Lectures on Materials Science for Architectural Conservation

Giorgio Torraca

The Getty Conservation Institute

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The Getty Conservation Institute works internationally to advance conservation practice in the visual arts—broadly interpreted to include objects, collections, architecture, and sites. The GCI serves the conservation community through scientific research, education and training, model field projects, and the dissemination of the results of both its own work and the work of others in the field. In all its endeavors, the GCI focuses on the creation and delivery of knowledge that will benefit the professionals and organizations responsible for the conservation of the world's cultural heritage.

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Foreword

"Everything happens at the atomic level," I used to tell my students. This means that if a bridge collapses, ultimately it is because a few atoms have let go of their bonds and started a small crack that continued to expand, resulting in disaster. If this paradox is true, an in-depth understanding of the mechanisms at work on a microscopic level is fundamental to the successful work of engineers and architects. The difficult part is bridging the gap between the microscopic and macroscopic levels from the atom to the building. Giorgio Torraca does this superbly.

For many years the Getty Conservation Institute has applied the expertise of scientists and conservators in bridging that same gap. The study of the mechanisms of salt crystallization and salt extraction in order to save thousands of square feet of mural paintings in the Mogao grottoes is a typical example. Other examples include the GCI's research into the influence of clay expansion with water and its effects on limestone in projects involving the conservation of churches and cloisters in Yorkshire and the great Maya pyramids at Copán. All of these conservation endeavors require the merging of knowledge from various branches of science.

Torraca's ability to synthesize concepts and knowledge from various fields and present them in plain, comprehensible fashion to the reader is remarkable. His previous books, *Porous Building Materials* and *Solubility and Solvents for Conservation Problems*, are the fundamental texts on which several generations of cultural heritage professionals have been educated. A characteristic that these books share with the present volume is the apparent unrefined quality of the figures and drawings. In an era of computer imaging, Torraca still draws his pictures by hand—a brilliant move that allows each illustration to convey the required concept with precision, clarity, and simplicity. Nothing is redundant.

Giorgio Torraca has been my mentor, colleague, and friend for more than forty years. During this time I have had the opportunity and good fortune to appreciate and benefit from his ability to tackle complex problems and immediately get to the core of them. This is what the reader will find in his *Lectures on Materials Science for Architectural Conservation*, which the GCI presents in the same spirit of bridging the fields of science and conservation. I am sure that architectural conservators, engineers, and conservation scientists not only will enjoy this work but will be enriched by the formative ideas presented within it.

Giacomo Chiari, Chief Scientist
The Getty Conservation Institute
March 2009

Preface

This text is based on notes and sketches I prepared for an undergraduate course titled "Chemistry of the Environment and of Cultural Property," which I taught at the "Valle Giulia" Faculty of Architecture, University of Rome "La Sapienza," from 2001 to 2004. The lecture notes were published in 2002 by the Scuola di Specializzazione in Restauro dei Monumenti, which kindly allowed the use of the material for an English version. The English text is not truly a translation because my intent was to find equivalent ways to express the concepts in a new language and not to translate the words; furthermore, several parts have been revised and some completely rewritten.

This work was produced with the support of the Getty Conservation Institute, and I am deeply grateful to Leslie Rainer for her accurate review of the text, pinpointing errors and suggesting improvements in the language, and to Giacomo Chiari for his enthusiastic support and suggestions (which would have increased the size of this text considerably had I the strength to carry out all of them).

In the Rome lectures, the chapters were organized according to the system used in the textbooks on materials science, starting with a summary of the scientific theory of the structure of materials, with some basic chemistry added as required by our field of interest. This order is maintained in the present version, but with some reservations on my part as, having taught technology to engineers and postgraduate architects for a long time, I know how allergic to chemistry they are; so, starting a book with a chapter that is essentially chemistry did not appear to be the best way to encourage a reader to advance further.

At some point I came to the conclusion that it would have been wise to relegate the chemistry to an appendix, but it was late in the project and I lacked the courage to do so mainly because it would have required renumbering all chapters and sections and correcting all cross-references (I use a lot of them), and most likely would have resulted in several errors.

As an alternative, I have a suggestion for the chemistry-wary reader: Start reading at part 2, using part 1 mainly for reference when encountering words or concepts with which one is not familiar. I have tried to support this method of reading by providing cross-references to relevant sections in part 1 whenever I thought that such a problem might arise.

In the Rome lectures, I tried to downplay the role of chemistry in the course by reducing its importance in the final exam; the students were told that the (oral) exam would start with a question on building materials and their properties, deterioration, and conservation (parts 2, 3, and 4, respectively), followed by a question on metals, corrosion, and conservation (part 5); then, for the last of the traditional three questions on Italian university exams, they would have to choose between structure of materials plus basic chemistry (part 1) and modern plastics (part 6), silicates, and silicones (part 7).

This system worked well because most students, encouraged by some success on the first two questions, managed to address the third without excessive damage. The fact that a vast majority chose structure and chemistry showed, however, that plastics was even more difficult for them, even if it is a more interesting topic to an architect.

In the present version, I attempted to reorganize parts 6 and 7 to improve readability, but still they are not as smooth and clear as they should be.

My problem in teaching technology is that I think the aim should be to provide ideas rather than information; although information is easily available in handbooks and on the Internet, what is missing for a student or a professional are the general concepts that allow him to organize the material in his mind so that he is able to pass an exam or use the information when evaluating problems on a drawing table or at a worksite.

In the case of modern plastics, the amount of information available is enormous, but it is not easy to extract from it guidelines that an architect or an engineer could use when evaluating their successes and their failures (e.g., simple models of molecular structures and relation between structure and properties). In the teaching of technology for architects and engineers, there is ample room for improvement, and not only in plastics.

The bibliography at the end of this text is meant in part to acknowledge the debt I owe to books and papers by several authors, and in part to suggest possible sources of ideas; this part of the project was made possible only by the efficient support of Marie-Christine Uginet, who brought in her intimate knowledge of the fine conservation library she grew at ICCROM over so many years.

Giorgio Torraca
April 2009

Part 1

Electronegativity, Chemical Bonds, Crystals, Molecules, and Chemical Reactions

1.1 Electronegativity

1.1.1 Orbitals

Atoms are composed of a **nucleus**, carrying a **positive charge**, surrounded by **electrons**, particles that are much lighter than the nucleus and carry a **negative charge**. An atom standing alone, which is a rather rare case, is electrically neutral, i.e., it carries no electrical charge. The charge of the nucleus is always a multiple of the charge of one electron, and the number of electrons is exactly what is needed to neutralize the charge of the nucleus.

Besides the electrical charge, each electron also possesses another property called **spin**, which may be roughly described as a rotation on its axis. Spin may have only two values, +½ or –½; as a very rough approximation we can say the electron may rotate one way or the opposite way.

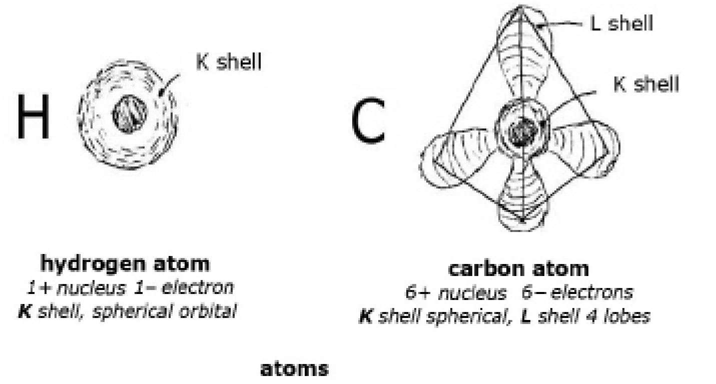
According to quantum theory, we can never know the exact position of an electron as it moves around the nucleus, so we cannot determine the actual path of its run (i.e., its "orbit"), but we can calculate the shape of a region of space near the nucleus where there is a high probability of finding it; this region near the nucleus is called an **orbital**.

Any orbital may hold up to two electrons, which must have opposite spin.

Different atoms have different numbers of positive charges in the nucleus and so also different numbers of electrons.

Around each nucleus the orbitals are organized in layers, **shells**, the outermost being the one that determines most of the chemical properties of each atom.

Figure 1.1



While shell K may accommodate a maximum of two electrons, shell L may fit up to eight electrons in its four orbitals. The next shell (M), with room for eighteen electrons, is normally considered as formed by two sub-shells, the first accommodating again eight electrons when filled up. The recurrence of the number eight as the number of electrons allowed in the second and third shell is the reason why an important rule of thumb was used to explain the properties of the most common atoms and was named the “rule of eight,” or “**rule of the octet.**”

The rule states that:

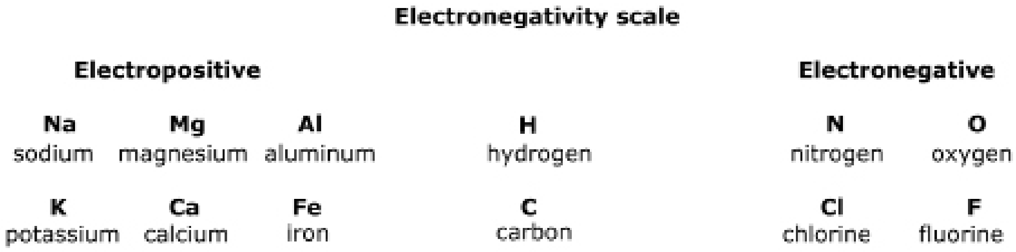
- as all atoms tend towards the most stable electronic structures, i.e., those in which the outermost shell is either full or empty;
- as all the most frequent atoms on the earth’s surface possess an outermost shell that may contain a maximum of eight electrons;
- **most atoms tend to acquire or to donate electrons in order to form an outermost shell containing either eight electrons or none.**

Among the most common atoms, the only exception is hydrogen, whose sole shell is K, which may accommodate two electrons only. Therefore hydrogen tends to acquire one electron or to give away the one it owns.

The tendency to acquire or to donate electrons is at the origin of all bonds between atoms. Atoms that have a complete outermost shell have no tendency to lose or acquire electrons and do not engage in bonds with other atoms (this is the case of the noble gases, e.g., helium).

1.1.2 The electronegativity scale

Atoms that have many electrons in their outermost shell tend to acquire more of them in order to fill it completely (**electronegative atoms**), while atoms that have only few electrons tend to donate them in order to create an empty shell (**electropositive atoms**, which are also called **metals**). In the electronegativity scale, these tendencies are given numerical values; as shown below in an oversimplified version, which is only qualitative:



Electronegativity scale

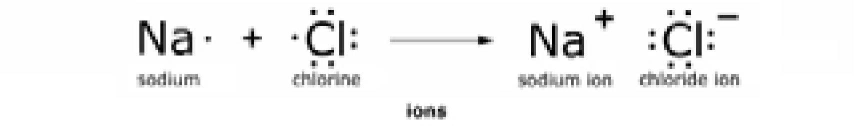
Electropositive				**Electronegative**	
Na sodium	**Mg** magnesium	**Al** aluminum	**H** hydrogen	**N** nitrogen	**O** oxygen
K potassium	**Ca** calcium	**Fe** iron	**C** carbon	**Cl** chlorine	**F** fluorine

1.2 Chemical Bonds

1.2.1 Ionic bond

One electronegative atom (e.g., chlorine) gets one electron from an electropositive atom (e.g., sodium); as a consequence, in both atoms the number of positive charges (nucleus) does not match the number of negative charges (electrons) anymore. Sodium remains, with a positive charge in excess (**sodium ion**) and chlorine with a negative charge (**chloride ion**).

Figure 1.2

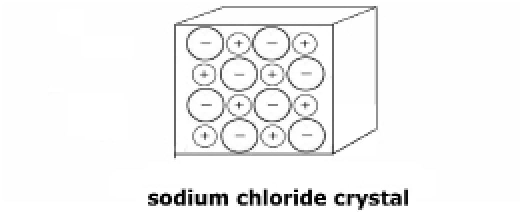


Atoms that carry an electrical charge at least equal to that of one electron are called **ions**.

As electrical charges of opposite sign attract each other, positive and negative ions get closer and form a bond. But, as in real life there is always a crowd of ions around when sodium and chlorine meet, even if the amount of matter involved is extremely small, it is not a couple of ions that is formed but rather a **regular, ordered structure of billions and billions of ions** in which ions with a charge of opposite sign stay as close as possible to each other, while ions of equal sign stay as far away as possible because they repel each other.

This regular structure is called a **crystal**; in the specific case of sodium and chlorine its shape is a cube: a crystal of sodium chloride, an **ionic crystal**.

Figure 1.3



The negative ions (**anions**, in scientific language) are larger than the positive ones (**cations**), because the electrons are less attracted by the nucleus and roam a little farther away.

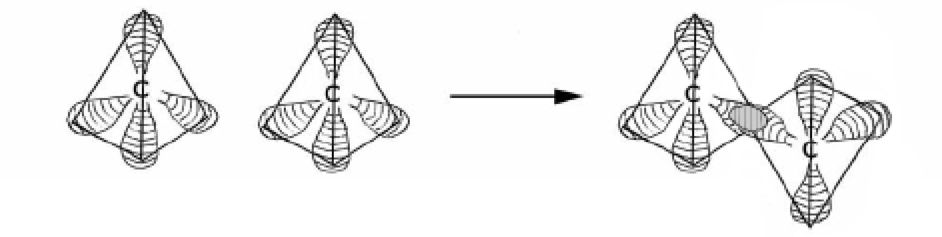
The force that keeps the ions together in the crystal is electrical attraction, a field force that works all around any electrical charge with no preferential direction. As a consequence the ionic bond is said to be a **non-directional bond**.

Inside an ionic crystal, however, some repulsive forces also work because electrical charges of equal sign repel each other; they act mainly between the larger negative ions that cover ("shield") the smaller positive ones.

1.2.2 Covalent bond

The covalent bond is formed between atoms that have approximately the **same electronegativity**. In this case an atom whose outer shell is missing some electrons may increase their number by **sharing electrons** with another atom which has the same tendency to attract them. This type of bond may be represented graphically as the **overlapping of two orbitals**, each containing one electron only, as shown in figure 1.4.

Figure 1.4



covalent bond between two carbon atoms

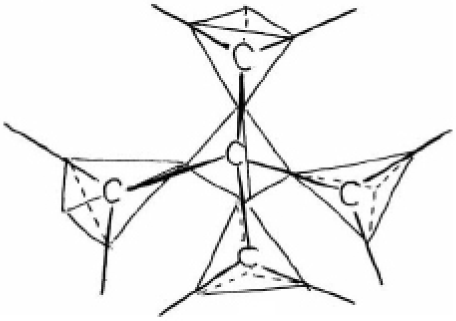
An orbital containing two electrons with opposite spin is thus formed between the two atoms. The four orbitals of shell L of the carbon atom are particularly suited to form this type of bond.

When carbon atoms are bonded, it is impossible to form couples of atoms because all four L-orbitals in each atom keep overlapping with those of other atoms so that, also in this case, an ordered structure, a **covalent crystal**, is formed.

In such a crystal, regularity is imposed not by electrical forces but by the fact that the bonds are **directional**, i.e., the connections are made only along definite directions, those imposed by the four L-orbitals that are directed towards the vertices of a tetrahedron whose center is occupied by the nucleus of the atom.

In nature this structure is found in the diamond crystal.

Figure 1.5



diamond crystal

Inside a covalent crystal no repulsive forces are active, so materials made of covalent crystals show great cohesive strength, and diamond is the hardest material we know.

In particular cases, carbon atoms may form a double covalent bond between them, but this will be discussed later (see section 1.4.5).

Covalent bonds are mainly formed by atoms found at the center of the electronegativity scale (the ones that have a half-full outermost electron shell) but also by electronegative atoms within their group; in the latter case, however, molecules are formed and not crystals (molecules are discussed in chapter 1.4).

Electropositive atoms form another type of bond, a metallic bond (see section 1.2.4), when they bind to each other.

1.2.3 Partial ionic character of covalent bonds

Covalent bonds may be formed also between atoms with a small difference in electronegativity. An example is offered by a bond between silicon (which stands at the center of the scale) and oxygen (one of the most electronegative elements).

Figure 1.6

polar covalent bond

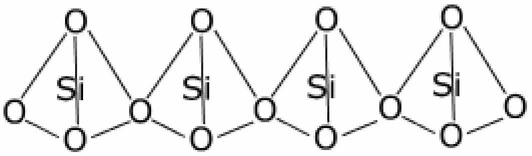
In the silicon-oxygen bond, the shared electrons tend to be closer to the more electronegative atom; as a consequence silicon remains with a slight excess of positive charge, while oxygen gets a small negative charge (these charges are much smaller than the unit charge held by one electron).

Such a couple of electric poles joined by a bond is called a **dipole**.

The outermost shell of the silicon atom (shell M) has four orbitals containing one electron each, just like the carbon atom; they are also oriented towards the vertices of a tetrahedron, a larger one though.

A silicon atom may form four bonds with four oxygen atoms, which in turn may each bind with another silicon atom; chains of silicon-oxygen tetrahedrons, and more complicated structures, are thus formed.

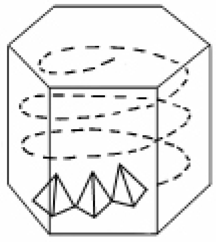
Figure 1.7



chain of silicon-oxygen tetrahedrons

The silicon-oxygen bond maintains the directional character, which is typical of the covalent bond, and crystals are formed. The chemical name of the silicon-oxygen compound is silicon dioxide (formula SiO_2) also known by its ancient name **silica**. In nature it is found in three different crystal forms, the most frequent being quartz, a hexagonal prism built up by a helix of chained tetrahedrons.

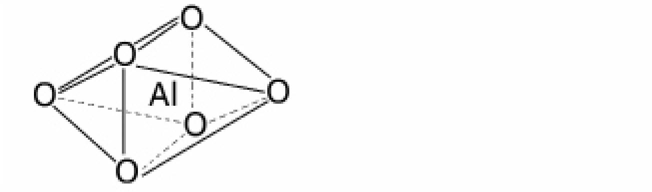
Figure 1.8



quartz

Another example of a structure formed by covalent bonds with ionic character is the octahedron formed by aluminum and oxygen. The chemical name is aluminum oxide (formula Al_2O_3), also known as **alumina**.

Figure 1.9



aluminum oxide octahedron

Si-O tetrahedrons and Al-O octahedrons constitute the backbone of a large number of minerals.

Covalent bonds with ionic character are strong, but not as strong as pure covalent bonds; the crystals they form are not as hard as diamond but harder than ionic crystals.

1.2.4 Metallic bond

The atoms of metals tend to donate the electrons of their outermost shell to electronegative atoms (acceptors), but if no acceptor is at hand they join and share the electrons that are not being accepted. The metallic bond is based on the **sharing of the electrons of the outermost shell** by a large number of atoms that join to form a **metallic crystal**.

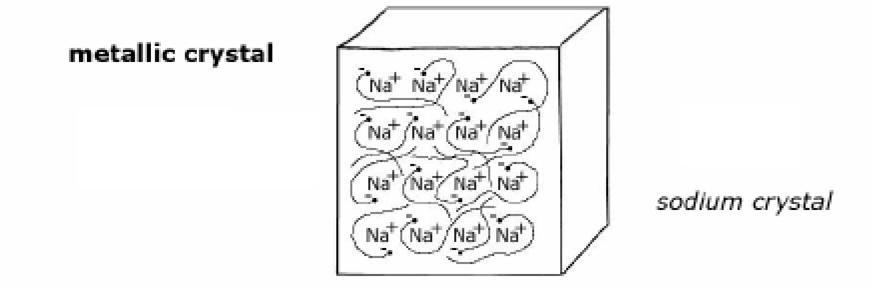
In metallic sodium, ten electrons fill the K and L shells and so are tightly bound to their atoms, while the single electron present in the M shell is shared among all atoms forming the crystal and is free to roam around together with the M-electrons provided by the other atoms.

In an oversimplified model of the sodium crystal, the atoms have lost one electron and are transformed into positive ions, which are kept in place by an **electronic cloud** (the term **electronic glue** is also used) that is free to move through the whole structure and even out of it in appropriate conditions.

The regularity of the atomic structure in a metal is due not to electrical attraction (as in the ionic crystal) or directional bonds (as in the covalent crystal) but rather to the natural tendency of atoms to arrange themselves in the **closest packed structure** that is possible, i.e., towards a maximum proximity of atoms in a solid.

In a typical piece of metal, the habit of the individual crystals is not visible because the simultaneous growth of many crystals when the material solidifies from a melt does not allow them to develop their geometric habit. The individual crystals may be observed under a microscope using special etching techniques on a polished cross section.

Figure 1.10



The metallic bond is **non-directional** because the attraction force due to the electron cloud is a field force evenly distributed inside the crystal.

This is an important characteristic because it allows metals to undergo plastic deformation (see section 1.3.2), a property that is not available in other types of crystals.

A more recent model of the metallic bond describes it as a covalent bond (because the atoms involved have equal or very close electronegativity), which is formed, however, between more atoms than the number of available electrons would allow (this happens because the close packing keeps many atoms very close to each other).

According to this view, there is a defect of electrons in the metallic bond with respect to the covalent one, and this helps to explain why metals are not as hard as diamond.

