension of the particles in a certain fraction.

7. THERMAL ANALYTICAL METHODS

Thermal analytical methods are used to research raw materials and green as well as baked products. Clays can be identified and you can determine which physical and chemical process take place in the clay when the temperature is raised.

Dilatometry

With a dilatometer you can measure the change in length of a test specimen during heat treatment. The oven atmosphere can be controlled. In this way it is possible to register the behaviour of a mass during the firing process (it may for instance shrink) and this process can then be adapted if necessary. The thermal expansion of a glaze can also be studied in this way.

Differential thermal analysis (DTA)

With the help of this analysis exothermic and endothermic process are measured which occur in a material as a function of the temperature. A ground sample is heated to a certain temperature and the temperature of the material is recorded in relation to the temperature of a reference substance, an inert material, very often corundum is used here.

When the material contains humus, this will burn at a certain temperature in a exothermic reaction.The temperature of the reference material consequently lags behind that of the sample. When there is question of an endothermic reaction, e.g. the decomposition of water, the temperature of the sample will lag behind. The diagram is a curve with many peaks.

The technique is used to study drying and firing behaviours, but it can also be applied to identify clays.

Differential thermogravimetry (DTG)

A DTG measurement is similar to a DTA measurement only changes in mass are also measured simultaneously. It is for instance possible to measure the water content.

Specific heat

When energy is supplied to a solid this may result in an increase in the vibrations of the electrons, ions, atoms or molecules of the sample. In a sample containing moving electrons this will lead to a strong heat conduction. Most ceramics do not conduct heat. The specific heat strongly depends on the porosity of the material.

Thermal conductivity coefficient

In a material, heat is transported from a high temperature area to a low one by means of vibrations of building blocks of the material or by means of moving electrons. As we know, most ceramic materials do not possess any moving electrons and, consequently, they are insulators. If, however, transport of energy does take place, this is due to thermal vibrations of the crystal lattice building blocks. The smallest amount of energy thus transferred is called phonon energy (cf. photon energy, the smallest energy amount in a bundle of light). A certain, minimal themperature is required for this energy exchange. Thermal conductivity is simple in materials with closely packed structures and high E-moduli. Lattice defects and porosity result in a decrease in thermal conductivity. Some ceramic materials have the same thermal conductivity value as metals. Nevertheless, aluminium nitride AlN and silicon carbide SiC are examples of electrical insulators and consequently suitable for electrical switches when heat dissipation is important.

Thermal conductivity is measured by placing a metal wire in the material. When a current flows through that wire, energy waves will move through the material. At certain distances from the wire thermometers are placed in the material.

8. SPECIFIC AREA

The specific area is measured in m^2/gramme. Its value can vary from 1–5 m^2/g in the case of, for example, coarse kaolin to about 100 m^2/g for certain plastic clay types. The measurement for example takes place by adsorption of gases like nitrogen. The adsorbed amount is measured as a function of the pressure. At a certain N_2 pressure nitrogen molecules at the surface of the solid particles are adsorbed and pressed into the pores. Consequently, this method is also suitable for measuring porosity and pore size distribution.

A second method is the adsorption of a dye from a solution, e.g. methylene blue, fuchsine, methyl violet and malachite green. A certain grain fraction of a dried clay is stirred for a certain time in a dye solution with a specific concentration. The reduction of the solution's colour intensity is a measure for the adsorbed amount of dye and it is measured spectrophotometrically. The dye molecules are much larger than nitrogen molecules and so they are only adsorbed and will not enter the pores.

9. HARDNESS

Usually, hardness is only measured on baked objects. This subject was already discussed in chapter 9 (see also no. 19 of this chapter). However, very little has been published about the hardness measurement of ceramic raw materials, i.e. powders. Such powders consist of miniature crystals and are sometimes used as abrasives. Obviously this use requires an extreme hardness.

Experiment: You can carry out a comparative hardness test on powders as described below. For this a porcelain jar is partially filled with spheres of a high hardness and the powder and then it is placed on two cylindrical rollers. By comparing the grain size distribution before and after the grinding process you can determine whether or not grinding took place and also to which extent. If not, then the powder is harder than the grinding spheres. If so, the degree of grinding is a measure for the hardness.

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10. DENSITY

A powder’s density is measured with a so-called pycnometer and the density of objects was described in chapter 9.

11. CRYSTAL STRUCTURE AND MINERALOGY

The crystal structure and mineralogy (nature and mass% of the minerals) are measured with the help of X-ray diffraction, a technique too complicated to be discussed within the framework of this book.

12. POLARISATION MICROSCOPY

I first came across this technique in mineralogy, a hobby which I took up long before there was question of incorporating ceramics into the curriculum of our students. This technique enables the mineralogist to determine the nature and the proportion of minerals present in a rock sample. A thin slice of rock is polished until light can pass through it. This is a very labour-intensive procedure. The slice is then placed under a microscope between two so-called polarisation filters. This is done is such a way that the sample can be rotated. The colours, the shapes of the crystal cross-sections and the angle at which the sample is place, all shed some light on the mineral composition.

I have worked out this technique. However, when I discovered that it was not used in ceramic applications, I refrained from incorporating it in this book. Yet I still think that this technique has educational value, both when applied on clay and on baked clay products.

13. RHEOLOGY

Rheology (the science dealing with the flow and deformation of matter) was already discussed in the chapters on colloid chemistry and clay. It is an important subject in clay casting.

14. PLASTICITY

Plastic clay is used in, for example, the manufacture of bricks and roof tiles. Each product requires a specific clay with a specific plasticity. In the chapter on clay and in the section on moulding (chapter 9, Ceramic in General) the subject was already discussed.

Determine the influence of the water content and humus (organic substances) content on the plasticity of clay. How can humus be made / obtained / imitated?

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15. SHRINKAGE

Drying and baking shrinkage are important phenomena in ceramics because they determine the dimensions of the dried and baked products and consequently the dimensions of the finished product. A dilatometer is used to measure shrinkage behaviour during heat treatment. By comparing the dimension before and after drying and baking you can calculate the drying and baking shrinkage as well as the total shrinkage. This is expressed in percentages.

A calculation example:

The drying shrinkage is 9% and the baking shrinkage is 6%. Calculate the total shrinkage.

Suppose the original length is L cm. 9% of L = 0,09L cm.

Length after drying = 0.91L cm. 6% of 0.91L cm = 0.0546L cm.

Length after baking = 0.8554L cm.

Total shrinkage = (L – 0.8554L)cm = 0.1446L cm = 14.46% of initial length.

16. POROSITY

Was discussed elaborately in chapter 9 (Ceramics in General).

17. FIRING COLOUR

The firing colour was discussed in the paragraph on coarse ceramics. Colours are measured quite often in the plastics industry, but I have not be able to find out if the method applied there is also applied in the ceramics industry. It is certain,however, that colours are measured visually in the brick industry, i.e. colour charts are used as reference

18. SURFACE ANALYTICAL METHODS

The coarseness of a surface and consequently the effect of surface treatment can be measured with a laser beam. In addition the surface is often investigated by means of various microscopic techniques. The nature of a surface can tell us something of the structure of the material. The information obtained depends on the treatment the area has undergone and the way in which the surface is examined. The researcher may want to determine how many phases there are present in the sample, how they are distributed throughout the sample or what the pores and the pores distribution are like. For these purposes many kinds of light and electron micros-copes are available.

The light microscrope can magnify up to 1,000 times and it has a resolution of 0.1 µ. This resolution is the minimum distance between two lines or points at which these lines or points can still be seen individually.

The electron microscope has a resolution of 10^{-3}–10^{-4} µ. A well-known example of an electron microscope is the TEM, the transmission electron microscope, which is used to study specimens a fraction of a micrometre or less in thickness, e.g. for depicting and recognizing clay minerals. Another type of electron microscope is used to depict surfaces and is often applied for ceramics. The surface of a slide is radiated with a beam of electrons. Some electrons are bounced back and due to the collisions of fast electrons secondary electrons are liberated from the surface. In this way you can obtain more information about the surface relief and the chemical composi-tion. The SEM, the scanning electron microscope radiates a surface with a controlled electron beam. In this way a certain part of the surface can be studied.

19. SURFACE HARDNESS

This determination should be carried out with care when dealing with porous materials in order to avoid executing the determination in or immediately above a pore. The surface hardness can be measured as:

scratch hardness which material can or cannot be scratched with another material of a known hardness. Mohs hardness scale applies here.

compression hardness a well-defined surface in forcefully pressed into the material to be researched. The depth of penetration is a measure for the hardness. Examples: Vickers hardness and Rockwell hardness.

wear resistance a) sand blasting method: loss of mass is a measure for strength; b) grinding methods: measure the loss of mass

In the case of floor tiles for instance any initial change in lustre and / or colour is first determined visually after which the loss of mass is measured.

20. ELASTIC PROPORTIES (INCL. YOUNG'S MODULUS)

How do materials behave when they are subjected to forces which act upon them? The resulting deformation can be: 1) reversible; as soon as the forces are removed, the deformation is completely undone. In this case there is question of an elastic deformation; 2) completely or partially irreversible; when the forces are removed, the

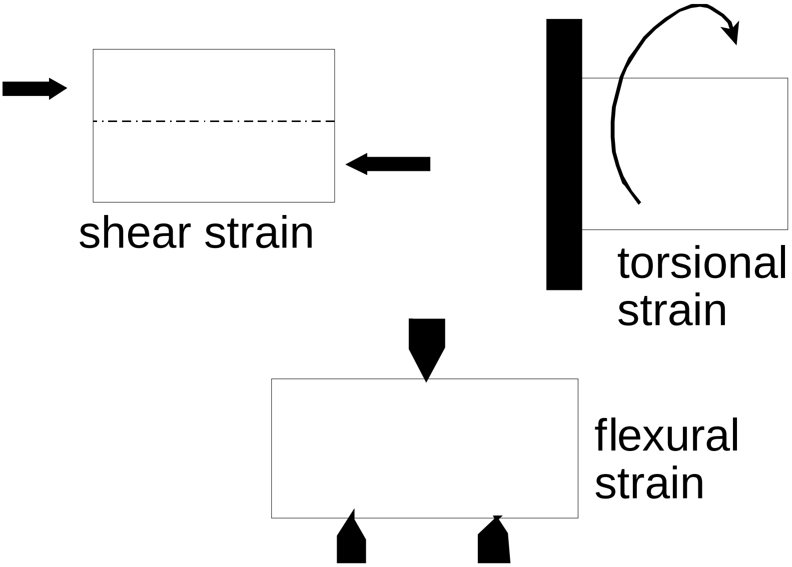

Fig. 13.6 Some ways of applying loads to ceramic test specimens.

deformations remain present and there is the question of plastic deformation. 3) The forces are so large that the cohesion within the material is lost; in that case we speak of fracture.

All sorts of factors affect the behaviour under stress: the kind of material used, the magnitude of the load, the temperature of the material and the speed with which the load is applied. In figure 13.6 some methods of applying loads are illustrated.

Most ceramic materials exhibit elastic deformations with slight elongations, followed by fracture. In chapter 9 we discussed E-modulus measurements on ceramic materials. This can e.g. be done by means of three or four point bending tests or by measuring the speed at which a sound wave passes through a material.

The general formula for the three point bending test is

$$\sigma = \frac{F \times L}{4 \times Y}$$

where L is the distance between the points on which the object rests; F is the applied force, Y is a factor which depends on the geometry of the object. In the case of a rod with width w and height h the following formula applies:

$$Y = \frac{w \times h^2}{6}$$

Consequently, the formula for sigma is:

$$\sigma = \frac{3 \times F \times L}{2 \times w \times h^2}$$

For a hollow tube with an outer diameter *D* and an inner diameter *d*, the following formulas apply:

$$Y = \frac{\left(D^4 - d^4\right) \times \pi}{32 \times D} \text{ and } \sigma = \frac{F \times L \times 8 \times D}{\left(D^4 - d^4\right) \times \pi}$$

\# Make clay rods with embedded, parallelly aligned flax fibres and compare their breaking strengths with those of fibre-less clay rods.