1.2.5 Non-crystalline solids, glasses

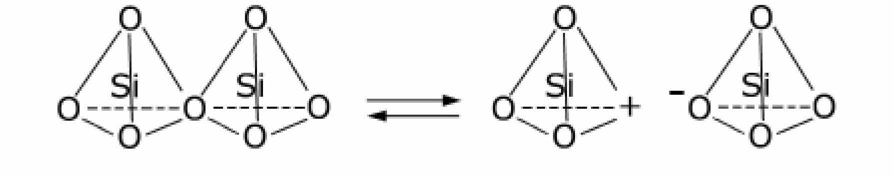
In many solid materials, atoms do not show a regular arrangement; the structure is not crystalline. These materials are called **amorphous**.

Many amorphous solids are composed of molecules (see chapter 1.4) and will be discussed later (see chapter 6.1 on polymers).

Glasses are amorphous solid materials produced by melting crystalline solids, which, upon cooling, do not succeed in re-forming an ordered structure. The most common glasses are produced by melting silica or silica containing mixtures.

The melting of the regular structures formed by the silicon-oxygen tetrahedrons, e.g., in a quartz crystal, is a process that occurs in steps through the progressive breaking of the connections between them, as shown in figure 1.11. The oxygen atom holds both electrons that formed the bond and gets a unit negative charge, while the silicon atom remains with one electron less, and gets a unit positive charge.

Figure 1.11



breaking of a silicon-oxygen chain

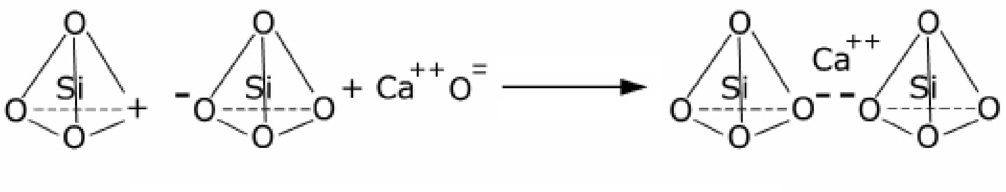
When the ruptures are few, as happens when the temperature is not very high, they tend to close again, because of the electrical attraction between the electrical charges on both sides of the break; but when a temperature near the melting point of the crystal is reached, the number of fractures is very high and the fragmented structure is deformed so that the rupture points cannot recombine easily. At the melting temperature (about 1700°C for silica) the network breaks simultaneously at several points, chains of tetrahedrons carrying positive and negative charges are formed, and the material becomes a paste first, then a very viscous liquid when the temperature is further increased.

If this liquid is rapidly cooled, the viscosity does not allow the chains of tetrahedrons to go back to the regular structure in such a short time. The solid that is formed has therefore a distorted, stressed, and potentially unstable internal structure in which the silicon-oxygen tetrahedrons are positioned in disorder and frequently distorted (**quartz glass**) but this strained condition can last for very long periods because of the enormous viscosity of the solid.

The addition of substances that stabilize the breaking points at temperatures well below the melting point of quartz makes it possible to achieve a complete disruption of the crystal and so its melting, at temperatures that can be reached even in a normal fireplace (600°C to 700°C). In antiquity the addition of lime and sodium carbonate to silica made the production of **soda-lime glass** possible at the beginning of the first millennium BCE.

The mechanism by which lime stabilizes the rupture points in the silicon-oxygen tetrahedron chains is shown in figure 1.12.

Figure 1.12



stabilization of a break in a silicon-oxygen chain

1.3 Properties of Materials as a Function of the Bond Type

1.3.1 Physical properties

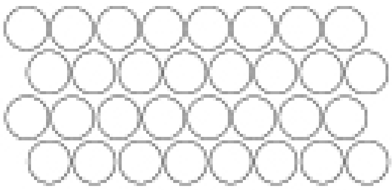
1.3.1.1 Melting point

The melting point of a crystal is a measure of the energy that is required to break most of the bonds that bind the atoms; therefore a strong bond results in a high melting point. In general, the melting points of covalent crystals and covalent crystals with partial ionic character are higher than those of metals, which in turn are frequently (but not always) higher than those of ionic crystals.

1.3.1.2 Density

The density of **metals** is frequently high because of the close packing of the atoms in the metallic bond (e.g., gold 19.3, iron 7.86). Aluminum (2.7) and titanium (4.5) are lighter, however.

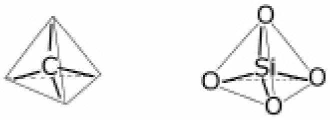
Figure 1.13



close packing in metals

Directional bonds such as **covalent**, or **covalent with partial ionic character**, must leave some unoccupied space around atoms, so the density of these crystals is low (e.g., diamond 3.0, quartz 2.6).

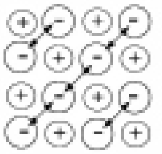
Figure 1.14



wider spaces around atoms in crystals formed by directional bonds

In **ionic** crystals, ions of equal sign are kept at some distance to reduce repulsion effects, so the density is low (e.g., sodium chloride 2.2).

Figure 1.15



repulsive forces in ionic crystals

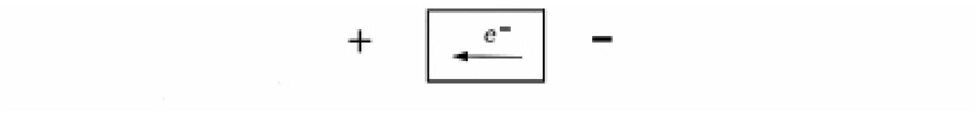
1.3.1.3 Electric conductivity

In **ionic crystals**, positive and negative ions cannot move out of their positions because of the electrical forces acting on them; electrical conductivity is not possible in normal environmental conditions. When the temperature is higher than 200°C, some smaller ions (e.g., sodium ions) may become mobile and a slight electric current may pass through the crystal. When an ionic crystal melts, both positive and negative ions are free to move and so all ionic materials become conductive in the molten state.

In **covalent crystals**, and in **covalent crystals with partial ionic character**, when their structure is completely regular there are no electrical charge carriers that are free to move in an electric field; they are perfect insulators. When a crystal has some defects in its lattice structure, e.g., different atoms introduced by chance or on purpose (doping), some electrons are set free in the crystal and a slight electrical conductivity may appear. These defective covalent materials are called **semiconductors**; some of them are very important in electronic technology.

Metals conduct electrical current because the electrons that create the metallic bond are mobile by definition and so they move towards the positive pole when an electrical potential is applied.

Figure 1.16



electrical conductivity of metals

1.3.1.4 *Thermal conductivity*

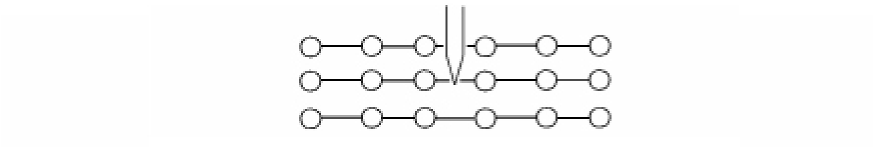
In **metals**, electrons are efficient carriers of thermal energy so thermal conductivity is high. In **ionic and covalent crystals**, heat is transmitted by the propagation along the crystal structure of the vibrations of the atoms around their equilibrium positions; this mechanism is not as efficient as the energy transport by electrons, as a consequence thermal conductivity is low.

1.3.2 Mechanical properties

1.3.2.1 *Hardness*

Hardness is frequently defined as the resistance of the surface of a material to the penetration of an extraneous body. As penetration requires the rupture of several bonds, a direct dependence of hardness upon bond strength is to be expected.

Figure 1.17



hardness of materials depends upon bond strength

Covalent crystals show maximum hardness, diamond being at the top of the hardness scale.

In the case of **metals**, penetration is achieved by plastic deformation (see section 1.3.2.4) so hardness is lower than in covalent materials, but it may be increased by mechanical (see section 5.1.2) and thermal (see section 5.1.3) treatments.

Ionic crystals frequently show low hardness, but it must be noted that the strength of the ionic bond is higher when it is formed between ions that carry a double electrical charge, and rather hard materials may be formed (e.g., white marble).

1.3.2.2 *Elastic deformation*

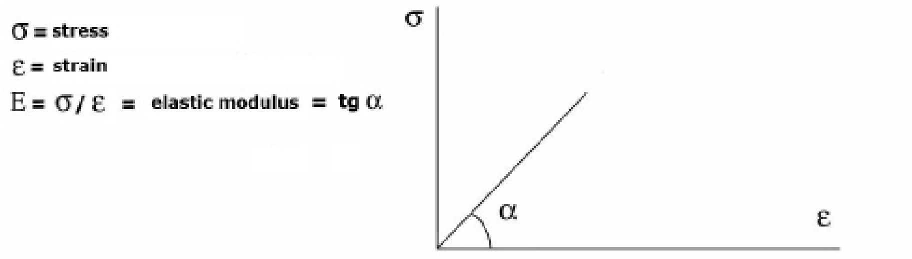
A material undergoing the action of a force that tends to modify its shape undergoes a deformation (**strain**) that is **proportional to** the force applied across its resisting cross section (**stress**) if the latter is not exceedingly great.

If the stress is not excessive, the deformation is reversible, i.e., the material reverts to its initial shape when the acting force is removed. A reversible deformation is called **elastic**.

The ratio between stress and strain (strain being defined as the ratio between the change in dimension to the initial dimension of the material) is called **modulus** (the complete name being “elastic modulus”) and depends directly upon the strength of the bonds inside the material that oppose the change of its shape.

The modulus is very large for covalent materials and progressively smaller for metals, covalent crystals with partial ionic character, and ionic crystals (diamond > steel > quartz > marble > salt).

Figure 1.18



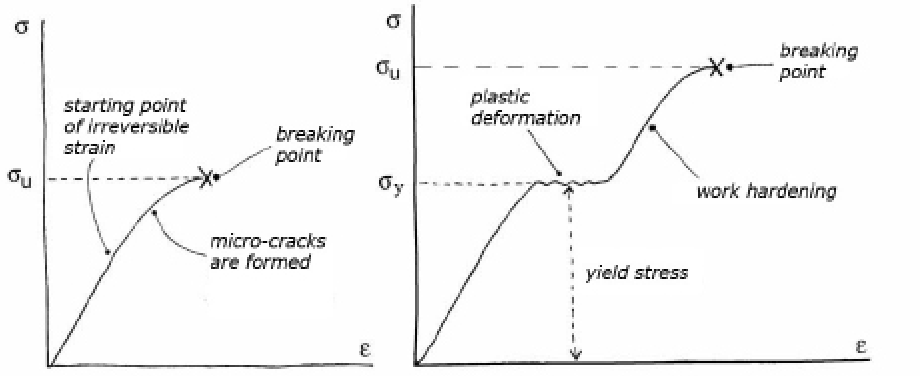
elastic deformation under a tensile stress

In the graphic representation of a test in which stress and strain are measured (as in figure 1.18), modulus is represented by the slope of the straight line, i.e., the tangent of angle α. Ideally it would be the stress required to cause a 100% elongation (i.e., a strain equal to 1) in a tensile strength test (most materials actually break before 10% strain is reached).

1.3.2.3 Irreversible deformation: Brittle and plastic materials

When stress overcomes the strength of the internal bonds of the materials, deformations become irreversible. In this phase, however, the behavior of metals (defined as **plastic**) is completely different from that of both ionic and covalent materials (defined as **brittle**).

Figure 1.19



brittle material **plastic material**

In **brittle materials**, a change of slope in the stress/strain diagram appears when the stress is still far from the magnitude that causes the rupture of the material (it may be 50% or even less); deformation is in excess with respect to what proportionality to stress would entail. The excess of deformation is not recovered when the stress is removed; it is irreversible.

Excess deformation is due to microscopic fractures that are formed inside crystals (cleavage) or between crystals, at points where stress is locally higher than the average value that is measured during a test.

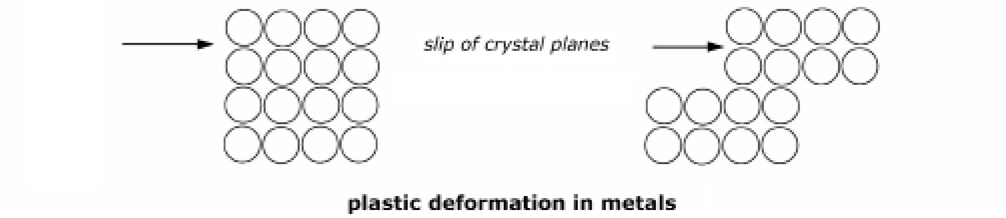
After a more or less extended phase of irreversible deformation, a brittle material breaks under stress values that are remarkably low under tension and much higher under compression (further discussion is found in section 3.1.1 dealing with the deterioration of brittle building materials).

In the case of **metals**, a dramatic change occurs when the **yield point** is reached: the material undergoes a rapid deformation while the stress is not increasing. This deformation is irreversible and is called **plastic deformation**. After this phase, the materials appear to regain strength and the stress rises again, producing only a limited amount of strain; the material has undergone a **work hardening**, a change in internal structure that made it more resistant but less deformable. When the stress reaches a high enough value (**ultimate strength**), the metal breaks.

1.3.2.4 Plastic deformation

Plastic deformations are caused by the **slip of atomic planes inside crystals**.

Figure 1.20

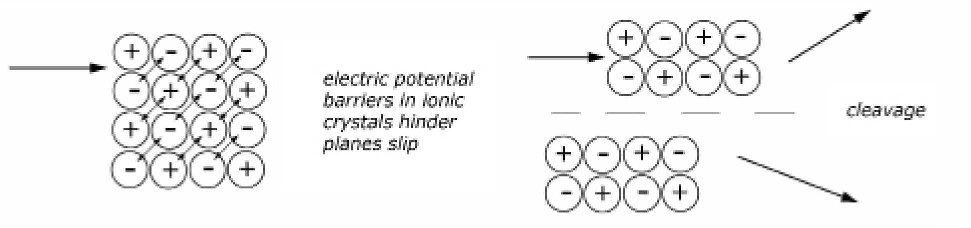


The slip of crystal planes is **possible in metallic crystals** because the bond is non-directional; when a plane slides under stress over another one, as in figure 1.20, it is easy to bind together the atoms again when the mechanical action is arrested because new bonds can be formed in any direction. Also, the close packing of atoms in metallic crystals favors sliding because planes that are full of atoms are well separated from one another and so they can be set in motion more easily.

The bonds in **covalent crystals** with or without some ionic character are directional in character; when a separation between planes is initiated, a new connection is not easily formed. Therefore, when the stress is large enough to pry an opening between two atomic planes, the crystal breaks (cleavage).

In ionic crystals, slip is not possible even if the bond is non-directional in character; the reason is that ions of equal sign should pass near each other to allow one plane to slide on top of its neighbor. As a consequence, a sequence of electrical potential barriers is created that is strong enough to inhibit slip. When the stress is large enough, cleavage of the crystal occurs, as in the case of covalent crystals.

Figure 1.21

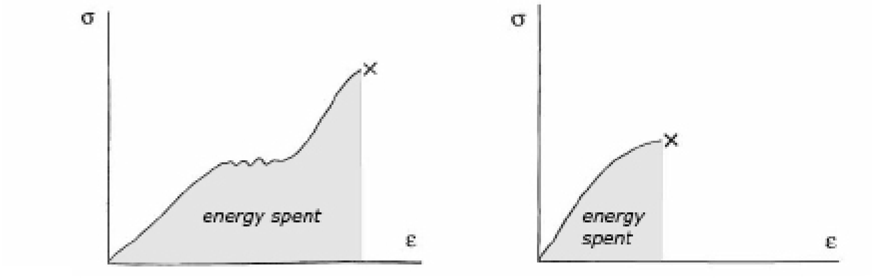


lack of plasticity in ionic crystals

1.3.2.5 Toughness

The toughness of a material is the overall energy required to break it under tensile stress. It is frequently measured by calculating the extension of the area underlying the stress/strain diagram resulting from a tensile strength test.

Figure 1.22



toughness

It is easy to see from the diagrams in figure 1.22 that the toughness of metals, when tested under tensile stress, is much larger than that of brittle materials; but it must be kept in mind that if a compressive strength test had been chosen to evaluate toughness, the result would be quite different.

The difference in the behavior of brittle materials under tensile and compressive stress is explained in section 3.1.1.

1.3.2.6 Creep

Plastic deformation and work hardening give metals the advantage of superior toughness over covalent and ionic materials, but in materials science advantages invariably come with strings attached; the unfavorable property connected to plasticity is creep.

Creep is a slow slip of atomic planes that may take place in metals under stresses much inferior to the yield strength measured in laboratory tests. This may happen under high stress continuously applied or when the temperature climbs above a limit that depends upon the nature of the metal. Creep causes serious dangers for metallic structures in the case of fires (refer to section 5.1.4 for a discussion of creep phenomena).

1.4 Molecules

1.4.1 Gases

The **covalent bond** may also form **molecules**, besides crystals, when a number of atoms of equal electronegativity are tied together. It must be noted that the term *molecule* defines an ensemble formed by a **definite number of atoms connected by covalent bonds** and is not applicable to ionic, covalent, or metallic crystals, as these are formed by a number of atoms that varies according to the dimension of the crystal and so it is not definite.

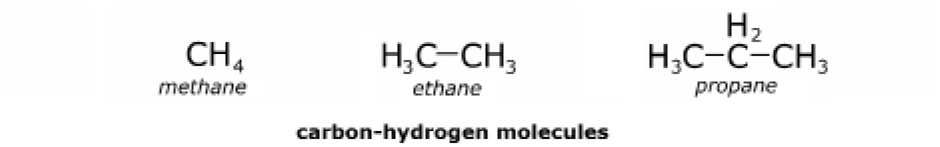
Figure 1.23

$H : H = H{-}H = H_2$ *hydrogen* N_2 *nitrogen* O_2 *oxygen*

molecules

A true covalent bond may be formed also between different atoms, provided their difference of electronegativity is very small; an example is offered by the carbon-hydrogen bond, which is a covalent bond because these atoms occupy positions very close to each other at the center of the electronegativity scale.

Figure 1.24



CH_4 *methane* $H_3C{-}CH_3$ *ethane* $H_3C{-}\overset{H_2}{C}{-}CH_3$ *propane*

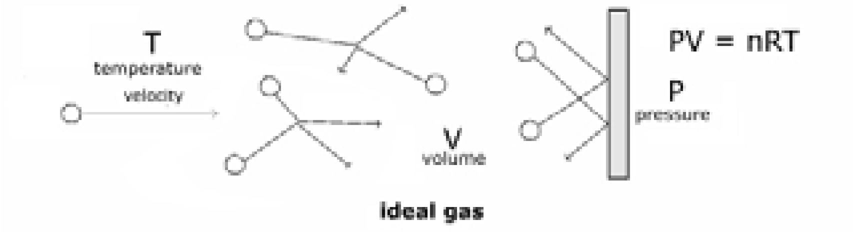
carbon-hydrogen molecules

Carbon-hydrogen and carbon-carbon bonds form the backbone of the molecules that constitute "organic chemistry."

The molecules shown in figure 1.24 form a **gas** when they are at room temperature. In an **ideal gas**, molecules move in straight lines until they meet an obstacle (the wall of a container or another molecule) and their velocity determines the temperature of the gas (greater velocity means higher temperature).

When two molecules meet, they rebound in a perfectly elastic way. When a molecule hits the wall of a container, it rebounds and transmits an impulse to the wall; the sum of these impulses is the pressure the gas exerts on the wall and is obviously related to the number of molecules that are present in a given volume of space and to their velocity (i.e., to the temperature of the gas).

Figure 1.25

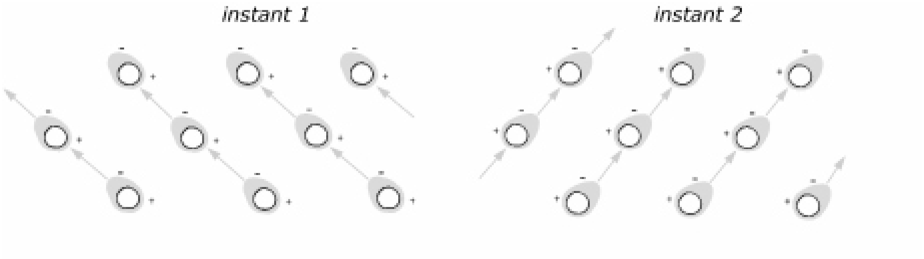


Real gases, however, behave according to the ideal gas law only at rather high temperatures and low pressures, discrepancies becoming more and more important as the pressure rises and the temperature is lowered.

This is due to the fact that the rebounds of the molecules are not perfectly elastic because there are forces of attraction between them.

The forces of attraction that are common to all types of molecules are called **Van der Waals forces** and also, frequently, **dispersion forces**. They originate from a fluctuation of the electrons around the nuclei, which creates instantaneous dipoles continuously changing their orientation so that on average the atoms remain electrically neutral. When two molecules are close, they influence each other so that the fluctuations of their electrons are consonant, the overall result being that in any instant there is the possibility of attractive forces between these tiny dipoles. Figure 1.26 is an attempt at a graphic explanation.