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21. RESISTANCE TO TEMPERATURE FLUCTUATIONS

In any material undergoing a temperature cycle, any changes caused by this can best be measured on its strength properties. Thermal treatment of a ceramic sample results in stress in the material due to a) temperature differences in the material, b) the fact that volume changes cannot take place evenly in the material as a result of certain external forces and c) different phases with different expansion coefficients. In pottery and porcelain the measurements take place as follows: heat to 100 °C and subsequently quench in cold water. Then each time increase the starting temperature by 10 °C and repeat this procedure until cracks appear in the material. Changes in properties are measured by means of the bending breaking strength and the *E* modulus as well as by measuring the loss of mass when the material is chipped.

22. NON-DESTRUCTIVE ANALYTICAL METHODS

In the case of non-destructive analytical methods the sintered object is subjected to an analysis which does not cause any damage to the sample. Until recently these techniques, like X-ray (diffraction) analysis, ultrasonic waves and CT scans, were only applied in the medical world, but now they are also used on ceramics. Sometimes even nuclear reactors are involved in these experiments.

X-rays are generated in a so-called X-ray tube. In this vacuum tube a cathode is heated and it will emit electrons. Due to the high voltage difference between the anode and cathode these electrons collide with the anode, at which point the kinetic energy of the electrons is converted into heat and X-rays. The latter are aimed at the object and pass through it, either completely or partially. We place a photosensitive plate under the object and this turns black when it is exposed to X-rays.

X–ray photograph of a hip joint, a rectangular piece of foam ceramics, a round glass reinforced with titanium fibers and a ring made of metal and ceramics (picture by J Bormans).

On the resulting photograph you can see an artificial hip joint made of titanium with a head made of dense, sintered aluminium oxide, a rectangular-shaped piece of Al_2O_3 foam ceramics made by ECN Petten, The Netherlands, a round glass disc reinforced with 10 volume percent of titanium fibres and a ceramic ring to which a metal ring has been attached. In this last object three rings can be distinguished: a thin ceramic inner ring, the metal outer ring and in between a thick ceramic ring.

In archaeological excavations pots with small necks are often founds whose interiors are difficult to measure. The CT scanning can be of assistance here. It appears that the 'slices' present a clear image of the structure of the pots. Numerous shades of grey can be seen on these slices and by linking each shade to a specific element scientists try to determine the composition of the clay.

Ultrasonic waves have frequencies which are beyond human hearing. These wave are able to penetrate matter to some extent and the rest is reflected. The *E* modulus and the density of the material both determine at which speed the waves move through the material. The intensity of the penetrated or reflected beam is measured. The method is for instance used to track defects/ flaws in the material and to measure the *E* modulus.

Some time ago the Technical University of München, Germany organized a project which was titled "Mit Neutronen zurück in die Vergangenheit" (Explore the past with the help of neutrons). Celtic ceramics and glass from Central Europe were researched by using neutron activation analyses to determine the content of trace elements in clay. In this way the origin of the clay and consequently of the ceramic objects could be determined. In addition the researchers were able to obtain more information on the colouring techniques for glass. For this a flow of neutrons originating from a reactor was aimed at a sample. This makes the atomic nuclei in the sample radio-active, causing them to transmit characteristic gamma radiations. The resulting spectra can be used to determine the elements of which the sample is built up both qualitatively and quantitatively.

14

Ceramic Composites

14.1 DEFINITION AND INTRODUCTION

A composite is a material kind built up of at least two different materials which has a set of properties which cannot be matched by the individual materials. These properties can be adjusted within a certain range. According to some reference books a composite is always artificial. However, according to the writer of this book, wood and bone should for instance also be rated among composites. In chapter 12.4 we shall use the structure of bone to justify this interpretation.

A composite mostly consists of two components, one of which in present in excess as far as mass and volume are concerned. This is called the matrix. The other component acts as the reinforcing factor. In figure 14.1 some examples illustrate how the properties of different materials can be merged to form one new product.

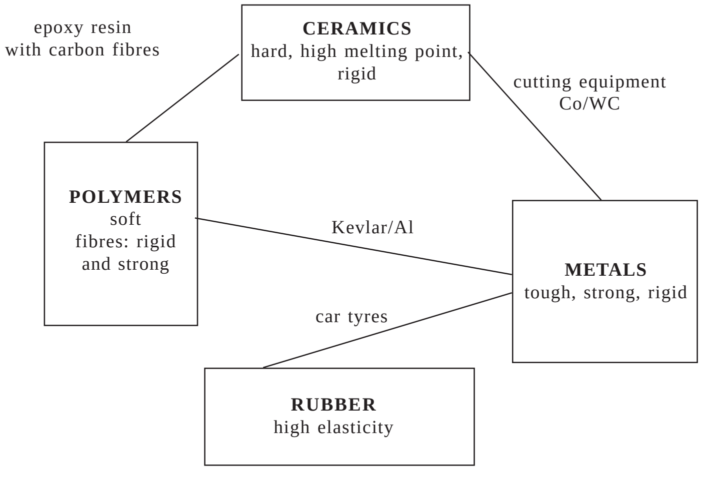
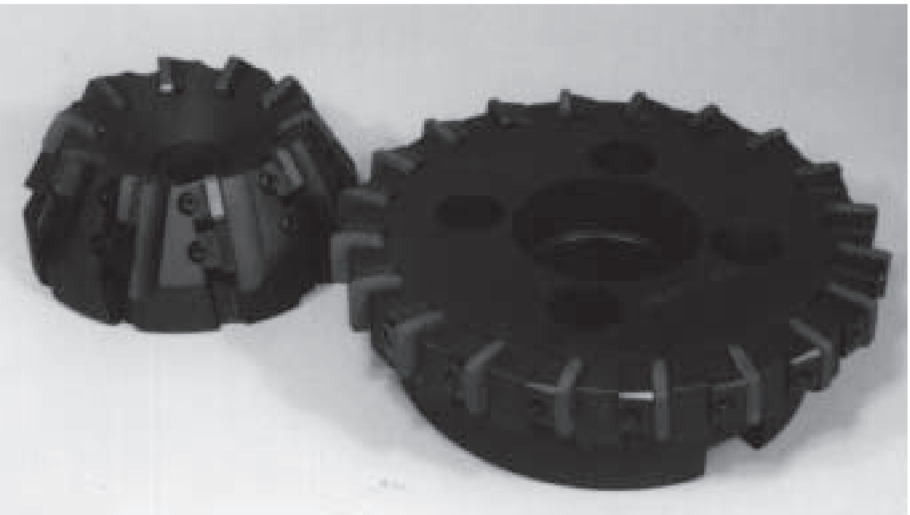


Fig. 14.1 Some examples of how materials can be combined to form composites.



Milling cutters for use with ceramic inserts (Courtesy of: Greenleaf Corporation, USA).

Fibres are added to a plastic or metal matrix, mainly to increase the strength of the material. In case of a ceramic matrix this is done to increase the fracture toughness of the brittle matrix.

A literature search will not result in an unequivocal definition of ceramic matrix composites or CMCs. The following definition which was presented at a symposium in Eindhoven, The Netherlands on 11 October 1994 gives us something to go by:

A ceramic matrix composite or CMC is composed of two or more solids, the matrix of which consists of a ceramic material or carbon. The crystalline, ceramic matrix is moulded and/or densified at a temperature of at least 1000 K. To the matrix one or more solid inorganic substances are added, e.g. in the form of particles or fibres in order to alter the (thermo) mechanical properties of the pure matrix. In the composite's microstructure these additives can still be distinguished by their chemicalcomposition or geometry even after they have undergone a temperature treatment of at least 1000 K.

Composites are both ancient and state-of-the-art. According to Ashby's graph (chapter 2) composites such as wood and bone were already used in around 10,000 B.C. In our present-day society we are especially familiar with plastic composites in e.g. surf boards and tennis rackets, with fibre glass used for boats and cars and with the long carbon fibres in a polymer matrix which are applied in aircraft construction. Electric contacts in switches must have a good electrical conductivity and should be resistant to wear. These properties can be realised by using a tungsten (resistant to wear) - silver (high conductivity) composite. In order to manufacture this composite the tungsten powder is compressed into a porous mould and its pores are filled with liquid silver in a vacuum. Reinforced concrete is a ceramic composite. And who is not familiar with plywood? In the space shuttle's nose and wing tips a carbon reinforced with carbon fibres and then coated with silicon carbide to prevent oxidation, is applied.

These last few decade the development of composites has boomed enormously because our technical progress and the demand for a constantly improving standard of living have created the need for new materials and because our increasing environmental awareness has led to a lot of criticism on the mining of oil-based fuels and on certain industrial activities. Composites satisfy our requirements for a number of reasons:

large components and complicated shapes can easily be made
flaws can easily be corrected
the production of small series is environmentally sound
interesting properties: good electrical insulator, extremely low heat conduction coefficient,
large heat capacity, good resistance to chemicals.

14.2 CERAMIC, SYNTHETIC COMPOSITES

In order to make brittle ceramic materials tougher, several techniques can be applied. All of these have in common that they reinforce the ceramic matrix by means of particles, fibres, irregular masses or by introducing a layered structure. All these possibilities can be seen in figure 14.2.

Let us have a closer look at the fibres and particles.

Ceramic fibres

Metal, glass and many polymer fibres are made by means of tensile processes, such as the one represented in figure 14.3.

Boron, carbon and ceramic materials are too brittle for this procedure and also too reactive and consequently their fibres must be produced differently.

Boron fibres are made by means of a CVD process, a Chemical Vapour Deposition process. Boron trichloride is heated in an oven and as a result it breaks down:

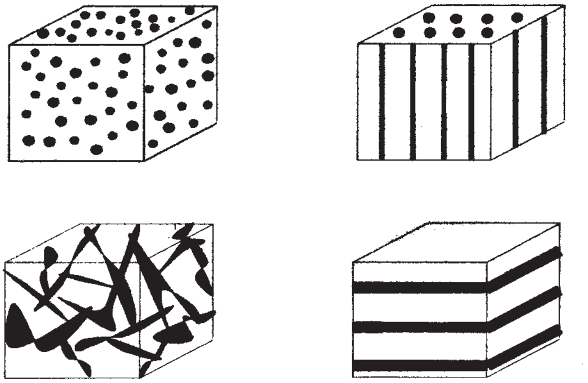


Fig. 14.2 Some examples of ceramic matrixes (cubes) which have been reinforced by particles, fibres, irregular masses or by means of a layered structure.

$$2\ BCl_3 \xrightarrow{T} 2\,B + 3\,Cl_2$$

The boron is deposited on a tungsten wire, the substate. In a similar way SiC vapour is deposited on C fibres.

Carbon fibres are made by carbonizing or pyrolyzing polymer fibres. I came across the chemical aspects of this process in the book “Principles of Polymerization” by G. Odian in which the author describes how these fibres are made of polyacrylonitrile (PAN) a polymer which is represented in figure 14.4 (see also chapter 3).

During an initial heat treatment this PAN chain is converted into a chain of 6 rings as can be seen in figure 14.5.

Then the material is heated to a temperature of 700 ºC and in this process each ring obtains a second double bond and hydrogen (H_2) is released (figure 14.6).