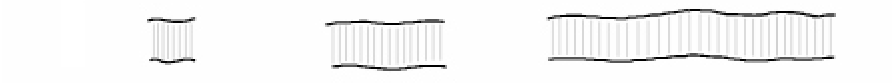
Figure 1.26



Van der Waals forces - a rough description

The force of attraction involved is extremely weak for each electron, but as the dimension of the molecules increases and so does the number of electrons involved, the forces sum up and influence in a sizeable way the properties of materials, in particular when the molecules are very large or, better, very long (as in polymers; see part 6).

Figure 1.27



the attraction between molecules is greater when they are longer

molecular bonds

As the molecules in a gas are moving more and more slowly (decreasing temperature) and collide more and more frequently with other molecules (increasing pressure), the probability increases that when two molecules meet, they remain together instead of rebounding. When this happens, the transformation of the gas into a liquid begins.

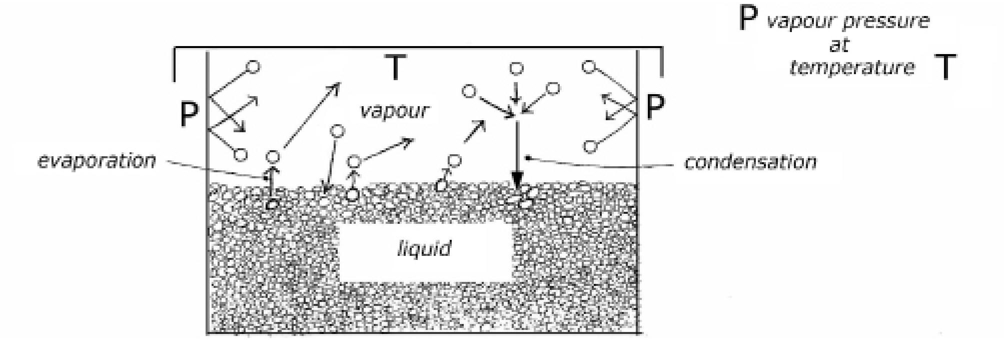
1.4.2 Molecular liquids

In a liquid, molecules are held within a limited volume by the forces of reciprocal attraction, but they enjoy a freedom of movement that increases when the temperature is raised. But even if the temperature remains constant, a liquid is never in a fixed, static situation because at any moment there is a passage of molecules through its surface, some molecules leaving the liquid and escaping into the air while other ones come in from the air.

Not all the molecules in a liquid possess the same energy: some of them have more energy than others (the distribution of energy among molecules is regulated by statistical rules) and are able to escape from the liquid into the gas surrounding it (this is called the **vapor** of the liquid).

At the same time, some molecules in the gas phase condense, i.e., they join together and reenter the liquid phase; if the liquid is kept in a closed container and the temperature remains constant, an **equilibrium** is established because the number of molecules escaping from the liquid into the vapor phase is more or less equal to that of the molecules that reenter the liquid by condensation, so that the number of molecules in the vapor phase is approximately constant. The pressure of the vapor phase in such equilibrium conditions is called the **vapor pressure of the liquid** at the temperature of measurement.

Figure 1.28



liquid-vapor equilibrium in a closed container

If the lid of the container is removed and a current of air is led along the surface of the liquid, most molecules that escape from the liquid are taken away as soon as they emerge, and very few molecules go back into the liquid; an equilibrium condition is never reached and the liquid progressively disappears (evaporates). The **evaporation rate** (velocity of evaporation) depends upon the vapor pressure of the liquid; a liquid with high vapor pressure evaporates more rapidly than one with low vapor pressure. The vapor pressure in turn depends upon the force of attraction between the molecules; if it is small, the vapor pressure will be high. The vapor pressure and the evaporation rate also increase when the temperature rises.

When the temperature is rather low, molecules can escape from the liquid only from the surface; if some gas is formed inside the liquid mass, the tiny bubbles are squeezed back into the liquid by the atmospheric pressure acting on it. But if the vapor pressure of the liquid becomes equal to the atmospheric pressure, gas bubbles do form and rise to the surface; the liquid has reached its **boiling point** and is rapidly transformed into vapor, while the temperature remains constant until all the liquid has disappeared.

The boiling point of a liquid provides some information on the energy that is required to detach its molecules from one another and also on the forces of attraction between its molecules.

As the forces of attraction increase with the size of the molecules, this also happens with the boiling points, a fact that is clearly observed in a series of molecules formed by carbon and hydrogen (**hydrocarbons**).

Boiling Points of Hydrocarbons		
methane CH_4 –161°C	**ethane** CH_3-CH_3 –88°C	**propane** CH_3-CH_2-CH_3 –42°C
butane CH_3-$(CH_2)_2$-CH_2 0°C	**hexane** CH_3-$(CH_2)_4$-CH_3 +69°C	**octane** CH_3-$(CH_2)_6$-CH_3 +126°C

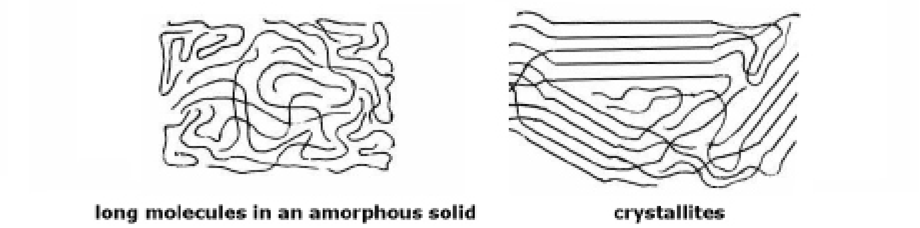
1.4.3 Molecular solids

When a liquid undergoes a decrease in temperature and the mobility of the molecules is progressively reduced, viscosity increases. At some point the energy the molecules possess is so low that it cannot overcome the forces of attraction anymore; at this point the molecules remain tied into fixed positions and the energy provided by heat (thermal energy) allows them only to vibrate. A molecular solid has been formed.

If the molecules are small, the creation of an ordered structure is possible; this would be a **molecular crystal**.

In the case of long molecules, like those of hydrocarbons with many carbon atoms, these may be arranged in a disordered (**amorphous**) state, but it is also possible that some parts of the molecules align themselves in regular bundles that are called **crystallites**, as some degree of order is achieved, even if it is different from the order existing in ionic, covalent, or metallic crystals.

Figure 1.29



long molecules in an amorphous solid

crystallites

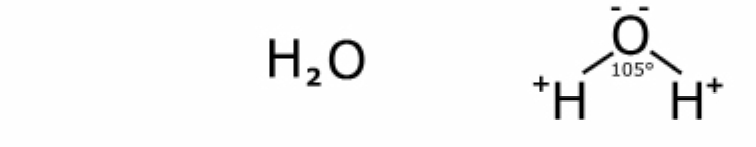
The melting points and the mechanical properties of these solids depend upon the force of attraction active between molecules, and we know that these forces are much weaker than the ones created by the chemical bonds between atoms. Molecular forces, however, increase progressively with the dimension of the molecules (in particular with their length), and so materials with interesting mechanical properties may be created also from molecular solids.

Among molecules made only of carbon and hydrogen atoms, solid **paraffin**, which contains chains of 22 to 30 carbon atoms, melts between 50°C and 60°C and is very soft, while **polyethylene**, a synthetic resin made of very long molecules (1000 carbon atoms or more), starts softening well above 100°C and shows mechanical properties that are good enough for many practical uses, even if its hardness is well below that of materials formed by primary chemical bonds (e.g., metals or ceramics).

1.4.4 Polar molecules

Molecules may be built also by covalent bonds with some ionic character, that is, bonds between atoms that show some difference in electronegativity (but not large enough to produce an ionic bond). This is the case with the **water** molecule.

Figure 1.30



the water molecule

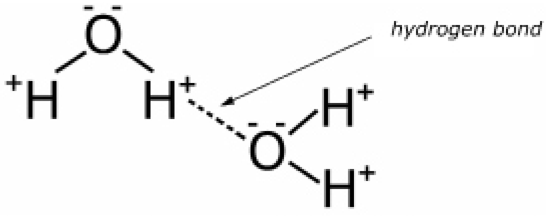
The covalent bonds between hydrogen and oxygen are directional and form an angle of about 105°. The bonds have some ionic character as the electrons tend to stay closer to the oxygen atom, and this results in a small negative charge on the oxygen and small positive charges on both hydrogen atoms.

This molecule carries **electric poles** on all its atoms and so we call it a **very polar molecule**.

Both hydrogen atoms show a strong tendency to attract the negative poles of other molecules because their positive nucleus is left almost without any electron cover (is not "shielded" by electrons) on the side opposite to the covalent bond formed with oxygen, as the single electron they own is now most frequently on the other side.

As a consequence, a **force of attraction** is established between water molecules that is much larger than the normal Van der Waals attraction that was discussed earlier. Also, this force acts along a single direction, between the hydrogen of one molecule and the oxygen of another molecule (it is not a "field" force active in all directions). For these reasons, the attraction determined by positive poles on hydrogen atoms is called a bond, even if it is about ten times weaker than the oxygen-hydrogen covalent bond. The name of this bond is **hydrogen bond**.

Figure 1.31

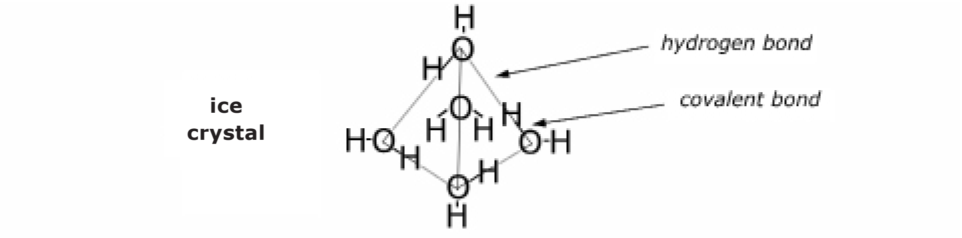


two water molecules linked by a hydrogen bond

The strength of the hydrogen bond explains why water boils at 100°C and freezes at 0°C while methane, which has the same number of electrons, and so presumably a similar Van der Waals attraction force, boils at –161°C and freezes at –184°C.

Solid water, i.e., **ice**, has a crystalline structure in which an oxygen atom is at the center of a tetrahedron whose vertices are occupied by four other oxygen atoms; the hydrogen atoms are located on the edges of the tetrahedron but not halfway because they are closer to the oxygen, with which they share the covalent bond.

Figure 1.32



There are a large number of molecules in organic chemistry that have a **partial polar character**, i.e., the electric poles exist only in part of the molecule while the rest is formed by covalent bonds with no ionic character.

An example is offered by the series of **alcohols** that are organic molecules, i.e., basically carbon-hydrogen covalent structures, connected to a polar group formed by one oxygen atom and one hydrogen atom. The **$^{-}$O-H^{+}** group, called the **hydroxyl group**, has a negative charge on the oxygen and a positive one on the hydrogen, and so a strong tendency to form hydrogen bonds with other molecules. The group formed by an atom carrying a small positive charge linked by a bond to an atom that carries a small negative charge is called a **dipole**.

The addition of the hydroxyl group to a hydrocarbon molecule causes an increase of the attraction between molecules and, as a consequence, of the boiling point of the liquid. The boiling point also increases as the length of the non-polar hydrocarbon chain is increased.

Boiling Points of Alcohols		
methane CH_4 –161°C	**ethane** CH_3-CH_3 –88°C	**propane** CH_3-CH_2-CH_3 –42°C
methyl alcohol CH_3-OH +65°C	**ethyl alcohol** CH_3-CH_2-OH +78°C	**propyl alcohol** CH_3-CH_2-CH_2-OH +97°C

All types of molecules that contain hydroxyl groups form hydrogen bonds between them and, in particular, with water molecules.

Also, a bond between nitrogen and hydrogen forms a dipole, **$^{-}$N-H^{+}**, found, for example, in the **amine group –NH$_2$**, which can form hydrogen bonds and so is able to attract water molecules.

Another possibility to form hydrogen bonds is with the **$^{+}$C-O^{-}** dipole, which does not contain a hydrogen atom but is able to attract the positive hydrogen of a dipole with its negative oxygen.

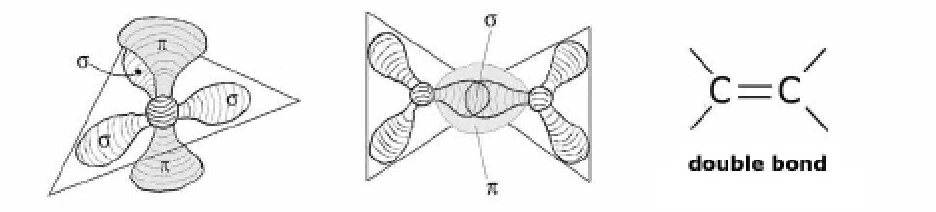
Other dipoles are formed by the linking of carbon with atoms other than hydrogen; the carbon-chlorine bond (**$^{+}$C-Cl^{-}**), which is found in many organic molecules (e.g., solvents and synthetic polymers), does not form hydrogen bonds so it does not attract water molecules.

1.4.5 Double bonds between carbon atoms

In the carbon atom, the tetrahedral structure of the orbitals in the L shell is not the only possible arrangement of the electrons around the nucleus. Another possible structure is a flat one, the nucleus being at the center of a triangle with three orbitals of the L shell directed towards its vertices. The three electrons belonging to these orbitals are designated by the Greek letter sigma (σ). The fourth electron of the L shell is to be found either above or below the nucleus in an hourglass-like orbital; this electron is designated by the Greek letter pi (π).

A bond may be formed between two carbon atoms, both having such a triangular arrangement, by the overlapping of two σ-orbitals as shown in figure 1.33; at the same time, the π-orbitals can overlap, forming a second bond parallel to the first.

Figure 1.33

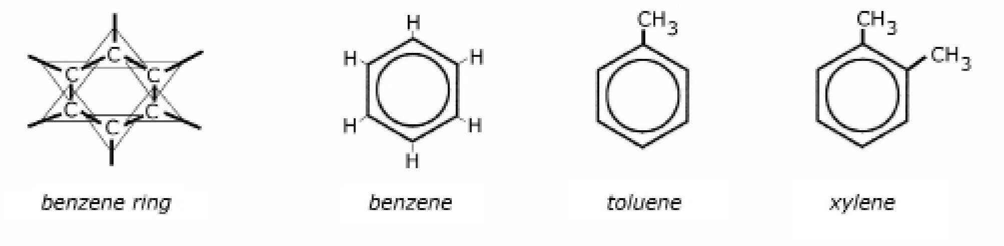


The double bond is somewhat stronger than a single carbon-carbon covalent bond, so the atoms stay closer to each other; the electronic structure, however, is not stable. A double bond in a molecule is an unstable region as it may easily be *activated* by heat, radiation, or catalysts, giving rise to chemical reactions, some of them quite useful in modern technology, e.g., addition polymerization (see section 6.4.1.1).

The benzene ring

Six carbon atoms, all in the "triangular" arrangement of the L-orbitals, may join and form a hexagonal ring, each atom bonding through two σ-orbitals to its two neighbors, while the six π-electrons become free to move around the ring, above and below the carbon atoms. The name of this molecular structure is a **benzene ring**.

Figure 1.34



benzene ring *benzene* *toluene* *xylene*

aromatic hydrocarbons

The benzene ring is flat; it is frequently represented by a hexagon in which a circle is inscribed, symbolizing the circular movement of the π-electrons. Contrary to the case of the isolated double bond, the benzene ring is not only strong but also chemically stable.

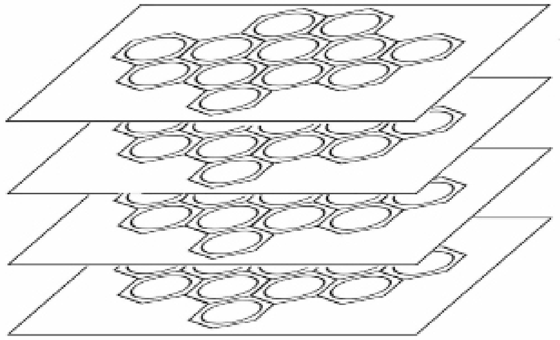
When the third σ-orbital of each carbon atom is used to create a bond with a hydrogen atom, the hydrocarbon **benzene** is formed. When one or more of the hydrogen atoms of benzene is substituted by groups of carbon and hydrogen atoms (e.g., the **CH_3** group, called the **methyl** group), other hydrocarbon molecules are formed; all hydrocarbons containing benzene rings are called **aromatic hydrocarbons** because of their characteristic smell.

1.4.6 Graphite

The triangular structure of the L-orbitals of the carbon atom is found also in a solid crystalline material, graphite, which is far more abundant in nature than the crystal formed by the regular tetrahedral arrangement of the L-orbitals (diamond).

The graphite crystal is a stack of planes formed by connected hexagonal rings of the benzene type.

Figure 1.35



graphite crystal

The planes of benzene rings are tied together by residual forces involving the π-electrons; these are much weaker, however, than the covalent bonds formed by the σ-electrons in the benzene rings. The consequence is that the crystal is easily cleaved under stress along the planes of hexagonal rings; this explains why a graphite pencil can write and graphite powder is a good lubricant.

Graphite can also conduct the electrical current because the π-electrons are free to move along the crystal planes when an electrical potential is applied to the material.

Graphite is formed from amorphous carbon (coal or carbon black) when it is subjected to very high temperatures (1500°C and higher) in the absence of oxygen (otherwise the carbon would be burned away, transformed into carbon dioxide gas).

1.5 Chemical Reactions

1.5.1 Acids

1.5.1.1 Strong acids and weak acids

Acids are defined as substances whose molecules split (the technical term is *dissociate*) when in contact with water, forming **hydrogen ions (H^+)** and a negative ion. Hydrochloric acid is a typical example.

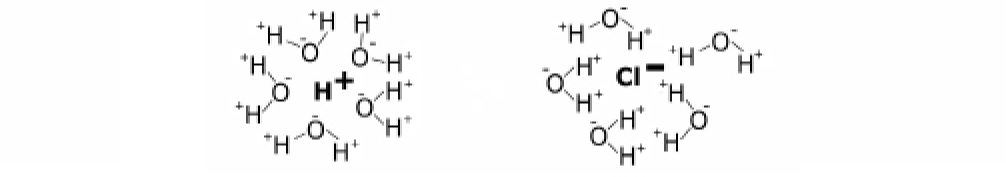
Figure 1.36

$$HCl + H_2O \longrightarrow H^+ + H_2O + Cl^-$$

hydrochloric acid

Positive and negative ions in the liquid are surrounded by water molecules attracted by the electrical charges of the ions.

Figure 1.37



ions in water (ion solvation)

Other examples of acids are sulfuric acid and nitric acid.

Figure 1.38

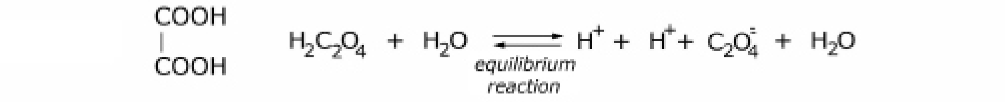
sulfuric acid $H_2SO_4 + H_2O \longrightarrow H^+ + H^+ + SO_4^{=} + H_2O$

nitric acid $HNO_3 + H_2O \longrightarrow H^+ + NO_3^- + H_2O$

These acids are **strong acids**; they dissociate completely into ions when they come in contact with water, forming all the hydrogen ions that are possible for them to produce.

Weak acids also exist, however; they do not dissociate completely when in contact with water and so they form fewer hydrogen ions than strong acids in water, at equal concentration. Oxalic acid is an example.

Figure 1.39



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \qquad H_2C_2O_4 + H_2O \underset{\text{equilibrium reaction}}{\rightleftharpoons} H^+ + H^+ + C_2O_4^{=} + H_2O$$

oxalic acid

The **–COOH** (**carboxyl**) group confers acid properties to organic molecules. All **organic acids** are weak acids because the dissociation of the carboxyl group is always an **equilibrium reaction**, i.e., a reaction that can proceed both ways, its final result depending upon the structure of the whole molecule and the surrounding conditions.

Figure 1.40

acetic acid CH_3COOH **citric acid** $$\begin{matrix} & & CH_2COOH \\ & & | \\ HO & - & C - COOH \\ & & | \\ & & CH_2COOH \end{matrix}$$

Acetic acid and citric acid are still weaker than oxalic acid; they may be used to season food because they have an acid taste but do not produce enough hydrogen ions to cause dangerous reactions.

1.5.1.2 Acids in the atmosphere

Carbon dioxide is a gas that is present in the air at a very low concentration (0.1% maximum); when it is dissolved in water, a very weak acid, carbonic acid, is formed, which provides carbonated mineral water with its pleasant taste.

Rainwater and dew are normally acid because of dissolved carbonic acid.

Figure 1.41

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
$$H_2CO_3 + H_2O \rightleftharpoons H^+ + HCO_3^- + H_2O$$
$$HCO_3^- + H_2O \rightleftharpoons H^+ + CO_3^= + H_2O$$

carbonic acid in water

Strong acids produced by the burning of fuels or electrical discharges may be present, however, in the rain or dew deposited in polluted urban atmospheres.