The heating process is continued at 400–600 ºC and then at 600-1300 ºC and the chains as shown in figure 14.6 ‘grow together’ to form the ultimate fibre with a graphite structure and N atoms on the

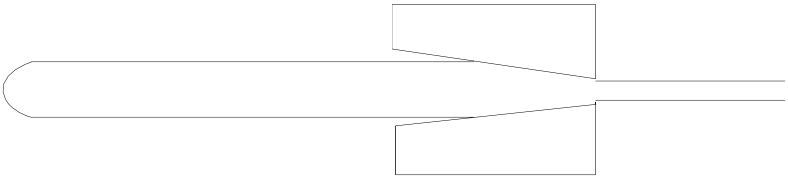


Fig. 14.3 Producing a polymer fibre by means of a tensile process.

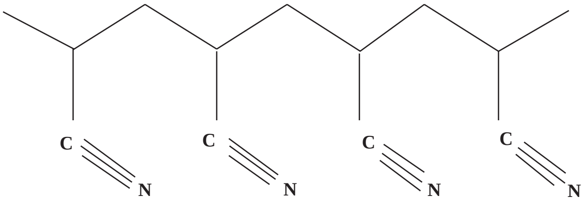


Fig. 14.4 A polyacrylonitrile chain.

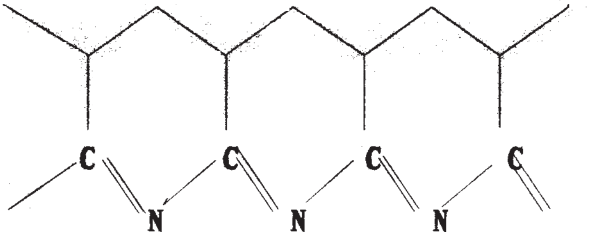


Fig. 14.5 PAN chain after initial heating.

outside (figure 14.7). The thickness of the fibre, and thus the number of PAN chains, can be varied.

Ceramic particles

The best known example of a ceramic particle is zirconium oxide (or zirconium(IV) oxide) ZrO_2. This compound exists in three crystalline forms which are stable at the following temperatures: monoclinic < 1170 °C, tetragonal 1170–2350 °C and cubic 2350–2700 °C. During the change from tetragonal to monoclinic, i.e. when the material is cooled, a volume increase occurs. According to various literature sources the size of this increase varies from appr. 3 % to appr. 9 %. Consequently it is impossible to make articles of pure ZrO_2, but by adding about 10 mole% of one of the oxides CaO, MgO or Y_2O_3 you can stabilize the cubic zirconium and then it can exist at room temperature. This stabilized zirconium can be used to manufacture products.

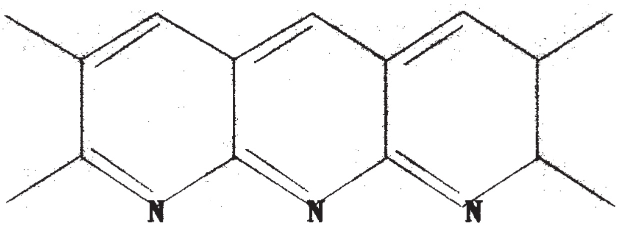


Fig. 14.6 PAN chain after heating to 700 °C.

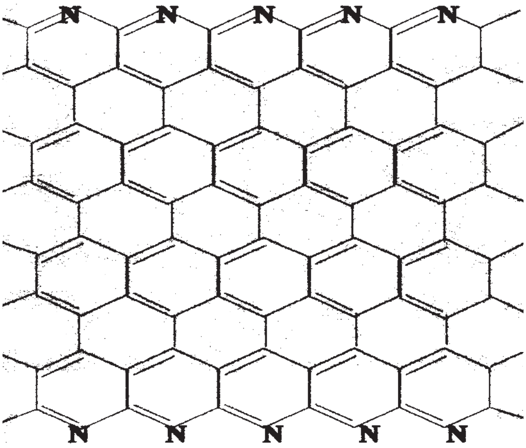


Fig. 14.7 Structure of a carbon fibre.

Synthesis of the composite

There are many methods to manufacture a CMC. Only a small selection is discussed in this section. Let us first have a look at the production process of a SiC matrix reinforced with SiC fibres. First a model is made of fibres, the so-called preform, then CVI (Chemical Vapour Infiltration) is applied to produce a coating on the fibres in order to ensure a better attachment to the matrix. The next step is resin infiltration. After pyrolysis (heating to a high temperature without oxygen) a network matrix of the porous carbon arises. Silicon which has first been melted in an oven is then introduced into this network; it reacts with the carbon to form the following matrix:

$$Si_{(l)} + C \rightarrow SiC \text{ (matrix)}$$

Other methods make use of CVD (Chemical Vapour Deposition), the precipitation or deposition of vapours on a surface. In this process reactive gases are passed along a heated substrate. The gases react on the hot surface and a solid is formed which is a deposit of a ceramic layer. In the following examples the formula of the deposited ceramic layer is printed in bold letters.

$$CH_3SiCl_{3(g)} \rightarrow SiC_{(s)} + 3\ HCl_{(g)}$$

$$CH_{4(g)} + 4\ BCl_{3(g)} + 4\ H_{2(g)} \rightarrow \underset{\text{boron carbide}}{B_4C} + 12\ HCl_{(g)}$$

$$TiCl_4 + 2\ BCl_{3(g)} + 5\ H_{2(g)} \rightarrow \underset{\text{titanium boride}}{Ti\ B_{2(s)}} + 10\ HCl_{(g)}$$

Properties of ceramic composites

We have already determined that ceramic objects are brittle. Ceramics can be made less brittle and consequently tougher by incorporating particles or fibres. This can for instance be crystals like zirconium oxide, which assume another crystal structure under the influence of a stress concentration. When a force is applied to a ceramic object a stress concentration is formed at the tip of the crack, i.e. the supplied energy concentrates in that particular spot. However, incorporated ZrO_2 crystals transform under the influence of the supplied energy to form crystals with a lower density. As a result, these crystals grow and the crack is prevented from expanding. The chance that a crack will occur is thus reduced (figure 14.8).

What exactly takes place here is not yet completely clear. For the transformation of the zirconium crystal in their free state a temperature of appr. 1200 °Cis needed. It will be clear that this temperature will not be reached in the situation of figure 14.8. Apparently we are not only dealing with a transfer of energy here. To end this item, one more technical term: ZTA (Zirconia Toughened Alumina), which is aluminium oxide which has been made tougher by adding zirconium.

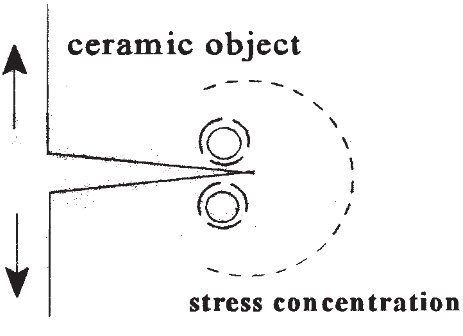


Fig. 14.8 Preventing the expansion of a crack by incorporating zirconium particles.

Simple mixing rules apply for some properties of composites, this means that those properties of composites can simply be calculated from the mixing ratio and the properties of both matrix and reinforcing component. The density of a composite is calculated as follows:

$$\rho_c = \varphi_m \times \rho_m + \varphi_{rc} \times \rho_{rc}$$

where ρ is the density; φ is the volume fraction (chapter 3) [c : composite, m : matrix, rc : reinforcing component].

A calculation example:

A composite consists for 80% (v/v) of a matrix with $\rho_m = 2.77$ g/cm^3 and for 20% (v/v) of SiC fibres with $\rho_{rc} = 3{\times}10$ g/cm^3 . When we assume that the composite does not possess any pores, then its density is:

$$\rho_c = 0.80 \times 2.77 + 0.20 \times 3.10 = 2.84 \text{ g/cm}^3$$

Some similar simple relations also hold for fibre-reinforced composites. When the fibres (f) are continuously and parallelly aligned, the following applies to the heat conductivity (hc):

$$hc_c = \varphi_m \times hc_m + \varphi_f \times hc_f$$

and for the *E* modulus in the direction of the fibres:

$$E_c = \varphi_m \times E_m + \varphi_f \times E_f$$

When a load is perpendicular to the direction of fibres, the components of the composite react independently:

$$\frac{1}{E_c} = \frac{\varphi_m}{E_m} + \frac{\varphi_f}{E_f}$$

For those readers who are not only interested in ceramics but also in formulas and mathematics the last but one equation is explained in the box below.

Suppose a tensile force F is applied in the direction of the fibres to a tensile test specimen made of a fibre-reinforced composite and the following formula applies $F = \sigma \times A$.

Then:

$$F_c = F_m + F_f$$

$$\sigma_c \times A_c = \sigma_m \times A_m + \sigma_f \times A_f$$

$$\sigma_c = \sigma_m \times (A_m / A_c) + \sigma_f \times (A_f / A_c)$$

in the case of a constant fibre diameter the following applies:

$$\varphi_m = \frac{A_m}{A_c}, \ \varphi_f = \frac{A_f}{A_c}$$

$$\sigma_c = \sigma_m \times \varphi_m + \sigma_f \times \varphi_f$$

$$\sigma = \varepsilon \times E$$

$$\varepsilon_c \times E_c = \varepsilon_m \times E_m \times \varphi_m + \varepsilon_f \times E_f \times \varphi_f$$

when the matrix is attached to the fibre the elongation will be the same for both of them:

$$\varepsilon_c = \varepsilon_m = \varepsilon_f$$

$$E_c = E_m \times \varphi_m + E_f \times \varphi_f$$

The properties of fibre-reinforced composites are for example determined by:a) length, diameter, orientation, volume fraction and properties of the fibres, b) the properties of the matrix and c) the nature of the bond between fibre and matrix. The ratio between length and diameter is an important fibre property. A small diameter means that the area is also small and consequently there is less chance of defects occurring in that area and so less chance of the fibre breaking.

Fibre ends take over less strain from the matrix than the rest of the fibre. In a certain fibre volume of fibres there are fewer ends when the fibres are long than when they are short and this will have an advantageous effect on the strength of het composite.

When the fibre direction is identical to the direction of the applied tensile force, the fibre has a so-called 0° orientation and the tensile strength is at its maximum. By altering the angle from 0° to 90° you can reduce the tensile strength from maximum to minimum.

When a composite is subjected to external forces, the energy of the matrix is only transferred to the fibres when there is question of a proper attachment. For that reason fibres are some-times provided with a layer of another material. An example: boron fibres in an aluminium matrix are provided with a silicon carbide coating and as a result the fibres are called borsic fibres. The thermal expansion coefficient of a fibre and its matrix must correspond. Figure 14.9 is a representation of what takes place when a crack in a fibre-reinforced matrix grows.

As you can see in the above figure, some fibres are somewhat pulled out of the matrix when a crack grows; this occurs under the influence of prevailing forces. This is called the fibre pull-out effect.

Finally a graph in which the tensile stress is plotted against the relative change in length of a so-called monolithic ceramic material (i.e. it only consists of matrix) and a fibre-reinforced ceramic material.

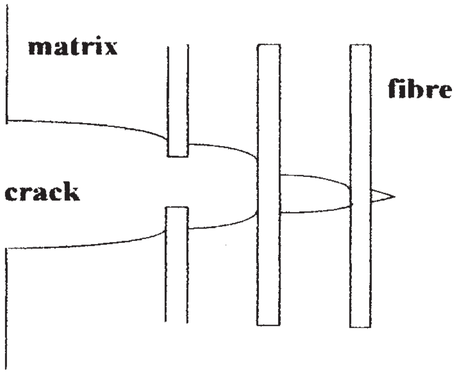


Fig. 14.9 Crack formation in a fibre-reinforced matrix.