Sulfur-containing fuels produce sulfur dioxide upon burning; this is oxidized in the air and, by adding a water molecule, is transformed into sulfuric acid.

Figure 1.42

$$S + O_2 \longrightarrow SO_2$$
$$SO_2 + O + H_2O \longrightarrow H_2SO_4$$

burning of sulfur-containing fuels

In air, electrical discharges and flames produce nitrogen oxides (**NO** and $\mathbf{NO_2}$) by a reaction between nitrogen and oxygen (air contains about 80% nitrogen and 20% oxygen). As the exact ratio between the two oxides is variable, when they are analyzed a combined formula is written $\mathbf{NO_X}$. After some time in the air, the nitrogen oxides are transformed into nitric acid by the action of oxygen and water.

Figure 1.43

$$N + O_2 \longrightarrow NO_2$$
$$2NO_2 + O + H_2O \longrightarrow 2HNO_3$$

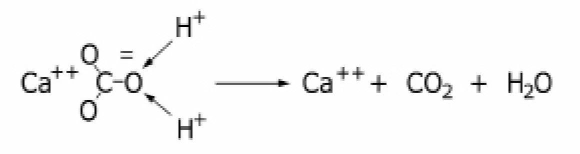
oxidation of nitrogen dioxide

1.5.1.3 Properties of acids

1. Acids have an acidic taste, as in lemon or vinegar.
2. Acids attack calcium carbonate and dissolve it.

Calcium carbonate ($\mathbf{CaCO_3}$), an ionic crystal, is insoluble in water because of the strong attraction between the calcium ion ($\mathbf{Ca^{++}}$) and the carbonate ion (**CO3—**), both carrying a double electrical charge. Hydrogen ions ($\mathbf{H^+}$), released from an acid dissolved in water, remove one oxygen atom from the carbonate ion, forming a molecule of water, thus transforming the carbonate ion into carbon dioxide ($\mathbf{CO_2}$), a gas, which forms bubbles in the liquid.

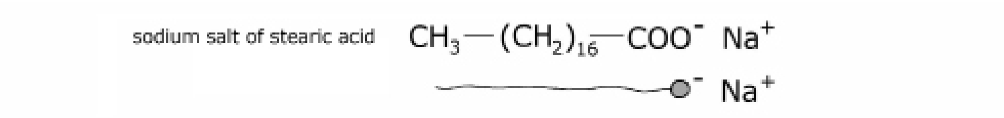
Figure 1.44



acid attack of calcium carbonate

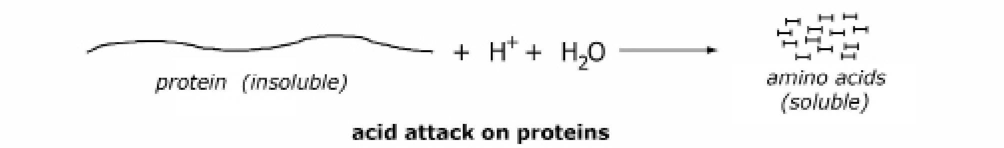
The calcium ions are surrounded by water molecules and attracted by the negative ions formed in the dissociation of the acid, so they disappear into the water; a crystal of salt will be formed if the water evaporates. If the acid is sulfuric acid, the salt that is formed is calcium sulfate that forms a crystal (gypsum) inside which two molecules of water are held near each calcium atom.

Figure 1.45



3. Acids favor the **corrosion** of many metals (see section 5.1.6.2).
4. Acids cause the breakup (**hydrolysis**) of long organic molecules such as **proteins** and **cellulose** (see section 6.2.1).

Figure 1.46

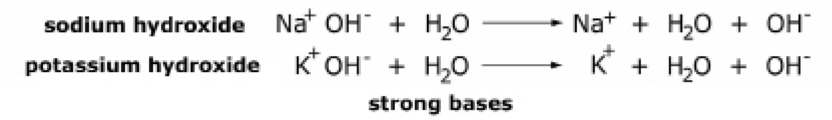


1.5.2 Bases

1.5.2.1 Strong bases and weak bases

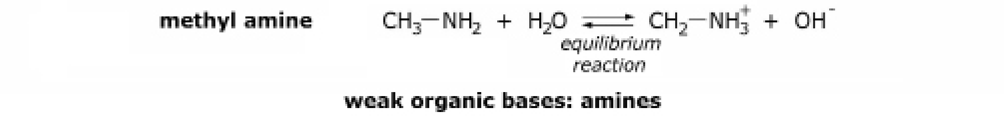
Bases are defined as substances that in the presence of water form **hydroxyl** (**OH^-**) **ions**. Strong bases dissociate completely in the presence of water, setting free all available hydroxyl ions. Examples of strong bases are sodium hydroxide (**NaOH**), also known as caustic soda, and potassium hydroxide (**KOH**), also known as caustic potash.

Figure 1.47



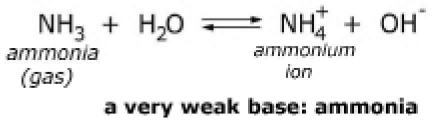
Many **weak bases** are organic molecules that contain the **amine group** (**$-NH_2$**). The amines form hydroxyl ions through an equilibrium reaction with water; the amount formed depends upon the type of molecule and the surrounding conditions.

Figure 1.48



Ammonia is a very weak base, weaker than the amines.

Figure 1.49

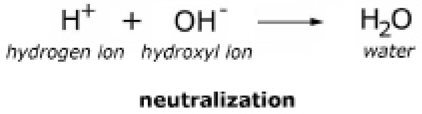


1.5.2.2 Properties of bases

1. Bases neutralize acids.

Hydroxyl ions join with hydrogen ions to form water molecules.

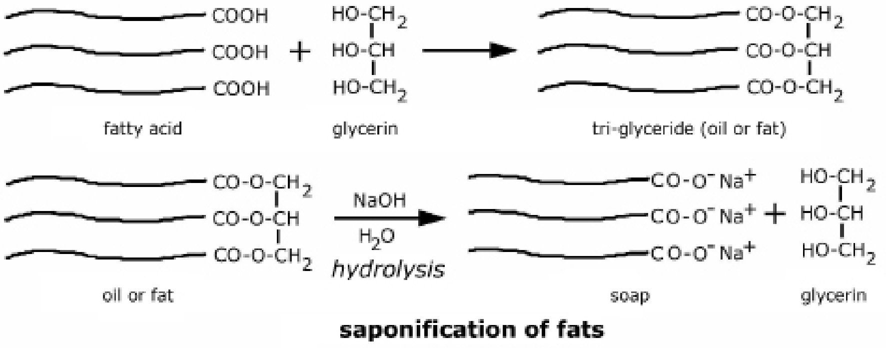
Figure 1.50



If the number of hydroxyl ions is equal to the number of hydrogen ions, the liquid they form is said to be neutral.

2. Bases can split ("hydrolyze") the molecules of fats and oils. This reaction was widely used in the past to make soap.

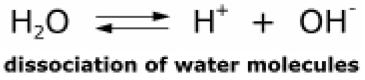
Figure 1.51



1.5.3 Evaluation of the acid or basic properties of a liquid; pH

In liquid water, a small quantity of hydrogen and hydroxyl ions is always available because water molecules dissociate according to an **equilibrium reaction**.

Figure 1.52



According to the law governing equilibrium reactions, the following relationship must be true:

$[H^+]$	×	$[OH^-]$	=	**constant = 10^{-14}**
concentration hydrogen ions		**concentration hydroxyl ions**		

Since the value of the constant must always be 10^{-14}, in the case of water, in a condition of neutrality the following relationship must also be true:

neutrality $[H^+] = [OH^-] = 10^{-7}$

If we add acid to a neutral liquid until the concentration of the hydrogen ion climbs up to 1 (one atomic weight, i.e., 1 g, per liter), according to the law of equilibrium the concentration of the hydroxyl ion must become 10^{-14}. The liquid is now very acid.

very acid liquid $[H^+] = 1$ $[OH^-] = 10^{-14}$

If instead a base is added to the neutral liquid until the concentration of the hydroxyl ion is brought up to 1 (one atomic weight of oxygen + hydrogen, i.e., 17 g, per liter), the concentration of the hydrogen ion must go down to 10^{-14}.

The liquid is now very basic.

very basic liquid $[H^+] = 10^{-14}$ $[OH^-] = 1$

As scientists prefer to use simple numbers in their work, it was decided that to measure acidity, or basicity, of a liquid, we should use the **logarithm of the inverse of the concentration of the hydrogen ion**. This number is to be called the **pH** of the liquid.

See below how it works.

a very acid liquid $[H^+] = 1$
$\log(1/[H^+]) = \log(1/1) = 0$ $pH = 0$

a neutral liquid $[H^+] = 10^{-7}$
$\log(1/[H^+]) = \log(1/10^{-7}) = \log 10^{+7} = 7$ $pH = 7$

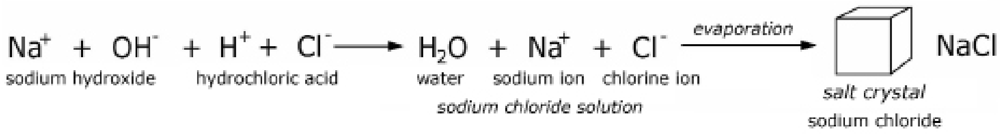
a very basic liquid $[H^+] = 10^{-14}$
$\log(1/[H^+]) = \log(1/10^{-14}) = \log 10^{+14} = 14$ $pH = 14$

Liquids that are more or less acid have pH values between 0 and 7, while liquids that are more or less basic have pH values between 14 and 7.

1.5.4 Salts

When an acid is neutralized by a base, or a base by an acid, water molecules are formed and the residual ions remain in the water. If the water evaporates, a **salt crystal** is formed. In the case of hydrochloric acid and caustic soda, sodium ions (**Na^+**) and chlorine ions (**Cl^-**) remain in the water after the neutralization and, when the water evaporates, a crystal of sodium chloride is formed.

Figure 1.53

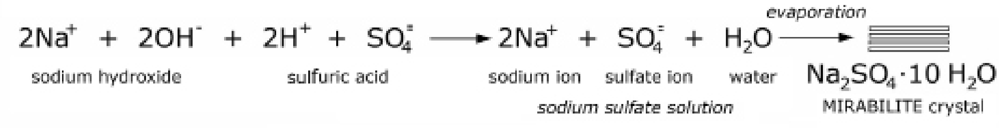


salt formation and crystallization

If **crystallization** takes place inside a porous material, like brick or stone, crystal growth may generate stresses that may be large enough to cause serious damage (see section 3.2.4).

In some cases, some water is held inside the growing salt crystal, tied to the ions in a precise ratio, and thus a **hydrated salt** is formed. An example is sodium sulfate, which is formed in the neutralization reaction of sulfuric acid and caustic soda.

Figure 1.54

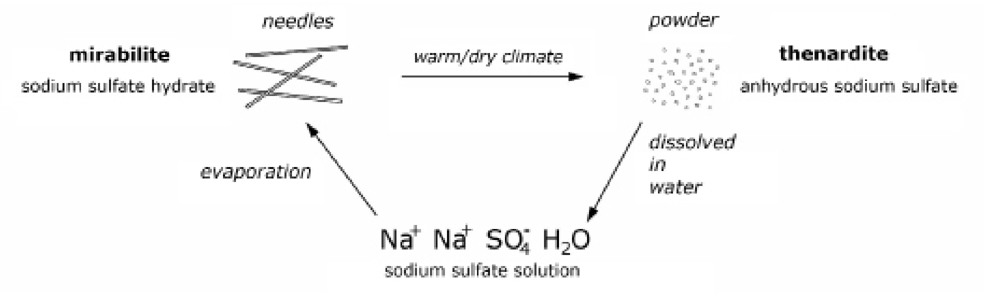


formation and crystallization of sodium sulfate

Crystals of salts are stable only within well-defined conditions of temperature and humidity; out of their field of stability, they lose the crystallization water (if they are hydrated salts) and are transformed into the corresponding **anhydrous salt** (when the air is too dry) or **deliquesce** (when the air is too damp), i.e., pick up water from water vapor in the atmosphere and dissolve in it.

As a cause of decay, hydrated salts are more dangerous than simple salts because their crystals occupy a larger volume and may grow very rapidly when the atmospheric conditions are suitable. An example is sodium sulfate that, lodged in the pores of stones or mortars, undergoes periodical phases of hydration, dehydration, and solution, causing stress at each cycle.

Figure 1.55



crystallization cycle of sodium sulfate

The table below lists, in order of frequency of the finds, the salts identified in the study of deterioration processes of stone, brick, or mortar in a single archaeological site (Herculaneum).

Salts Causing Deterioration of Stone or Mortar in One Archaeological Site		
Formula	**Chemical Name**	**Mineral Name**
Na_2SO_4	sodium sulfate	thenardite
$Na_2SO_4 \bullet 10H_2O$	sodium sulfate hydrate*	mirabilite*
$CaSO_4 \bullet 2H_20$	calcium sulfate hydrate	gypsum
$NaCl$	sodium chloride	halite
$NaNO_3$	sodium nitrate	niter
KNO_3	potassium nitrate	saltpeter
$Na_3(SO_4)(NO_3) \bullet H_2O$	sodium sulfo-nitrate	darapskite
$K_3Na(SO_4)_2$	potassium sodium sulfate	aphtitalite
$MgSO_4 \bullet 6H_2O$	magnesium sulfate hexa-hydrate	hexahydrite
$MgSO_4 \bullet 7H_2O$	magnesium sulfate hepta-hydrate	epsomite
$CaCO_3$	calcium carbonate**	calcite***
$CaCO_3$	calcium carbonate**	aragonite ***

* Mirabilite frequently loses its crystallization water during transportation to the laboratory, so it is transformed into thenardite when the sample is analyzed.

** Calcium carbonate is insoluble in pure water but is transformed into soluble calcium bicarbonate when carbon dioxide is dissolved in the water (see section 3.3.1). It is well known that the crystallization of calcite crystals caused by the evaporation of calcium bicarbonate solutions can cause damage inside porous materials.

*** Calcite and aragonite have the same chemical composition but different crystal structure. Calcite is the most frequent form; aragonite is found in shells, corals, stalagmites in caves, and other special occurrences.

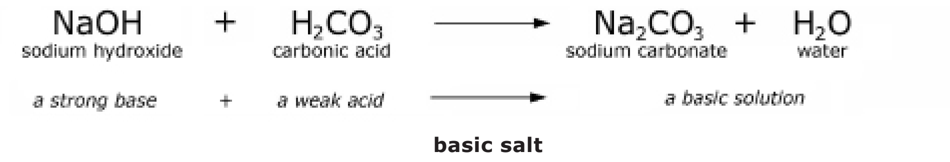
The list of salts involved in the deterioration of building materials would be much longer if all the findings reported in the technical literature were included.

1.5.5 Acid salts and basic salts

If the acid and the base that neutralize each other and form a salt are not of equal force the solution of the salt in water is not neutral.

In the case of **sodium carbonate**, the base is stronger and, as a consequence, its solution in water is **basic**. In the past, sodium carbonate, whose current name was *soda*, was widely used as a cleaning agent.

Figure 1.56

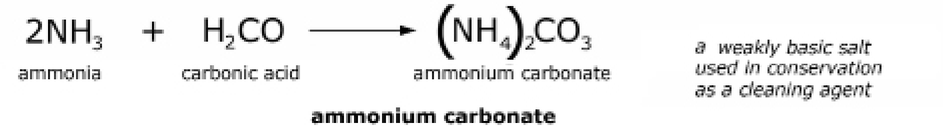


Sodium bicarbonate, which is formed by neutralizing only half of the potential acidity of carbonic acid, is only **weakly basic**.

Figure 1.57

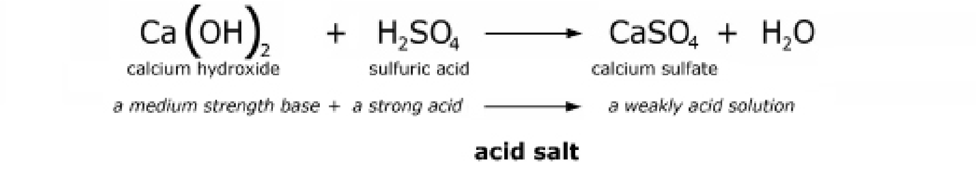
If carbonic acid is neutralized by ammonia, which is only slightly stronger than the acid, the result is **ammonium carbonate**, a **very weakly basic salt** that today is widely used for cleaning surfaces of historic or artistic importance.

Figure 1.58



Acid salts are formed by acids neutralized by weaker bases. An example is calcium sulfate, which is formed by a strong acid (sulfuric acid) and a medium strength base (calcium hydroxide).

Figure 1.59



Gypsum, when in contact with water, forms a weakly acid solution that may favor the corrosion of iron.

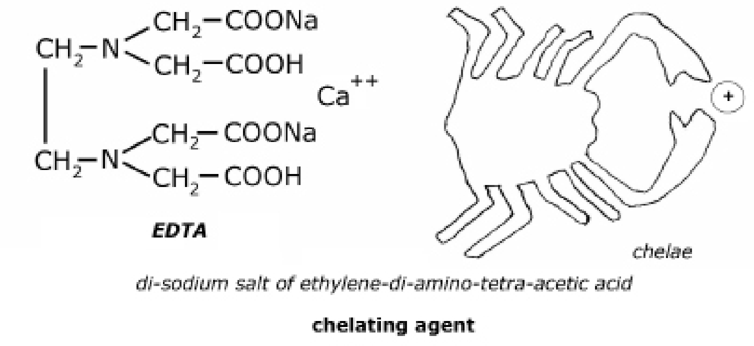
1.5.6 Chelating agents

Salts of organic acids, which have many acid groups (–COOH) in each molecule, are able to pick up atoms of metals from insoluble inorganic incrustations (e.g., calcareous crusts on stones or rust layers on iron), thus allowing for their easy removal from the affected surfaces.

The multiple acid groups in these molecules act like the pincers of a crab, grabbing atoms one by one and transporting them into the liquid, hence the name *chelating agents*, derived from *chelae*, the pincers of crustaceans.

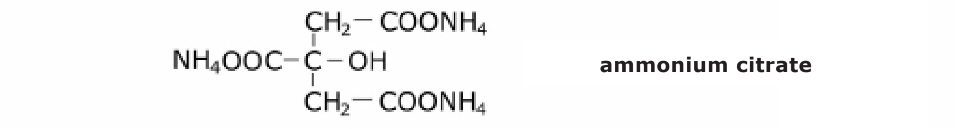
The best-known chelating agent in conservation is **EDTA**, most frequently used with only half of its four acid groups neutralized.

Figure 1.60



Salts of other organic acids were used in the past for the same purpose before the introduction of EDTA and are occasionally still used today. An example is ammonium citrate (and other salts of citric acid).

Figure 1.61


$$NH_4OOC-\overset{\displaystyle CH_2-COONH_4}{\underset{\displaystyle CH_2-COONH_4}{C}}-OH$$

1.6 Physical Transformations—Solutions and Emulsions

1.6.1 Solutions

Dissolution is a process in which the molecules of a liquid (**solvent**) completely separate the particles (atoms, ions, or molecules) that constitute a solid (**solute**) and cause its disappearance. The liquid into which the separated particles are dissolved is called a **solution**. If the liquid evaporates, the solid material is re-formed with the same chemical composition it had before being dissolved.

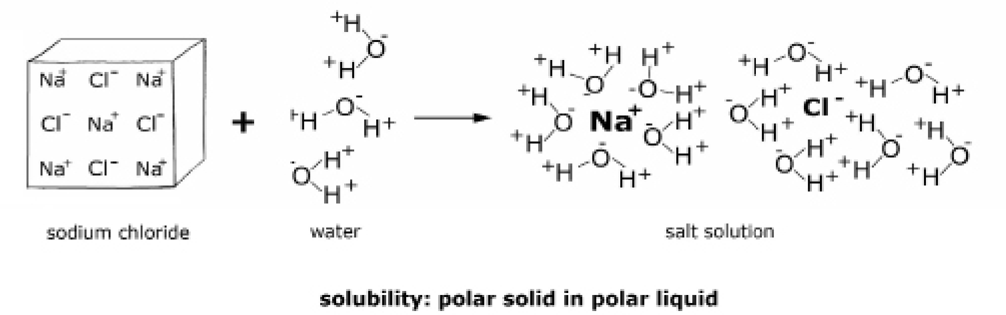
According to this definition, the chemical attack of a solid material by an acid (as in the case of calcium carbonate and hydrochloric acid) and its disappearance into the water is not a case of "solution" because, when the water evaporates, the chemical composition of the solid residue will be different from the one of the initial solid.

The general rule governing the solubility of solids may be stated as: **a solid is dissolved by a liquid of "similar nature."**

The "similitude" is determined by the presence, or absence, of electrical charges, or dipoles, in the liquid and in the solid.

An ionic crystal, such as sodium chloride, is full of electrical charges and can be dissolved only by a liquid whose molecules possess a lot of dipoles; water is the only common liquid qualifying under this requirement.

Figure 1.62



Considering the transformation depicted in figure 1.62, one may ask why the process should proceed in the direction indicated by the arrow, i.e., towards the dissolution of the solid into the liquid.