A professional example

By making use of the Internet I have searched all over the world for photographs of ceramic composite structures. In the end I received some from Mr K. Yoshida of the Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Japan. These are photographs

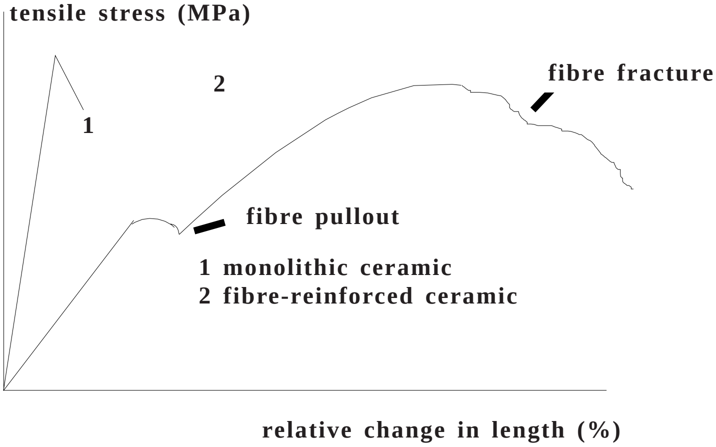


Fig. 14.10 Tensile stress as a function of the relative change in length of a non-reinforced (monolithic) and of a reinforced ceramic material.

of silicon carbide composites after breaking. Silicon carbide (SiC) is one of the main ceramic materials used as high temperature structural ceramics. It is characterized by good mechanical properties at high temperatures, a high thermal conductivity and a high resistance to corrosion and wear. In order to be applied in nuclear reactors it also has to be resistant to high energy neutron radiation. However, monolithic SiC is brittle and consequently requires re-inforcement. This is done by adding fibres and the composite is then called SiC / SiC_f.

The composite can be synthesized by means of a) CVI and b) hot compression. The advantage of the first method is that it can be done at low temperatures and so the fibre will not be affected. The reinforcing phase is a two-dimensional (2D) tissue of Hi-Nicalon fibres with right angles (90^o) between the fibres. Hi-Nicalon is the trade name of the SiC fibre made by Nippon Carbon Co. Ltd., Japan. These fibres have been provided with a C-coating. The composite is referred to as a CVI–SiC / SiC_f composite. The interface between the fibre and the matrix plays an important part here. When the interfacial bonding is too strong, the breaking energy in the matrix will continue in the fibre without exhibiting any fibre pull-out. The result is that the composite breaks like monolithic ceramics do, i.e. by means of a brittle break. In case of correct bonding and temperatures up to 1500 ^{o}C a non-brittle fracture with accompanying fibre pull-out occurs. At temperatures $\geq$ 1600 ^{o}C the break is brittle due to decomposition of the fibre.

Method b, the so-called hot pressing method is suitable for making dense composites. A 2D woven Hi-Nicolon tissue with or without a boron nitride coating (BN) is used as reinforcement. All of this is illustrated by the following photographs.

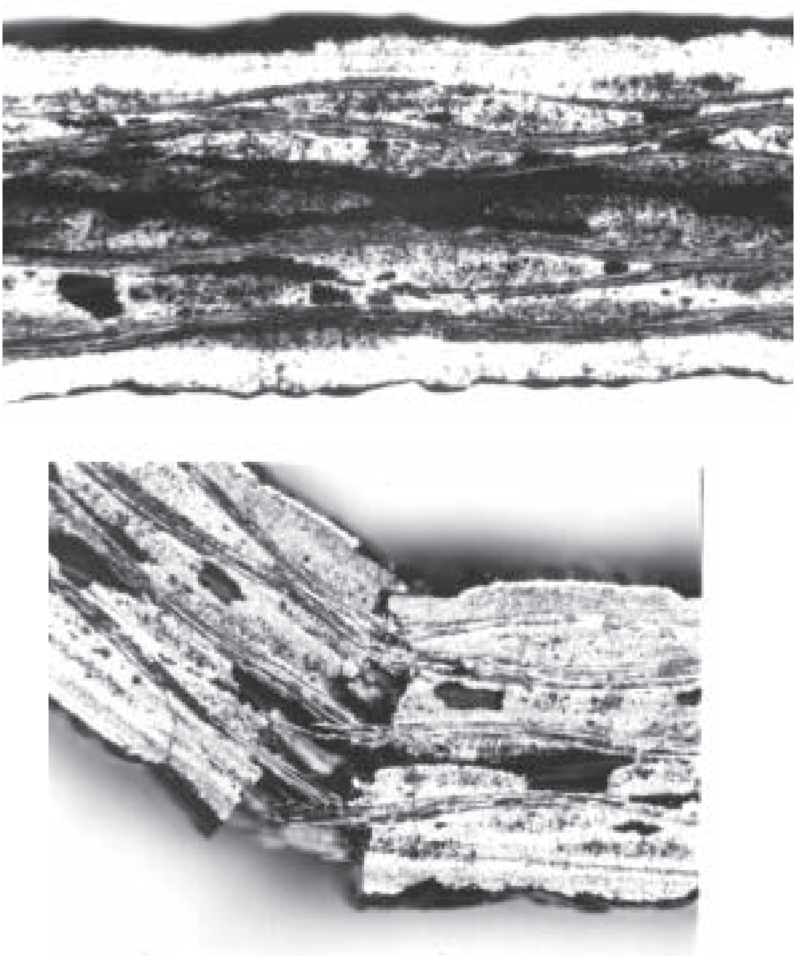
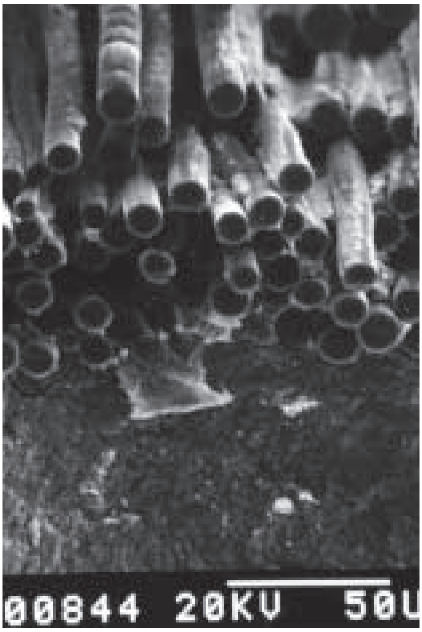
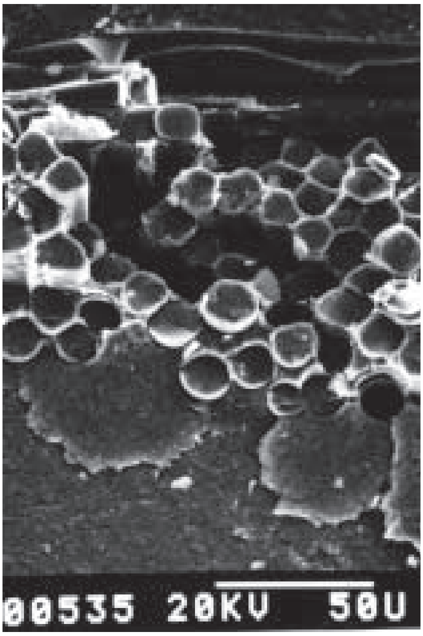


Photo **14.1 / 14.2** Optical micro-photograph of a SiC/SiC$_f$ composite, made by means of CVI before and after a three point bending test (source: Ube Industries Co Ltd Japan).

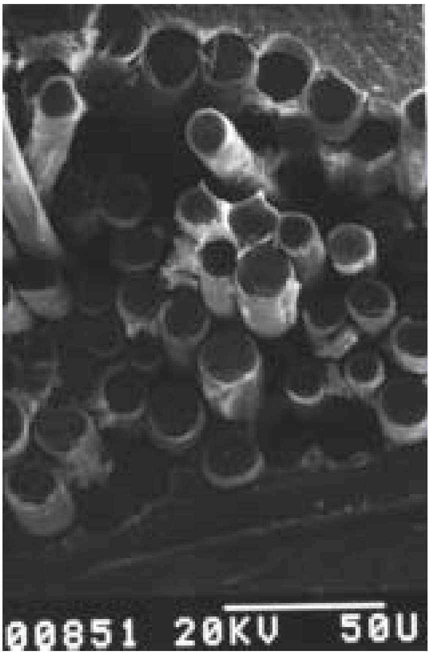
The photographs 14.3 and 14.5 clearly show the fibre pull-out, both in coated and non-coated specimens. In photograph 14.4 little pull-out can be seen because the temperature is high.



14.3



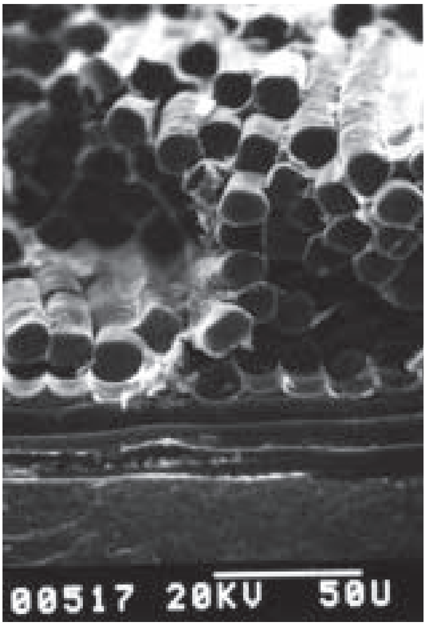
14.4



14.5

Source: Nippon Carbon Co Ltd Japan

14.3 SEM photograph of the fracture surface of a SiC/SiC_f composite, hot-pressed during 1 hour at 1650 °C, non-coated Hi-Nicalon.
14.4 As in 13.3, but at 1750 °C, not coated.
14.5. As in 13.3, but at 1750 °C, BN-coated.



14.7

14.8

14.6 As in 14.3, but during two hours at 1750 °C, not coated.
14.7 SEM micrograph of BN-coated Hi-Nicalon fiber for use as a reinforcement of a SiC/SiC-composite. (Source: Nippon Carbon Co Ltd Japan).

An educational experiment: cement rods with flax fibres

The purpose of this educational experiment, which was developed in the materials science laboratory of my school, is to instruct and illustrate. Preferably simply experiments should be done to support theoretical knowledge.

Within the framework of ceramic composites we embedded flax fibres in cement rods and then investigated whether or not this substantially changes their breaking strength. In addition we tried to apply a SiO_2 coating onto the fibre in order to improve its attachment to the matrix since this largely consists of oxides too. The tensile strengths of both the coated and non-coated fibres were measured. Both the manufacture of the rods and the application of the fibres were done manually and it was impossible to select fibres with uniform diameters. Furthermore each fibres consists of many smaller fibres, which proved to be a factor beyond our control. All these experimental inadequacies affected our tensile strength and breaking strength measuring results: the differences between the maximum and minimum values amounted to as much as 60%. Obviously our results (average values) can only serve as indications.

Results:	Tensile strength of the fibre σ (average) =	612 MPa
	Tensile strength of the wrapped fibre	125 MPa
	Tensile strength of the fibre after treatment with water glass	1914 MPa

We were unable to explain the large difference in the tensile strengths of a ‘single’ fibre and a wrapped fibre, nor the high tensile strength of the fibres treated with water glass. The latter was contrary to our expectations that the concentrated alkali in the water glass would affect the fibre structure.

The cement rods were subjected to a three point bending test. The breaking strength and the E modulus were calculated using the following formulas:

breaking strength $\sigma = \frac{3\times F\times d}{2\times w\times h^2}\ \mathrm{N\ m^{-2}}$ (Pa); $E = \frac{F\times d^3}{4\times w\times h^3\times Y_c}\ \mathrm{N\ m^{-2}}$

where F is the maximum applied force w, h is the width, height of rod, d is the distance between supports, Y_c is the deflection of the object at $F_{\max}$ ($F_{\max}$ is the maximum applied force) .

Results:

Cement rods σ (average) = 3.04 MPa, E (average) =		316 MPa
Cement rods with transverse fibres	3.14	234
Cement rods with diagonal fibres	4.36	208
Cement rods with longitudinal fibres	11.8	977

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