The answer to such a question depends upon the calculation of the **free energy** of the system water-salt in the two possible states (separation, i.e., insolubility, or solution). The direction of all natural processes is always towards the state in which the free energy is lowest.

Free energies may be exactly calculated, but we can gather a general idea of the direction of natural processes without going into such specialized analysis and considering instead the definition of free energy offered by the **Gibbs-Helmholz equation**:

$$F = U - TS$$

where:

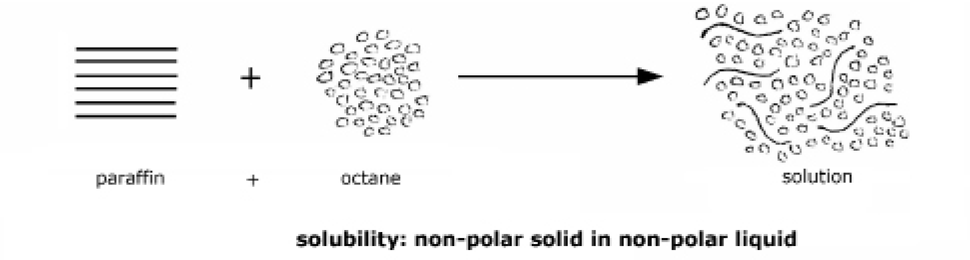
- **U** is the **internal energy** of the system, which in the cases that interest us is essentially determined by electrical attraction—the higher the electrical attraction, the lower the value of U;
- **S** is the **entropy** of the system that depends on the condition of order (or disorder) of the system—the greater the disorder, the larger the value of S;
- **T is the absolute temperature in Kelvin degrees (i.e., Celsius degrees + 273).**

In the case of the dissolution of sodium chloride in water, as electrical attraction forces are more or less equal in both states (solubility or insolubility), the deciding factor becomes entropy, which appears with a negative sign in the equation and so favors the most disordered state, i.e., the solution.

We note also that the temperature has a multiplying effect on entropy, which means that the tendency towards disorder (solution) is increased by an increase in temperature, a fact that is confirmed by experience.

Free-energy-based considerations also lead to the conclusion that a non-polar solid should be dissolved by a non-polar liquid.

Figure 1.63

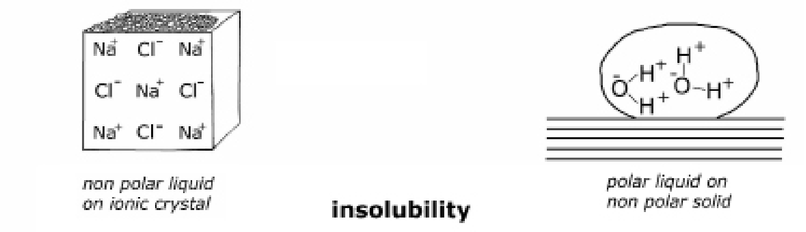


In this case, electrical attraction forces are weak but, again, more or less equal in both situations (separated solid + solvent versus solution), therefore entropy (i.e., the tendency to disorder) is the deciding factor and favors solution.

A **large difference in the polar character** of solid and liquid leads instead to **insolubility**.

In the case of an ionic crystal in contact with a non-polar liquid, the electrical attraction in the solid is far larger than the very weak Van der Waals attraction that might be exchanged in a solid-liquid mixture; as a consequence, the internal energy would be the deciding factor and solid and liquid would remain separate (insolubility). The same reasoning would apply to the case of a polar liquid (like water) and a non-polar solid (like paraffin), leading to the conclusion that insolubility is going to be the outcome of any encounter of such substances.

Figure 1.64



We have seen, however, that also **molecules with partial polar character** exist in which part of the structure is non-polar and part polar. Several solid substances that are of interest in conservation belong to this category, for instance, most of the natural and synthetic resins.

A similarity rule, in general, is valid also in these cases, i.e., an intermediate polarity solvent is needed to dissolve an intermediate polarity solid.

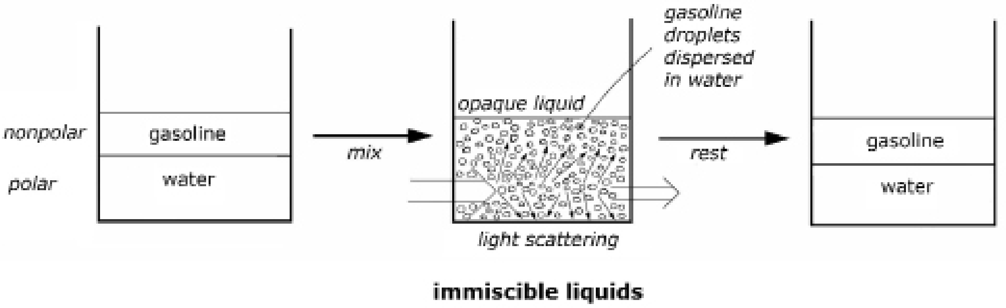
This explains why **intermediate polarity solvents** are required to dissolve the resin components of adhesives and paints whose molecular structure is normally a carbon-hydrogen non-polar chain with polar groups attached.

1.6.2 Miscibility

Miscibility (i.e., the mixing of two liquids resulting in a single liquid phase) follows the same rule as the solution of a solid. **Liquids of similar polarity form a single liquid** when mixed, while liquids with a strong difference in polarity if poured into the same container form two separate liquid layers.

In the latter case, if we try to force mixing by mechanical action, it appears initially that mixing is achieved, but the single liquid layer that is formed is not clear anymore; a closer examination reveals that its opaqueness is due to tiny droplets of one liquid floating inside the other. The opaque liquid is called a **dispersion** of one liquid into another. The dispersion is not stable unless we add some agent to stabilize it (see section 1.6.3); after some time the droplets join together to form again a separate liquid layer.

Figure 1.65



The opaqueness of the dispersion is due to the droplets of the dispersed liquid, which, being larger than the wavelength of the light, cause a phenomenon known as **scattering**, i.e., the deviation of fractions of the light beam in all directions, thus reducing its intensity in the direction of transmission (see figure 1.65).

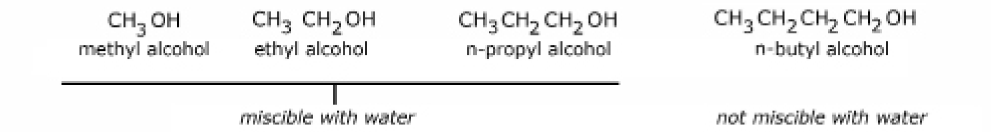
Intermediate polarity liquids, such as ethyl alcohol and acetone, are miscible both in water (very polar) and in low-polarity liquids such as benzene.

Figure 1.66

solvents of intermediate polarity

In the series of alcohols, as the length of the hydrocarbon chain is increased, while the polar group remains a single one, the ability to mix with water is progressively reduced; a complete mixing is impossible when the chain is four carbon atoms long.

Figure 1.67



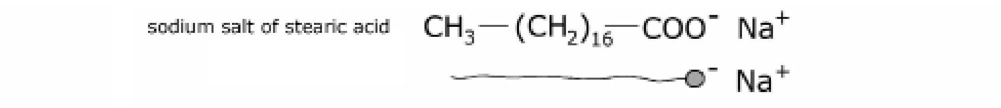
miscibility of alcohols with water

1.6.3 Surface active agents, emulsions

Surface active agents (surfactants) contain in their molecule both a non-polar section and a polar one and so are able to act as intermediates between a non-polar substance and water, allowing the formation of stable dispersions (frequently called **emulsions**). The non-polar section is frequently rather long, while the polar group is short.

The most widely known surface active agent is common **soap**, which is the **sodium, or potassium, salt of a fatty acid**, i.e., a molecule containing a 15 or 17 non-polar carbon atom chain, and a carboxyl group (**–COOH**).

Figure 1.68

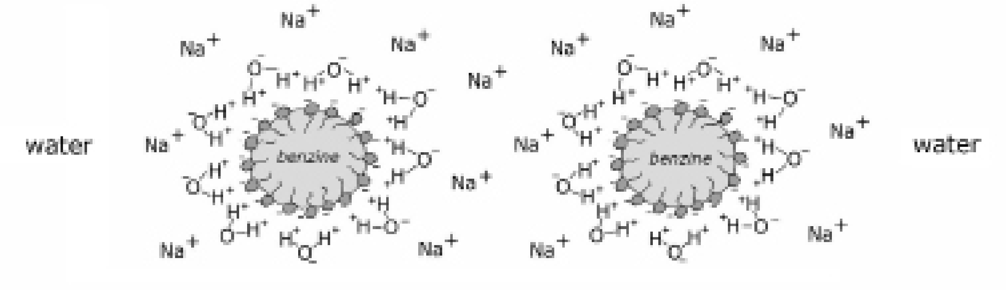


common soap

In modern surface active agents (or "surfactants"), the ionic part is frequently the sodium salt of a sulfonic acid group (**$–SO_3Na$**) created by the reaction of sulfuric acid with an organic molecule.

The molecules of the surface active agent stabilize a dispersion of non-polar droplets by adhering to them with their long non-polar "tails" and orienting the ionic "heads" towards the water, while the positive ions (sodium or potassium) are surrounded by water molecules and dispersed in the liquid.

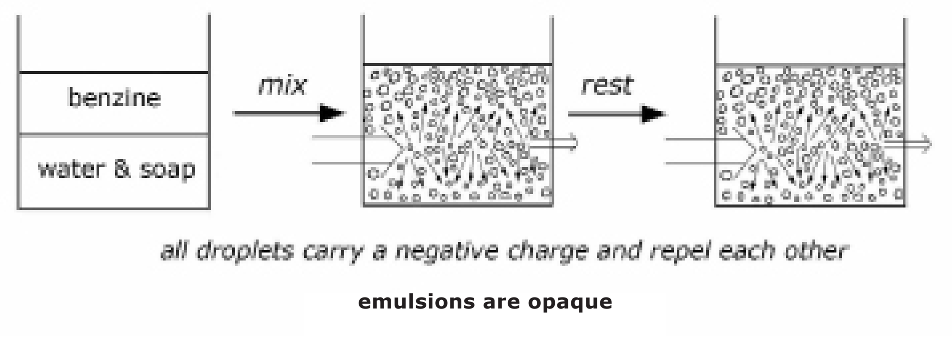
Figure 1.69



emulsion

As a result, all droplets are coated by a layer of negatively charged ionic groups that can attract water molecules; the droplets repel each other because they all have the same electric charge.

Figure 1.70



Today, water emulsions of adhesives and paints that are insoluble in water frequently substitute true solutions in industrial uses and also in conservation because **solvents**, besides being **expensive**, are also **toxic** (most of them) and **flammable**. They are also considered as **atmospheric pollutants** by the most recent legislation aimed to impose limits on the use of volatile organic compounds (**VOC**).

Emulsions are easily recognized from solutions because they are opaque and milky white (milk is an emulsion of fats and proteins in water) and almost odorless, while solutions are clear liquids that smell of solvent.

There are also disadvantages, however, in the use of emulsions in conservation. One is that several admixtures (surfactants, stabilizers, biocides) are always added to emulsions in order to improve their shelf life, and these may impair the aging properties of the adhesive or paint that has been emulsified.

A second disadvantage is that the dispersed particles of an adhesive in an emulsion are much larger than the isolated molecules of the same adhesive in a solution; hence the penetration of emulsions into porous solids is more difficult.

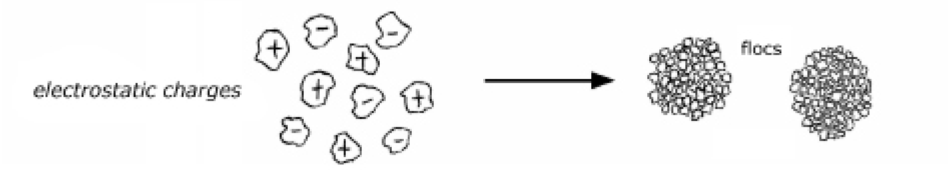
1.6.4 Water reducers, plasticizers

Water reducers are polar organic molecules that are used in building technology to ease the mixing of mortars and concretes, allowing a reduction of the amount of water that is necessary to achieve a satisfactory result.

As will be discussed further on (see chapters 2.4, 2.5, 2.6, 2.7), any reduction in the amount of water used for mixing causes an increase of the strength of the hardened paste.

Water reducers adhere to the surfaces of the grains of binders and sand, forming an extremely thin film that improves the attraction to water and helps dissolve flocs, which are formed by the electrical attraction of positive and negative charges created by grinding processes or attrition between particles.

Figure 1.71



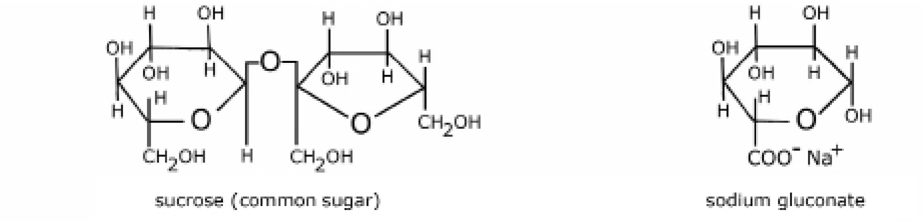
formation of flocs in the fine aggregate of mortar or concrete

The amount of a water reducer added to a mortar or a concrete is always very small, in the range of 1% of the weight of the binder (lime or cement); an excess would result in inferior mechanical properties of the hardened mortar.

Hints in the technical literature and surviving traditions among masons point to the fact that water reducers must have been widely used since antiquity to improve the performance of lime mortars and concretes. The most likely candidates for such a role are sugary juices from plants and fruits.

Today, we know that sucrose (common sugar) is a fairly effective water reducer, and the first industrial water reducer of modern times is a derivative of glucose, **sodium gluconate,** still used in conservation as an admixture for grouts used in the consolidation of detached plasters (see section 4.3.2).

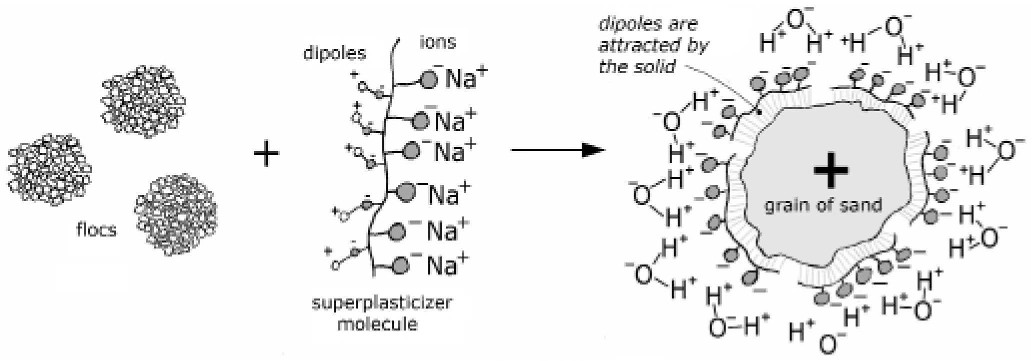
Figure 1.72



sugar and sugar derivatives used as water reducers

Superplasticizers, presently used in modern concrete, are linear synthetic polymers (see chapter 6.5); very long, dipole-rich molecules to which many acid groups neutralized by sodium ions have been attached. In the earliest types the **sulfonic acid** group (–SO_3Na) was used, but now the up-to-date superplasticizers are **acrylic polymers** in which the neutralized carboxyl group (–COONa) is the active element.

Figure 1.73



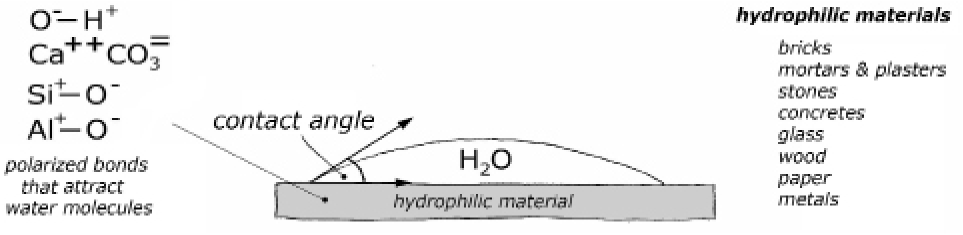
superplasticizer

1.7 Hydrophilic and Hydrophobic Materials

1.7.1 Hydrophilic materials

The surface of most architectural materials is rich in groups of atoms, such as the hydroxyl group ($^{-}$O-H^{+}), which carry electric charges and are able to attract water molecules. These materials are said to be **hydrophilic**; water spreads on their surfaces, wetting them. If a drop of water is deposited on the surface of a hydrophilic material, the **contact angle** of the drop is **small**.

Figure 1.74

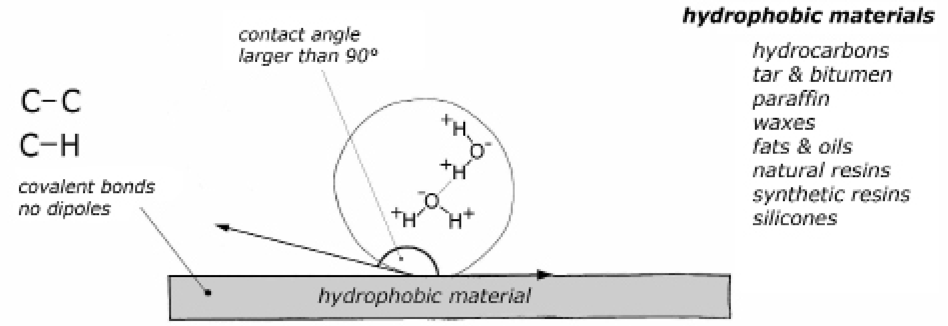


Bricks, stones, plasters, concretes, gypsum, glasses, paper, and wood are all hydrophilic materials. Also, metals are hydrophilic if their surface is slightly oxidized (as happens to most metal surfaces when in contact with air).

1.7.2 Hydrophobic materials

Materials that show on the surface very few (or no) electrical poles, or ions, are unable to attract water; these materials are called **hydrophobic**.

Figure 1.75



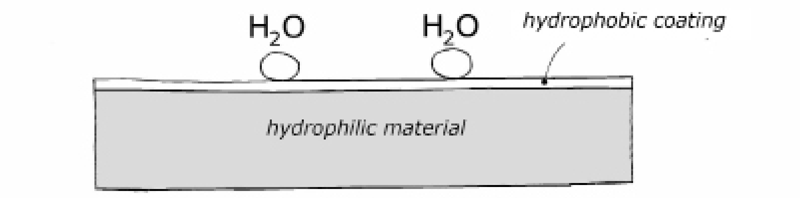
Water does not wet their surfaces, spreading as a continuous film, but rather contracts into isolated drops whose contact angle is large (over 90°).

A hydrophilic material whose surface is dirty may appear to be hydrophobic because most of the surface is covered by a film that doesn't attract water (grease, smoke, dust); cleaning with water containing a surface active agent removes the film of dirt, and the hydrophilic character of the surface is observed again.

Surfactants may also be used to improve the wetting by water of a hydrophobic surface.

A hydrophobic film may be intentionally applied to an architectural surface to protect it against physical and chemical decay processes activated by their contact with water (see chapters 3.2 and 3.3 for rigid and porous building materials and section 5.1.6.2 for metals).

Figure 1.76



If the surface of the material is vertical, the water drops are unable to adhere to it and roll down. Unfortunately, the water-repellent effect of hydrophobic films is not permanent because the organic non-polar groups that produce the hydrophobic effect are chemically modified by the action of oxygen and solar radiation (a process called **oxidation**), and after a few years the surface slowly reverts to its normal hydrophilic condition (see chapter 6.6 on the oxidation of organic molecules).

Part 2

Mortars, Bricks, and Concretes: Earth, Gypsum, Lime, and Cements

2.1 Earth as a Building Material

2.1.1 Soil classification

Origin

Earth (soil) is the product of the deterioration of rocks caused by chemical, mechanical, and biological processes such as frost, thermal cycles, rainwater, dew, microorganisms, and plants. The material resulting from the initial breakout of the rocks undergoes further transformations as it is transported away, deposited as a sediment, compressed by further sedimentation, or modified by chemical processes (diagenesis) or biological colonization.

Composition

- Fragmented minerals from the original rock (volcanic or sedimentary).
- Minerals formed by chemical decay processes (e.g., clay; see section 3.3.3 for more details on such processes).
- New minerals formed by contact with water and substances dissolved in it.
- Organic molecules formed by biological processes (e.g., humic acids in agricultural soils).

Geotechnical classification

When the mechanical properties of a soil are considered in geotechnical studies, it is found that these depend essentially upon the dimension of its particles; therefore soils are classified by geotechnical engineers according to the grain size of their constituents, without reference to their chemical composition.

Soil materials are defined as follows according to the Unified Soil Classification System (USCS):

Unified Soil Classification System	
Name of soil fraction	**Grain size**
gravel	75–2 mm
sand, very coarse	2–1 mm
sand, coarse	1–0,5 mm
sand, medium	0.5–0.25 mm
sand, fine	0.25–0.125 mm
sand, very fine	0.125–0.075 mm
silt	0.075–0.004 mm
clay	< 0.004 mm

Slightly different size intervals are specified in other classifications used in Europe and in the United States, but the names of the fractions are the same.

The main components of the finer fractions, silt and clay, are **clay minerals**; soils in which the fine fractions prevail become sticky and plastic when they are wet. Silt and clay are the binders that bind the grains of the coarser fractions of the soil and allow its use as a building material.

The coarse fractions, gravel and sand, have no cohesive force by themselves, but they constitute the inert filler that limits the shrinkage of wet, plastic earth when it dries. Sand alone is like the sand on a beach: you can build sand castles with it when it is damp, but it disaggregates as it dries.

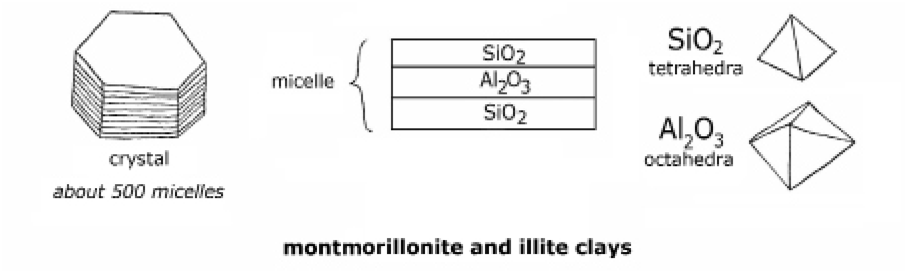
2.1.2 Clay minerals

Clay minerals are called simply clays in mineralogy, a fact that may give rise to some misunderstandings because the term is not exactly equivalent to "clay" as defined by geotechnical engineers.

Actually the "clay" fraction of soils contains also some minerals that are not clay minerals, while the "silt" fraction always contains a significant amount of clay minerals besides the non-clay components.

Clays are **aluminum silicates with a layer structure** (the technical term is *phyllosilicates*); clay crystals are formed by a stack of extremely thin layers, up to 500 of them. Each layer is called a **micelle** and is itself a stratified structure: the basic unit in the crystal of the most common clays (**montmorillonite**, **illite**) is a **three-layer micelle**, a sandwich in which the outer layers are formed by silica tetrahedrons and the central one by alumina octahedrons.

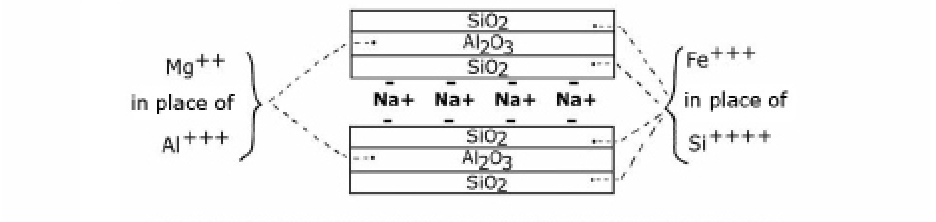
Figure 2.1



In montmorillonite and illite clays, some **silicon** atoms in the silica layers are **substituted by iron** atoms and some **aluminum** atoms **by magnesium** in the alumina layer; as the substitutes carry a smaller positive charge than that of the normal occupants of these positions, the net result is a **negative charge of the micelle**.

The assemblage of the micellae to form the clay crystal is made possible by **sodium ions** (occasionally other ions, e.g., potassium) with a **positive charge** inserted between the micellae.

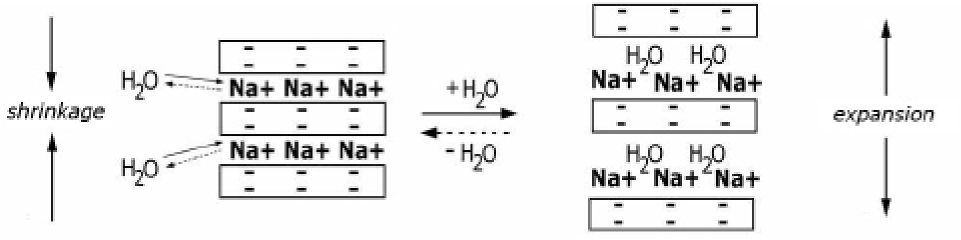
Figure 2.2



electrical attraction between micellae in the clay crystal

When clay is moistened, water molecules are attracted by the sodium ions and penetrate between the micellae, causing an increase of the distance and a weakening of the connection between them. The clay crystals swell when they are damp, but they go back to their initial size when the water evaporates.

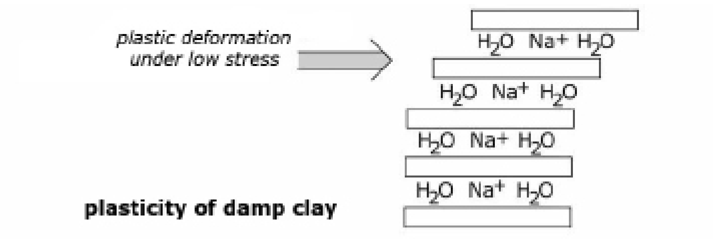
Figure 2.3



clay expansion and shrinkage

In damp conditions, clay is plastic, i.e., it can be easily deformed and will hold its new shape when dried. The flat clay crystals and the wet micellae slide easily under weak pressure, as when clay is modeled by hand. Dry clay is brittle instead.

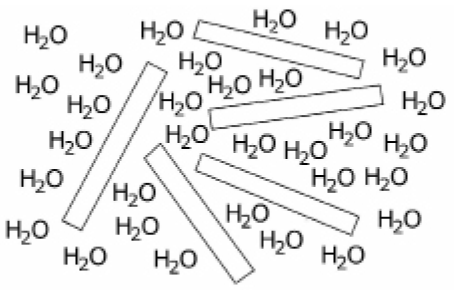
Figure 2.4



plasticity of damp clay

In the presence of a large excess of water, however, all connections between the micellae are severed and the clay micellae are dispersed into the water; the presence of the clay in the liquid is betrayed only by its opalescence.

Figure 2.5



clay dispersion in water

2.1.3 Earth as a building material

Earth used for construction must be rich enough in clay to be plastic when wet and hard when dry, but an excess of clay must be avoided because it would cause shrinkage and cracking when the wet material dries.

The composition of earth used in construction falls normally within the limits listed below.

Earth for Construction	
clay + silt	20–30%
sand	70–80%

Such a ratio may be found in natural sediments, but if these are not available in the area near the building site, a correct mix is made up by mixing sand with soil, which contains an excess of clay.

Since very ancient times, other materials have been added to the mix to improve the final properties of the hardened material in quality construction:

- **Vegetal fibers**, such as straw (quoted in the Bible) or hay chopped to 5 to 10 cm in length, improve mechanical properties, in particular tensile strength, which is very low in the hardened raw material. The mechanism is quite similar to the one induced by fibers (glass, carbon, or synthetic resins) in thermosetting resins or cement mortars in modern technology (see section 6.5.4 for a discussion of the properties of composite materials).
- **Dung** improves resistance to water, hindering the dispersion of clays in an excess of water.
- **Lime or cement** in modern earth construction technology improves both mechanical properties and water resistance. The material obtained by the addition of up to 20% lime, or 10% cement, is called **stabilized earth**.

Traditional earth construction technology includes an initial “weathering” step in which the raw material is kept under water for a long time (up to one year in some cases) to improve the plasticity of the clay. This appears to be justified by a rearrangement of the clay crystals in parallel layers, a condition that appears to improve soil plasticity when wet.

The best earth structures are built using **mud bricks** (or **adobe**) that are made by pressing the soil/fiber mixture into bottomless wooden molds, frequently 1-foot-square ones, and then drying the molded bricks under the sun. This material can easily reach compression strength values around 3 MPa. Vitruvius mentions mud brick buildings rising up to five stories high, and living examples of high buildings are visible in Yemen, Iran, and elsewhere.

An important function in earth buildings is performed by the **plasters** that must be applied to avoid damage to the core structure when the walls are hit by heavy rains. Traditional plasters are made of clay-rich soils mixed with long vegetable fibers; in external exposures they act as sacrificial protection layers that are periodically substituted when the superficial earth has been washed away and the fibers are visible. Inside the buildings, however, such plasters may well have decorations, in relief and with colors, which are intended to last; when the buildings were kept in good shape by an adequate maintenance, such decorations did indeed survive for centuries.

The use of cement or lime plasters on the external surfaces of earth buildings, contrary to expectations, proved to be less efficient than the traditional system in experiments carried out by the National Park Service on ancient constructions in New Mexico. Actually, a water-resistant plaster keeps longer but transfers the risk of damage to the internal core whenever a local failure of the outer shield—which in the long run is inevitable—opens the way to water penetration. Furthermore, internal damage may easily escape detection until very serious consequences make it evident.

2.1.4 Clay as a moisture barrier

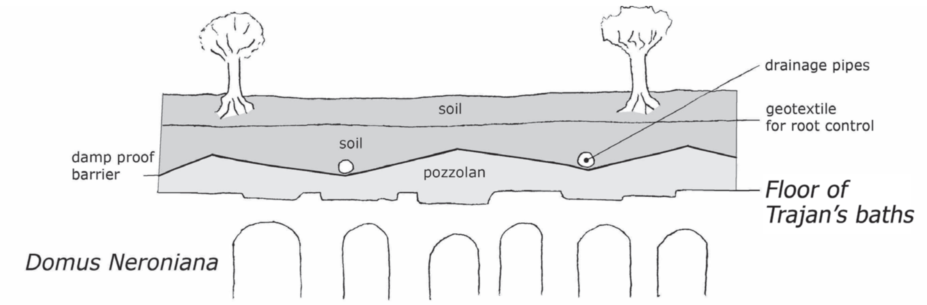
The swelling of clay when in contact with water may be exploited to arrest its penetration into built structures because the swollen clay tends to inhibit the passage of water if it is lying under other materials (such as sand, gravel, or earth) that exert pressure strong enough to impede its expansion.

A special clay, **sodium bentonite**, is particularly suited for this task, as it expands its volume over twenty times when it absorbs water and is free from constraints.

Such a water barrier offers the advantage over the current ones based on organic water-repellent materials of being practically immune from aging processes (oxidation or biological attack).

Figures 2.6 and 2.7 show the application of a bentonite barrier designed by I. Massari to avoid rain penetration in the buried structures of the Domus Aurea, the emperor Nero’s palace in Rome, which survived with most of its interior decorations having been included in the foundations of Trajan’s baths.

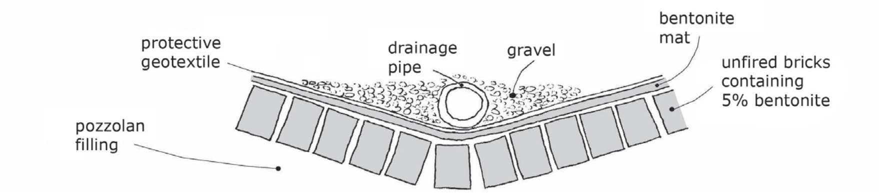
Figure 2.6



protection of the Domus Aurea from rain infiltration

Bentonite may be applied as a powder, but in this particular case another commercially available form was used, consisting of a layer of clay enclosed between two polypropylene geotextile sheets sewn together. This sort of quilt was laid on top of a floor of unbaked bricks upon which some bentonite powder had been spread.

Figure 2.7



detail of the damp proof barrier over the Domus Aurea
(design by I. Massari)

The barrier is built with appropriate slopes that allow the flow of rainwater through the main drainage pipes connecting to the sewage system; the regularity of the flow is ensured by a network of minor drainage pipes feeding the major ducts. The whole drainage system is covered by a bed of gravel and an earth fill that contains another geotextile sheet that should impede the penetration of roots from the garden vegetation into the water barrier.

2.2 Ceramic Materials

Ceramics are produced by firing metal oxides, or mixtures thereof, at temperatures that are high but not high enough to cause complete melting of the solid (although partial melting may occur).

Architectural ceramics are mostly made by firing clays that are shaped in the wet condition, then dried and fired; the properties of the final products depend upon the type of clay and the temperature of firing.

2.2.1 Terra-cotta and bricks

Composition

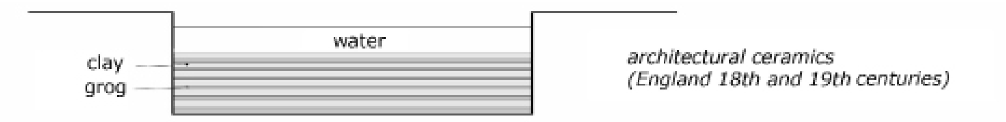
Terra-cotta products such as bricks and floor or roof tiles are made from natural clays of the illite-montmorillonite type, with the addition of fillers, inert materials that do not undergo transformations or shrinkage up to the firing temperature.

The filler material may be siliceous sand or, quite frequently, **grog** (called **chamotte** in France and Italy), which is made by grinding fired terra-cotta from previous production. Ancient Roman bricks and tiles frequently contain pozzolana as a filler.

“Weathering”

As was mentioned earlier, the plasticity of clay improves after a period of immersion in water. An example of such a practice is offered by the manufacture of stoneware in England in the eighteenth and nineteenth centuries. Clay was laid down in pits, in layers alternating with layers of grog of appropriate thickness, covered with water and left there for at least twelve months. At the moment of use, carving into the layered material yielded “weathered” clay and grog in the appropriate proportions.

Figure 2.8



“weathering” clay in a pit

Mixing, filtration, and air removal

Preparation of the clay for molding in the required shape is a critical step that conditions the success of the whole process. After an accurate mixing, the clay is filtered to remove mineral fragments or vegetal inclusions and then air bubbles are removed by pressure filtration and gas removal under vacuum. In the past, clay would be passed through sieves and then laid down in flat sheets and beaten to expel all entrapped air.

Molding

In the past, bricks and tiles were formed by hand, but today molding is fully mechanized. Clay is pressed into molds or extruded and cut, the latter, e.g., in the production of hollow bricks.

The dimensions of the clay objects before firing must be calculated, taking into account the shrinkage that is foreseen in the drying and firing stages.

Drying

In order to avoid cracking or deformation caused by the shrinkage of the clay, drying must be very slow. Since the nineteenth century, the drying process has exploited the hot gases exiting from the firing furnace; this is achieved either by moving the clay objects slowly towards the fire or by moving the fire towards the clay (as in the Hoffman furnaces).

Firing

Today, firing temperatures are in the 1000°C to 1100°C temperature range; stoneware is produced from similar clay mixtures at slightly higher temperatures (1100°C to 1200°C). Lower temperatures were normally used in the past, furthermore, temperature was not constant inside old furnaces, so bricks from different positions inside the furnace would have different properties, those fired at higher temperatures showing greater strength. The produce of a firing could be easily sorted according to the color; a yellow color, resulting from a lower firing temperature (possibly 700°C to 800°C), suggested lower quality, whereas red and pink colors (firing up to 1000°C and more) would indicate better mechanical properties.

The color of the fired clay depends also, however, upon the chemical composition of the initial material: the iron content determines the intensity of the red hues, while calcium and magnesium tend to lighten the color by forming white products. Iron-free clays must be used to obtain a white ceramic body.

In the course of the firing, several transformations occur:

- around **500°C the crystal structure of the clays is destroyed** and amorphous (non-crystalline) silica and alumina are formed;
- at **600°C to 700°C** sodium or potassium ions present in the clay cause the **melting of part of the silica** which will form a glass in the cooling phase;
- starting from **800°C to 900°C** solid-state reactions start happening involving silica, alumina, and some metal oxides present as minor components in the initial mixture. Aluminum silicates like **diopside** or **gehlenite** may be formed.

The identification of such crystalline materials in a terra-cotta may provide an indication of the firing temperature.

Properties

Firing transforms the plastic clays into a hard, brittle, porous material that can withstand contact with water without excessive loss of strength.

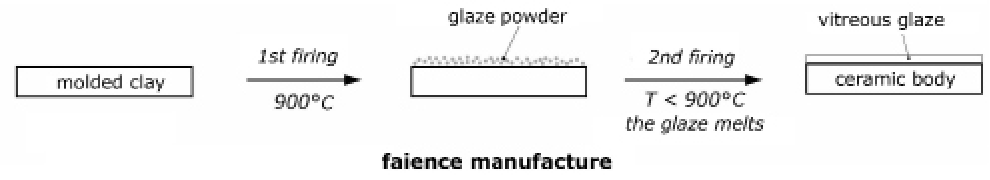
Terra-cotta does not swell like clay under the action of water and cannot be used to form a moisture barrier; on the contrary, capillary forces attract water into the pores and may cause serious decay processes (see chapter 3.2).

Compressive strength varies according to the firing temperature and the quality of the clay, but for an average brick it may be estimated around 30 MPa. Also, the resistance to abrasion (an important property when terra-cotta tiles are used for floors) is improved by firing at higher temperature.

2.2.2 Faience (majolica)

Faience is made by creating a **glaze** (a thin layer of glass) on a fired clay body. The glaze seals the pores of the surface and allows one to decorate it.

Figure 2.9



Majolica glaze is made up of a **low melting** compound, frequently **tin oxide,** which forms a glass on cooling. Various metals are added, mainly as oxides, to give a **color** to the glass: e.g., cobalt for blue, iron for green, lead and antimony for yellow, gold for red. An easily burning organic binder may be added to improve adhesion of the raw enamel to the fired clay (it would disappear in the second firing).

The vitreous layer is formed by a second firing at a temperature that is lower than the one applied when the ceramic body was created.

Important **wall and floor decorations** were created with faience tiles in Asia (e.g., Iran), Europe (e.g., Germany, Italy, Spain, Portugal), and South America (e.g., Brazil). Their conservation is not easy when they are directly exposed to the external environment because a combination of physical, chemical, and biological processes leads to the detachment of the glaze from the ceramic body: a slow process that may require some centuries to develop.

Also, floors in both external and internal environments are easily spoiled by pedestrian traffic because of the **low resistance to abrasion** of the tin oxide glaze; the only effective conservative provision is the prohibition to walk on such surfaces.

2.2.3 Gres (clinker)

Gres is a modern type of glazed ceramic that is fired at a much higher temperature (1300°C to 1400°C) than the majolica bodies. Also, the **glaze** is different, being composed largely of **silica with suitable admixtures** that allow melting at a temperature somewhat lower than the one used to fire the ceramic body, but much higher than the one used for the tin oxide glaze.

As a result, **more resistant bodies and surfaces** are produced, which allow the use of these tiles in heavy traffic areas (stations, airports, supermarkets, and museums).

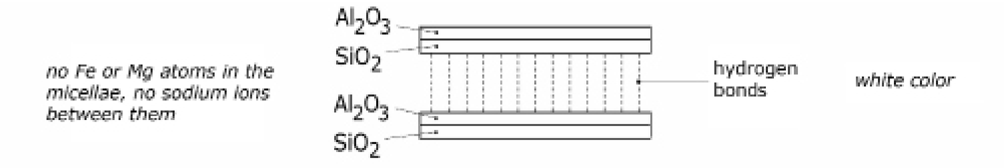
2.2.4 Porcelain

Porcelain is made using a different type of clay from the ones employed in the production of terra-cotta, majolica, and gres.

The main component of **kaolin clay**, or China clay, is a mineral named **Kaolinite**, made up of a stack of silica/alumina layers like all other clays but with a **two-layer** structure inside the **micellae**, one of silica tetrahedrons and one of alumina octahedrons. The micellae are not electrically charged and, as a consequence, sodium ions are not found between them; they are assembled to form the crystal by hydrogen bonds between the alumina layer (which carries many polar $^{-}$**O-H**$^{+}$ groups) and the negative oxygen atoms of the silica layer of the next micella.

The clay crystals contain very few extraneous atoms; in particular the **absence of iron** results in a colorless material that, on firing, produces white ceramic bodies.

Figure 2.10



kaolinite

Kaolin clay is less plastic than the clays of the montmorillonite type, because water does not penetrate easily between two micellae; it is harder to mold but produces ceramic bodies with better mechanical properties.

Porcelain is manufactured by firing at a high temperature (about 1400°C) a mixture of **kaolin**, **quartz**, and **feldspar** (an aluminum silicate rich in potassium).

In the firing process, kaolin is decomposed around 500°C and feldspar melts not much above that temperature, because of the abundance of potassium in its composition; the molten material dissolves some of the silica and alumina from kaolin. Above 1200°C a new crystalline composition of silica and alumina is formed, called **mullite**.

Upon cooling, the residual molten material forms a **large amount of glass** that fills the free spaces between the crystals (quartz and mullite) so that the final body is almost free of pores.

A high-melting, silica-rich **glaze** is applied in a **second firing** at a temperature above 1000°C; this improves the imperviousness of the surface and makes it possible to apply a decoration, if desired.

2.3 Gypsum

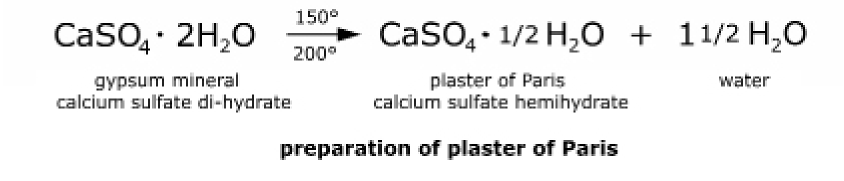
Gypsum is the most ancient artificial binder used to make mortars and plasters (e.g., a mortar between blocks in the Cheops Pyramid, about 2900 BCE).

The mineral gypsum, chemical name calcium sulfate dihydrate, is the raw material used to prepare the gypsum binder used to make gypsum mortars and stuccoes; the use of the same name for the mineral, the binder, and the final product (plaster or mortar) may easily cause confusion. Many trade names have been used in the past to designate various types of gypsum, but these hardly help to understand the real nature of the material involved.

2.3.1 Hemihydrate gypsum (plaster of Paris)

The mineral is heated at a moderate temperature (150°C to 200°C) and is transformed into the binder through the removal of three-quarters of the water it contains. The chemical reaction is usually written as shown in figure 2.11.

Figure 2.11



$$CaSO_4 \cdot 2H_2O \xrightarrow[200^\circ]{150^\circ} CaSO_4 \cdot 1/2\,H_2O + 1\,1/2\,H_2O$$

The partially dehydrated calcium sulfate, whose name in chemistry is calcium sulfate hemihydrate, takes up again the water it lost as soon as it gets a chance; the speed (the technical term is *rate*) of this reverse reaction depends upon how it was previously heated.

If the humidity of the air in the oven is not controlled and drops because of the rise in temperature, small crystals are produced and the specific surface of the binder is high; as a consequence it is very reactive. This type of gypsum, whose chemical name is β- (beta) **gypsum** (class A in British Standard BS 1191), is the most common one and is frequently called plaster of Paris (in some nations the name of the city would be of a local one, e.g., *gesso di Bologna* in Italy). It reacts with water and hardens ("sets") quite rapidly (3 to 4 minutes).

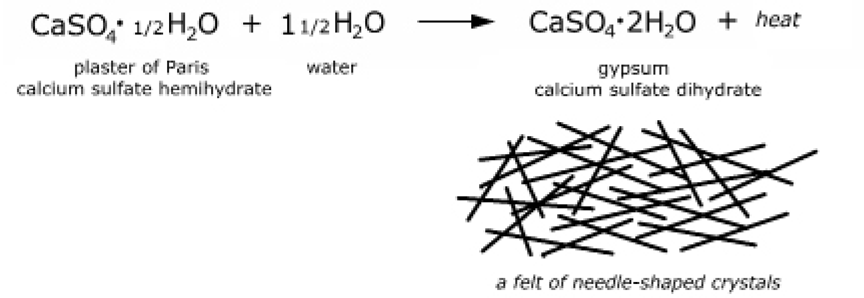
When a time-consuming job must be made with the mortar, the setting reaction is retarded by the addition of some organic material (class B gypsum in BS 1191).

If the air in the oven is kept damp, the crystals of the hemihydrate are formed slowly and grow to a larger dimension than in the previous case; the specific surface is therefore smaller than in the β type. This type of gypsum, which is called α- (alpha) **gypsum**, hardens slowly when mixed with water.

2.3.2 Hardening reaction

When in contact with water, calcium sulfate hemihydrate returns to the fully hydrated form whose needle-like crystals grow rapidly, forming a felt-like mass in which some water is trapped inside the solid. The temperature rises due to the heat produced by the hydration reaction, and the trapped water evaporates, leaving behind many microscopic voids.

Figure 2.12



hardening of gypsum

As a consequence, plaster of Paris does not undergo a reduction of volume (shrinkage) upon hardening, a property that sets it apart from all other materials used as binders in mortars.

2.3.3 Overheating of gypsum

Surprisingly enough, heating gypsum mineral at higher temperatures does not improve its hardening properties. Above 200°C, complete removal of the water from the crystal begins and the anhydrous sulfate that is formed (called anhydrite III) still reacts with water but quite slowly.

The slow setting of anhydrite is compensated by the addition of setting accelerators (frequently aluminum-potassium sulfate, alum) to produce plasters with better mechanical properties (class C of BS 1191). A somewhat higher firing temperature, and again the addition of an accelerator, is used for the production of Keene's Cement (class D of BS 1191), a material mentioned in both U.K. (BS) and U.S. (ASTM) specifications.

Also to this class belongs a material that was used in Italy and mixed with glue, unheated gypsum as a filler, and pigments to prepare a slow-setting stucco used to produce colorful surfaces (e.g., tabletops), called **scagliola**.

Above 300°C, the products formed (anhydrite II first, then anhydrite I at higher temperatures) do not react with water anymore so that the material may be used as an inert filler or a white pigment only. In Italy it is called *gesso cotto a morte*, i.e., “fired to death” gypsum.

A different type of reaction with water is made possible when gypsum is fired at a much higher temperature, e.g., around 1000°C. Calcium sulfate is in part decomposed into calcium oxide and sulfur trioxide, a gas. The resulting mixture of calcium oxide and anhydrous calcium sulfate reacts with water and sets to form a material that is hard enough to be polished; when it is analyzed after setting, it is found to be a mixture of almost equal parts of calcium carbonate and calcium sulfate. This material enjoyed a period of fashion for the production of decorated floors in northern Italy in the nineteenth century, when it was sold under the trade name *gesso idraulico* (hydraulic gypsum).

2.3.4 Properties of gypsum

The rapid setting and the absence of shrinkage (there is even a **slight expansion** when a gypsum/water paste hardens) make gypsum a very useful material for several jobs, e.g., making molds or casting stucco decoration.

Gypsum may thus be used without fillers or admixtures, but its mechanical properties, after setting, are **rather weak** (its surface may be scratched by a fingernail). Gypsum is also slightly soluble in water, and its weak mechanical strength is further reduced in a damp environment.

Several formulas were developed since ancient times to improve gypsum’s hardness and water resistance.

The addition of alum (a sulfate of aluminum and potassium) causes an increase of hardness and, as mentioned above, accelerates the setting reaction. Potassium and sodium silicates are mentioned in the technical literature as consolidants. Synthetic resins are now frequently added to gypsum as emulsions in water.

As calcium sulfate is an acid salt (see section 1.5.5), **damp gypsum is weakly acid**, a property that is a negative factor if the mortar is to be used in contact with iron or steel parts, as their corrosion is favored by an acid environment.

Today, strong objections are raised against the use of gypsum mortar in architectural conservation; calcium sulfate is a **soluble salt**, even if only weakly soluble, and it is known to cause damage to lime plasters, bricks, or stones (see section 3.2.4).

2.3.5 Lime-gypsum mortars

Documents from the seventeenth and eighteenth centuries show that in Italy, masons needing a fast-setting, reliable material for masonry repair jobs frequently used lime/gypsum mixtures in variable ratios.

Actually, the use of such mixes has some good points because gypsum ensures a fast initial setting, while lime improves mechanical properties and water resistance.

Also, the occasional use of lime-gypsum-pozzolan mixtures for large repair jobs has been proved by the analysis of baroque façades in Rome.

When modern hydraulic binders such as hydraulic limes and Portland cement became available, such practices disappeared from the trade.

2.4 Lime and Lime Mortars

The most ancient use of lime in building technology, as far as we presently know, goes back to the fourth millennium BCE in Anatolia and Palestine, but, at that date, lime appears to have been only a medium to paint walls.

Lime as a binder in mortars applied on wall surfaces, i.e., plasters, is found in the Knossos palaces of the Minoan age (around 1700 BCE), but the use of lime mortars to build walls is far more recent; the thin layers of almost pure lime between stone blocks, as in the republican walls of Rome, appear to be more an aid for setting them in the right position than a structural component of the masonry. A structural function of lime mortars and concrete is not documented earlier than the third century BCE in Rome and coincides with the addition of pozzolanic materials, which modify the chemistry and technology of lime (lime/pozzolan mixtures will be discussed separately in chapter 2.5).

In the chemical language, the term *lime* is applied only to calcium oxide (formula CaO), but in the current use by architects and engineers its use is extended to other members of the family of materials derived from calcium oxide; this may give rise to awkward misunderstandings as the same name may be applied to materials exhibiting quite different properties. A correct use of the technical names of lime products is shown in the following table.

Limes		
Technical name	**Chemical name**	**Chemical formula**
quicklime	calcium oxide	CaO
hydrated lime	calcium hydroxide	$Ca(OH)_2$
lime paste	calcium hydroxide + water	$Ca(OH)_2 + H_2O$
natural hydraulic lime*	di-calcium silicate + calcium hydroxide and/or calcium oxide	$C_2S^* + CH^*$ some C^* and a little C_3S^*
hydrated hydraulic lime* or hydraulic lime*	tri-calcium silicate + di-calcium silicate + calcium aluminates + inert fillers	$C_3S^* + C_2S^*$ and others

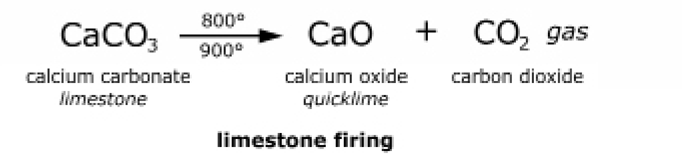
***Hydraulic lime** is a hydraulic binder that is discussed in chapter 2.6 (for a definition of hydraulic binders see section 2.5.2); the modified chemical formulas used for hydraulic limes in the table above are consistent with the simplified system currently used in the cement industry (see section 2.6.1).

2.4.1 Lime manufacture

2.4.1.1 Firing (calcination)

Lime is prepared by firing limestone composed mainly of calcium carbonate at temperatures above 700°C; in the calcination process, calcium carbonate is decomposed, losing gaseous carbon dioxide and 40% of its weight. The residual stone is surprisingly light and is called quicklime because of the rather violent reaction that occurs when it is immersed in water.

Fgure 2.13



As the temperature inside ancient lime kilns was far from constant, it frequently happened that part of the limestone charge would receive insufficient heat and would not be transformed into quicklime. This material could be sifted out of the paste that is formed in the second phase of lime manufacture and found occasionally some special use (e.g., mosaic tesserae in Venice).

A worse problem could be caused by the overheated parts in which calcium oxide would undergo "**sintering**," i.e., coalescence into very compact nodules that would not react with water in the second phase of the process. They would react much later (even centuries), increasing in volume and shattering any set mortar in which they might have been included.

Also, these nodules would be sifted away when lime paste was purified in a good technology, but notable exceptions occurred in the past in times of hasty or careless production.

2.4.1.2 Slaking

As mentioned above, calcium oxide reacts rapidly with water, producing a large amount of heat; the temperature of the water may well soar above its boiling point and dangerous droplets of hot caustic liquid may be sprayed all around. This operation, called slaking, would be carried out in the past in a pit excavated in the ground in order to keep the operators at a safe distance.

Figure 2.14

The product of slaking is "lime paste," a smooth white paste that contains calcium hydroxide, water, and a little calcium carbonate. An average composition is shown below.

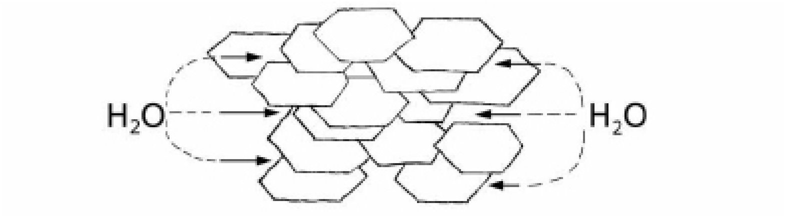
Lime Paste	
calcium hydroxide	40–45%
water	50–55%
calcium carbonate	2–5%

Lime paste is said to be "plastic" because when squeezed between fingers it feels greasy. This is an important property as it allows to mix the paste with sand to make a mortar of high quality without requiring any addition of water (besides that which the paste already contains).

Silica-rich impurities in the limestone that is fired result in a "lean" lime paste of reduced plasticity not suitable for the production of fine mortars (e.g., for plasters and stuccoes).

The quality of lime paste appears in general to be improved by keeping it under water for a rather long time (Vitruvius suggests one year); this may be explained by a change in the shape of the calcium hydroxide crystals (mineralogical name Portlandite). Portlandite hexagonal prismatic crystals split, producing thin hexagonal plates of sub-microscopic dimension (they are visible only under the electron microscope); it is believed that these would slide easily around each other thanks to the interposed water molecules (a mechanism similar to the one that explains the plasticity of wet clay).

Figure 2.15



plastic behavior of lime paste

Today, slaking is performed mostly by blowing steam over the quicklime; the result is a less violent reaction whose final product is a powder of "hydrated lime," which is the type of lime more widely available.

According to most masons, hydrated lime powder is not as easy to mix with sand as a good lime paste; it requires more water and so it produces mortars of inferior quality. This problem, however, may be solved by the addition of a water reducer or a superplasticizer, as suggested in the next section. An advantage of hydrated lime powder is that it can be distributed in bags and stored in the air.

2.4.2 Formulation of mortars

Inert materials must be added to lime paste to reduce the shrinkage it undergoes upon hardening.

The typical formulation of a mortar is as follows:

Lime Mortar	
lime paste	1 volume
sand	2 to 3 volumes
water	0

No water should be added because the lime paste contains enough of it to allow mixing, even if with some difficulty. Mechanical mixing and water reducers can make this operation quite easy, however.

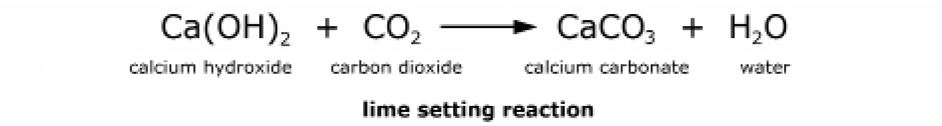
Water must be added if hydrated lime powder is used, but its volume should not exceed the volume of the lime by much. Mixing might be quite difficult with such formulations, but water reducers or superplasticizers (see section 1.6.4) and mechanical mixing normally solve this problem.

Sand should be of mixed grades of fineness in order to fill space in the most efficient way. When the volume to be filled by a mortar is large, larger fragments of stones or bricks are added; when these have dimensions above a few millimeters (4.75 mm in the European specifications), we should speak of a concrete rather than of a mortar.

2.4.3 Hardening of lime mortars

Lime hardens by contact with carbon dioxide molecules present in the air. The reaction is shown in figure 2.16.

Figure 2.16



$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Lime mortars are usually classified as air-setting mortars. When the water in the fresh mortar evaporates, air can enter the open pores and carbon dioxide can react with lime also inside the material and a complete hardening is achieved.

Hardening is accompanied by an important reduction of the volume as both the water formed in the reaction and the water present in the paste disappear; if the right amount of sand is used, shrinkage is contained within acceptable limits, although in most cases tiny cracks appear on the surface of hardened mortars (e.g., in plasters).

If water is added to the lime paste, e.g., to aid mixing, an excess of porosity is formed when it evaporates and the resulting mortar shows inferior mechanical properties. As a consequence of the nature of the setting reaction, **lime mortars do not harden properly in a very damp environment**, because water does not leave the pores open to air penetration.

Also, **lime mortars cannot be used in bulk** or in the core of thick walls because carbon dioxide would not produce the hardening in a reasonable time. Actually, unreacted calcium hydroxide is frequently found in the core of ancient walls.

2.4.4 Properties of lime mortars

When tensile and compressive strength of lime mortars is tested using the standard European test sample (4 × 4 × 16 cm prism), very low values, in the range of 1 MPa, are found, but the cross sections of the samples, swabbed with an indicator (phenolphtalein) that stains in violet all the areas where calcium hydroxide is still present, reveal that the cores have not reacted with carbon dioxide even after sixty days (not to mention the twenty-eight days prescribed by the specification).

If a lime mortar is applied as a rather thin layer, e.g., not thicker that 10 mm, and this is kept in a dry environment, much higher values should be reached, but they cannot be measured according to the present specifications.

The highest hardness is obtained with calcareous sands; “marmorino” layers, composed of lime paste and marble powder (or clear calcite crystals, crushed) were used since antiquity to simulate marble by applying a thin, hard white layer over a stucco body made with a hydraulic mortar. Also, the surface on which painted decoration was applied was a hard white layer based on the same formula, with the occasional addition of white clay (kaolin) that would allow polishing to a glossy finish.

Considering the general characteristics of lime mortars, the conclusion is reached that their most appropriate use is on the surface of masonry walls rather than in their core, provided the climatic conditions allow a proper hardening. Lime mortars are the most suitable material to make renderings as the porosity of the hardened mortars allows for an easy evaporation of the moisture that may affect the core of the walls, thus contributing to the creation of a healthier interior environment.

2.4.5 Mixed mortars

The use of lime-gypsum mortars in the past is discussed in section 2.3.5. Lime-cement mixtures have been used frequently in architectural conservation either when good quality lime was not available or when an insufficiently trained workforce appeared to be unable to produce a decent result with lime alone.

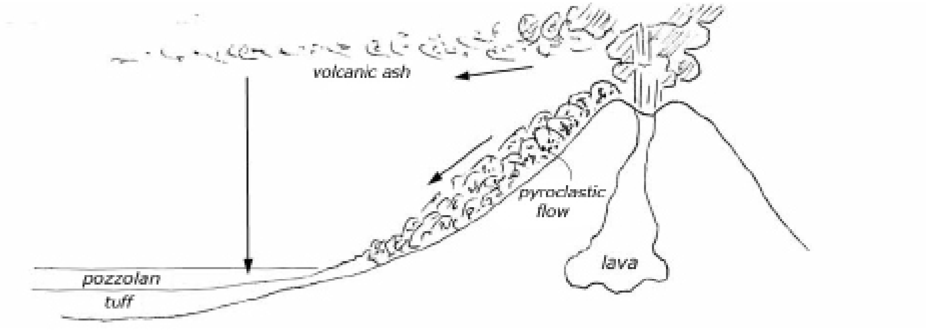
Contrary to what is frequently written in the current technical literature, lime-cement mixes rich in lime may perform quite well, if the strength requirements are not too high. A lime-cement-sand mix with the ratio 3:1:10 was tested at length in the ICCROM (International Centre for the Study of the Preservation and Restoration of Cultural Property) lab, providing compressive strengths in the standard EN test in the range of 3 MPa when a water reducer was added; it was also used to re-plaster a Tuscan villa, yielding a hard and pleasant finish, with no ill effects appearing after over twenty years.

2.5 Pozzolanic mortars

2.5.1 Pozzolan

The original "pozzolana" is a soil found near the Roman town of Puteoli (today Pozzuoli) formed by the deposition of volcanic ash, i.e., small and medium-size particles of molten siliceous material thrown into the air by a volcano during an eruption.

Figure 2.17



pozzolan

The siliceous lava, which also contains aluminum and smaller amounts of other metallic atoms like iron and potassium, upon rapid cooling in the air forms some crystalline silico-aluminates, but a large fraction solidifies as amorphous glassy particles, roundish in shape, in which some gas bubbles were trapped (**pumice** is the term used by geologists).

Pumices may be gray as in Pozzuoli, or whitish as in the Mediterranean islands, or, if iron is an important component, they may assume various colors from yellow to red to brown to black, as in the Rome area (pozzolans from the Alban Hills).

The property that made pozzolan precious in the classic age and still quite useful today is the ability of the glassy material to react with lime and water at room temperature, forming a hard mass. The setting reaction does not require the presence of air, so it may happen in a very humid environment, or even under water, or in the core of a thick wall.

Such setting characteristics allow the use of a building technique called by Vitruvius *opus caementicium*, something very similar to modern concrete technology.

Judging from surviving buildings, the earliest use of pozzolan as an addition to lime may not have happened before the middle of the third century (250 BCE), but most likely its use spread only in the second century BCE.

The claim that the concrete technique should have originated in the Greek world is not substantiated by existing buildings of such an early age, nor by the ancient literature. Another type of pozzolan was used in central Italy, in the Renaissance; it was produced by volcanoes north of Rome. In this case, the active component appears to be thin glassy fragments, frequently bent and forming stacks of loosely adhering sheets, which are called **shards** by geologists (they are found for instance in the mortar on which *The Last Judgment* was painted in the Sistine Chapel).

In the course of history, other volcanic materials were found possessing the same surprising properties as the Italian pozzolans; an important example is **trass** from the Rhine valley (also called *tarras* in the past), which was used in northern Europe and England up to the time when modern hydraulic limes were introduced.

Also, fire made by men may produce glassy materials that can react with lime at room temperature. Since ancient times **crushed bricks or tiles** were used for their pozzolanic activity (*cocciopesto* mortars are discussed in section 2.5.4) and, occasionally, also **iron slag**, a by-product of ironworks.

Presently, the demand for pozzolanic materials is again high, for reasons that are explained elsewhere in this text (see section 2.8.2), and other industrial by-products, such as **fly ash** or **silica fumes**, are widely used throughout the world.

2.5.2 Lime-pozzolan mortars

Amorphous silica and probably also amorphous alumina from the vitreous pumices react with water and lime to form hydrated calcium silicates and hydrated calcium aluminates whose formula has not been exactly defined so far.

Figure 2.18

$$Ca(OH)_2 + H_2O + SiO_2 \cdot Al_2O_3 \text{ glass} \longrightarrow \text{hydrated calcium silicates, hydrated calcium aluminates}$$

lime - pozzolan reaction

As the setting reaction does not depend upon carbon dioxide, hardening may well take place even if air is not available (e.g., under water). Mortars like these, which set by reaction with water, are called **hydraulic**, a category that includes all mortars made using the modern hydraulic binders, i.e., hydraulic lime and cement.

The calcium silicates and aluminates formed in the setting reaction are not stable when exposed to air and carbon dioxide; a phenomenon called **carbonation** affects all hydraulic mortars, both ancient and modern. As air penetrates slowly into the core of the mortars after they have dried out, the hydrated calcium silicates and aluminates are transformed into calcium carbonate while silica and alumina are left in amorphous conditions; these remains are the only surviving traces of a hydraulic reaction which took place in the past. This topic will be discussed again later in these lectures (chapter 2.7) because of the importance it has in the deterioration of modern reinforced concrete.

Since a large part of the pozzolan does not react with lime, it works also as an inert filler, reducing shrinkage; the addition of sand, therefore, is not required and, as far as we know, it was not usual in the Roman technology. Sand is occasionally added to the mix in Italy today.

The typical composition of a lime-pozzolan mortar is shown below.

Lime-Pozzolan Mortar	
lime paste	1 volume
pozzolan	2–3 volumes
water	0

No water should be added in the preparation of the mix, but water is to be used later once the mortar has been set in place, to keep it wet because it is important to avoid rapid drying. The setting reaction is not very fast and requires the presence of water for a rather long time; quick drying would lead to insufficient hardening, or no hardening at all. The problem was well known by the ancient builders, as shown by the contract made to build the lateral walls of the church of Sant'Andrea della Valle in sixteenth-century Rome, which stipulates that all masonry must be kept wet for a month after construction.

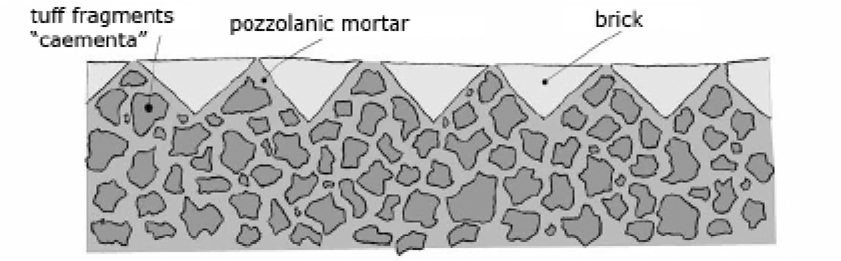
Compressive strength tests of lime-pozzolan standard bars, held twenty-eight days under water, showed values in the range of 6 MPa.

2.5.3 *Opus caementicium*

The concrete used in republican times in ancient Rome to build the cores of walls was made of a lime-pozzolan mortar and an aggregate of large splinters of volcanic tuff, called *caementa* in Latin, a word apparently derived from the verb *caedo* ("to split").

In above-soil structures, the concrete core would grow parallel to the facings of the walls, as the more or less flat splinters were laid down carefully and all voids were filled with the mortar. Facings would be made up of dimension stone in the early times, but later more refined and more economic methods were used; the oldest, **opus reticulatum**, was made of small truncated tuff pyramids, shapes laborious to make (slaves work) but easy to assemble. Later, in **opus testaceum** the facing was made of triangular bricks easily prepared by splitting along the diagonals the standard one-foot-square brick. An ideal cross section of a Roman concrete wall with a brick facing is presented in figure 2.19.

Figure 2.19



cross section of a Roman concrete wall with brick facing

In Rome some variations of the initial technique appeared in the imperial architecture; courses of bricks might alternate with *opus reticulatum* bands in the facings, while material recovered from demolition, stones, and also fragments of old concrete were frequently used in the cores.

The mechanical resistance of these structures is often quite high; compressive strengths of 15 to 20 MPa have been occasionally measured on samples cored out of the walls.

The structure of the foundations was not as well cared for; mortar and aggregates were mixed and thrown in the excavated pits, often lined with planks, more or less like it is done today with modern concrete.

2.5.4 *Cocciopesto*

Firing of clay-based ceramics involves a partial melting of the clay and the glass formed in the cooling can react with lime at room temperature; therefore ground terra-cotta shows some pozzolanic activity. The reaction with lime, however, is much slower than in the case of volcanic ash and a long permanence of mortars in moist conditions is required in order to develop a high mechanical resistance. When such conditions are realized, however, the strength of the final product is quite impressive. Samples from mosaic foundations in Sicily showed compressive strength well above 10 MPa.

A traditional *cocciopesto* (literally, "crushed shard") mortar would be composed of lime paste, finely ground crushed brick or tile, and larger fragments of the same added in amount and size appropriate to the volume to be filled. Recent experiments show that only the fine fraction shows a pozzolanic activity, the shards acting only as a low-porosity aggregate.

In refined work, in the Rome area, fine red pozzolan (the most active volcanic ash) would be added, very likely to accelerate the setting of the mortar.

Classic Roman technology used *cocciopesto* whenever a piece of masonry in service conditions would always, or at least frequently, be in contact with water. So, not only was the interior lining of cisterns (some of them still active), fountains, or swimming pools made of *cocciopesto* but also the foundations of floor mosaics, the renderings of walls built against damp soil, the pointing mortar in the brick facings of fortification structures, and the capping on top of unprotected walls.

The reason *cocciopesto* was preferred to a normal pozzolanic mortar for water containment is probably the fact that the brick or tile fragments, which are far less porous than the large pumices found in pozzolan, were thought to be able to contain water just as the ceramic vessels in everyday use did.

Today, *cocciopesto* mortars are the preferred materials for the capping of ruined walls or the paving of walkways in archaeological sites in Italy; unfortunately, their service life is frequently shortened by a faulty technology (excess water in the mix, unsuitable terra-cotta material, miscalculated fragments/fines ratio).

2.6 Hydraulic Lime

2.6.1 Symbols used in the chemistry of modern hydraulic binders

In industrial practice, technology textbooks, and most of the current technical literature, the chemical formulas of hydraulic binders are simplified thanks to the adoption of symbols that are different from the standard ones. The new symbols and the equivalent standard ones are listed in figure 2.20.

Figure 2.20

$C = CaO$ calcium oxide
$S = SiO_2$ silica
$A = Al_2O_3$ alumina
$F = Fe_2O_3$ iron oxide
$H = H_2O$ water
$\bar{C} = CO_2$ carbon dioxide
$\bar{S} = SO_3$ sulfur trioxide

symbols used in the chemistry of hydraulic binders

2.6.2 History of hydraulic lime

If a clay-containing limestone is fired in a lime kiln, a silica-lime reaction takes place at high temperature, producing di-calcium silicate (C_2S, if the special symbols are used). In the slaking phase, di-calcium silicate reacts with water at room temperature, forming hydrated calcium silicate.

If the limestone that is fired contains a small amount of clay, a fact that frequently happened in the past, the resulting lime will be "lean": when slaked in water, it will produce a paste that contains some hydrated calcium silicate and is less plastic than a paste made of pure lime. It would be less suitable to make renderings and its market price would be lower.

Firing of limestone containing 10% to 15% clay yields a type of quicklime that is quite different from ordinary quicklime; it cannot be slaked in a pit because it would harden and become unusable. If it is slaked by spraying with a small amount of water, a powder is obtained; this should be mixed with sand in a dry condition and, when water is added, the mixture should be applied immediately. It hardens best in a wet condition and produces a mortar of superior strength.

The studies of Smeaton (around 1750), Vicat (1800–1810), and several others brought about a complete explanation of the behavior of this type of lime, which today is called hydraulic lime; but it had already been known and had received different names in earlier times.

Analysis of mortars in medieval structures show that **hydraulic lime technology was actually used before the modern discovery of the process**; it is quite likely that the knowledge would be of empirical nature (e.g., limestone from some special quarry could produce such a kind of material) and did not circulate freely. In the Palladio treatise on architecture (printed 1560), clear reference is made to a lime that could be used in very damp conditions (*calce nigra*), which was produced from a limestone quarried near Padua.

In seventeenth- and eighteenth-century Italian documents, the term *calce forte* (strong lime) appears occasionally, well distinguished in name and price from *calce per ricciare* (lime to make renderings), which was the most expensive type.

2.6.3 Manufacture, setting, aging

Today, hydraulic lime is prepared by firing clay-rich limestone (marliaceous limestone) or a mixture of limestone and clay. At high enough temperatures, the reaction between lime and silica is possible and calcium di-silicate is formed.

Figure 2.21

$$\underset{\text{limestone}}{\mathrm{C\bar{C}}} + \underset{\text{clay}}{\mathrm{AS}} \xrightarrow[1100°]{1000°} \underset{\text{di-calcium silcate}}{\mathrm{C_2S}} + \underset{\text{lime}}{\mathrm{C}} + \underset{\text{alumina}}{\mathrm{A}} + \underset{\text{carbon dioxide}}{\mathrm{\bar{C}}}$$

production of hydraulic lime

As an excess of calcium carbonate is present with respect to clay, firing produces also a sizeable amount of calcium oxide (quicklime). Slaking of the latter with a calculated amount of water breaks up the burnt stone into a powder whose main components are di-calcium silicate, calcium hydroxide, and occasionally also some remains of calcium oxide.

Hydraulic lime hardens (sets) by the reaction of di-calcium silicate with water; the reaction product, hydrated calcium silicate, is also known by its mineralogical name, **tobermorite**. Also some hydrated lime (**free lime**) is formed, in addition to the one already present in the powder before the reaction.

Figure 2.22

$$\underset{\text{di-calcium silicate}}{\mathrm{C_2S}} + \underset{\text{water}}{\mathrm{H}} \longrightarrow \underset{\text{calcium silicate hydrate}}{\mathrm{CSH}} + \underset{\text{free lime}}{\mathrm{CH}}$$

setting reaction of hydraulic lime

The fresh mortar is basic after hardening, because of the initial calcium hydroxide and the free lime added by the reaction, but this condition changes progressively on aging because carbon dioxide penetrates into the mortar once it has dried and transforms the hydrated lime into calcium carbonate, which is only very slightly basic, almost neutral. Carbon dioxide also splits the hydrated calcium silicate into calcium carbonate and amorphous silica.

Figure 2.23

$$\underset{\substack{\text{hydrated calcium}\\\text{silicate}}}{\mathrm{CSH}} + \underset{\text{free lime}}{\mathrm{CH}} + \underset{\text{carbon dioxide}}{\mathrm{\bar{C}}} \longrightarrow \underset{\substack{\text{calcium}\\\text{carbonate}}}{\mathrm{C\bar{C}}} + \underset{\substack{\text{amorphous}\\\text{silica}}}{\mathrm{SH}} + \underset{\text{water}}{\mathrm{H}}$$

carbonation of hydraulic lime after setting

Amorphous silica formed by the aging of hydraulic binders is called soluble silica because, contrary to crystalline silica (e.g., quartz), it is soluble in dilute acids. Its presence in ancient mortars, if abundant, supports the hypothesis that a hydraulic binder was used.

Under the general term of *hydraulic lime* or *hydrated hydraulic lime* today, another type of hydraulic binder is marketed, which is obtained by downgrading the mechanical strength of Portland cement (see chapter 2.7) thanks to the addition of suitable inert materials or by the recycling of below-grade cement (more information in the next section).

2.6.4 Hydraulic lime mortars

As hydraulic lime undergoes some shrinkage in the hardening process, the addition of a non-shrinking, inert filler is required to produce a material with acceptable mechanical properties. In worksite practice, the amount of sand added is frequently less than in the case of lime paste mortars.

Hydraulic Lime Mortar	
hydraulic lime powder	1 part (volume)
sand	1 to 3 parts (volume)
water/hydraulic lime ratio	⅓ to ½ part (volume)

Both the amounts of sand and that of water influence the mechanical strength of the material after setting. The highest strength values are obtained, keeping sand to the lower limit and using very low water-to-lime ratios, but a water reducer or a superplasticizer (see section 1.6.4) must be added to produce a workable mix in such conditions.

Siliceous sand should produce the best results in theory, but other factors also influence the results (e.g., types of minerals, shape and size distribution of the grains).

The European specification EN 459 introduces a distinction between three categories of hydraulic limes:

- **NHL**: “natural hydraulic limes,” which are made from marliaceous limestone only;
- **NHL-Z**: if other hydraulic materials (i.e., cement) or pozzolanic ones are added, up to a maximum of 20%, to a natural hydraulic lime;
- **HL**: “hydraulic limes,” which are made up starting from “appropriate materials.”

Each category is then subdivided into three classes (2 MPa, 3.5 MPa, 7 MPa) according to the minimum compressive strength shown by a standard mortar after twenty-eight days. It is important to note that for each class a maximum value that must not be exceeded (7 MPa, 10 MPa, 15 MPa) is specified.

The ASTM specification C 141-97 (reapproved 2006) defines only one category and one class of “hydrated hydraulic lime,” with only a minimum requirement of compressive strength that would make it equivalent to the European category HL, class 3.5 MPa, but with no maximum strength requirement.

The maximum strength requirement is important for conservation purposes because hydraulic lime mortars offering mechanical strengths between 5 and 8 MPA appear to be more compatible with traditional masonry materials than mortars based on modern cements.

Not all hydraulic limes found on the market, however, are suitable for use in the conservation of ancient buildings because the most common types produce soluble salts in the course of the setting reaction. This is the consequence of the presence of alkali metal compounds (mainly sodium) in the raw materials (clay, limestone) or in the ashes of the fuel used to fire them. Also, the addition of calcium sulfates to control the rate of the setting reaction (which is necessary when cement is used instead of natural hydraulic lime as the active component) contributes to the presence of soluble salts.

For these reasons, the present trend in architectural conservation in Europe is towards the use of limes of the NHL or NHL-Z categories of EN 459 specification. A performance-based choice of materials would be certainly preferable to a choice based on a nominal classification, but this is not yet possible because of the level of quality control currently available in architectural conservation works.

2.6.5 Grouting mixtures

In the conservative treatment of architectural surfaces, the use of superficial injections of suitable fluid mixtures (**grouts**) to reinstate adhesion of parts that are partly detached from the wall structure (e.g., plasters or decayed stone surfaces) is gaining a widespread acceptance (see section 4.3.2).

The active component in the first hydraulic grouts that were successfully used, and in most of the ones that are presently available on the market, is a natural hydraulic lime that should be as much as possible free from potentially dangerous impurities such as soluble salts.

Other usual components of the grouts used in superficial consolidation are:

- a **pozzolanic material** passing through a fine sieve (the mix must pass through an injection needle), which is needed to react with all the calcium hydroxide present in the hydraulic lime, or formed as free lime in the setting reaction, in order to avoid the appearance of a white halo of calcium carbonate around the point of injection;
- a **water reducer** or a **superplasticizer** to minimize the amount of water required to achieve the desired fluidity;
- a **water-retaining agent** to hold the water in the mix, avoiding its loss by suction into the porous materials surrounding the injection point.

2.7 Cement

Modern cement is manufactured by firing mixtures of limestone and clay, just as in the case of hydraulic lime but with more clay (around 22%) and at a higher temperature (1450°C). The patent for Portland cement was awarded in 1827 to Joseph Aspdin, who claimed that his invention could produce an artificial stone as good as Portland stone (the best limestone used in construction in England).

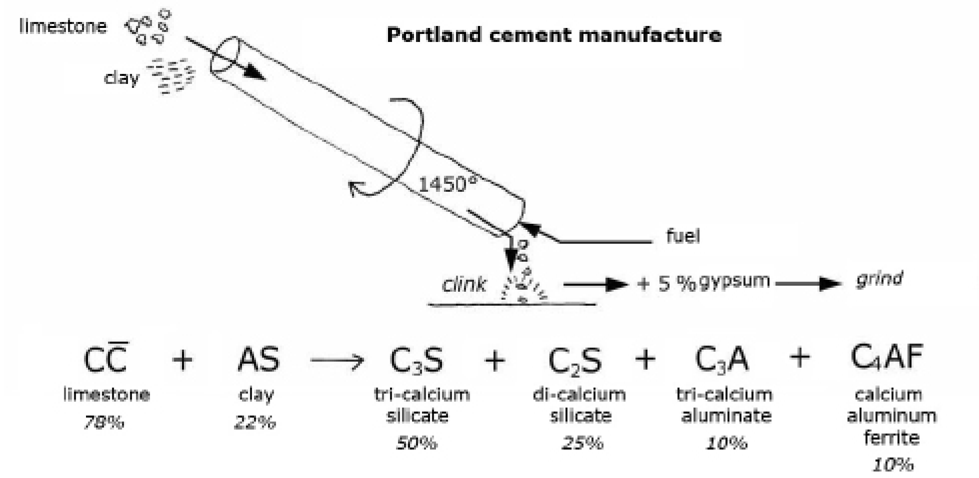
This was not yet the real thing, however, as it was only in 1845 that I. C. Johnson produced a material comparable to the present cement by reaching such a high temperature that an almost complete melting of the mixture was achieved and, on cooling, the final product of the firing was a vitrified mass. This was called "the **clinker**" because of the sharp sound it produced when it was discharged from the cold kiln and hit the floor of the shop.

2.7.1 Manufacture of cement

A clay-rich limestone, marl-stone, or most frequently a clay-limestone mix, is fired in kilns that often are large rotating tubes of great length (up to 90 m).

Clinker is very finely ground and mixed with a calculated amount of gypsum (up to 5%), which is required to reduce within acceptable limits the speed of the setting reaction that starts when the powder comes in contact with water.

Figure 2.24

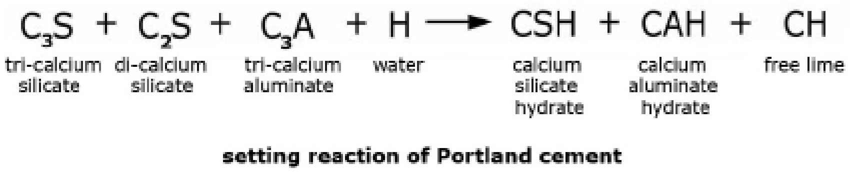


At the higher temperature reached in the firing, tri-calcium silicate, tri-calcium aluminate, and calcium alumino-ferrite are formed, all these compounds being highly reactive with water, besides the slower reacting di-calcium silicate (which is the only active compound in hydraulic lime).

2.7.2 Setting reaction

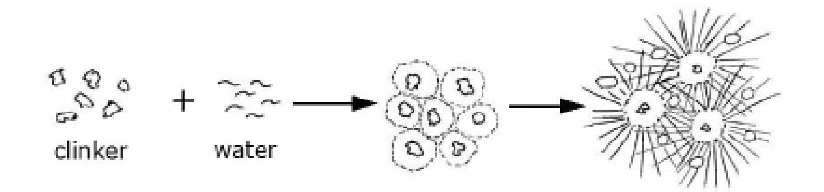
The hardening of a water-cement paste is determined mainly by the formation of hydrated calcium silicate and hydrated calcium aluminate.

Figure 2.25



The study of the hardening reaction with a scanning electronic microscope (SEM) allowed the observation of a first stage in which gelatinous globules are formed around the clinker grains and a successive one in which a great number of fibers of hydrated calcium silicate (**tobermorite**) break out of the globules and spread around, causing the hardening of the paste. The fibers are, at least in part, crystalline. Hexagonal crystals of hydrated lime (**portlandite**) are also visible among the fibers.

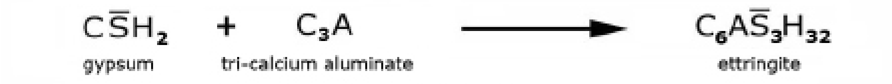
Figure 2.26



hardening of cement paste

Gypsum retards the reaction by rapidly forming around the jelly globules a skin of hydrated calcium sulfo-aluminate (**ettringite**), which delays the penetration of water into the clinker grains.

Figure 2.27



$$C\overline{S}H_2 + C_3A \longrightarrow C_6A\overline{S}_3H_{32}$$

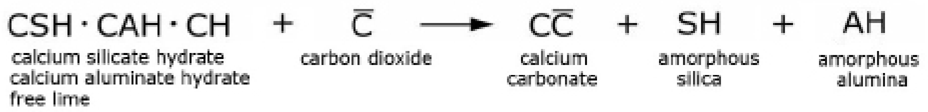
formation of ettringite in the setting reaction

The free lime that is formed, together with some caustic soda originating from the sodium ions contained in the clay, determines a very basic condition in the setting cement, pH being as high as 12 or even 13.

2.7.3 Carbonation

The chemical composition of cement does not remain constant as the hardened material undergoes, upon aging, the action of carbon dioxide gas, which slowly penetrates into its mass. Carbonation affects not only the free lime but also the hydrated calcium silicate and aluminate, converting all calcium compounds into calcium carbonate and both silicates and aluminates into amorphous silica and alumina. The aging of cement is thus similar to that of hydraulic lime.

Figure 2.28



$$CSH \cdot CAH \cdot CH + \overline{C} \longrightarrow C\overline{C} + SH + AH$$

cement carbonation

Carbonation does not impair the mechanical strength of cement mortars and concretes, but, by changing their chemical character from strongly basic to almost neutral (pH drops from 12–13 to around 8), it affects the durability of reinforced concrete, as will be discussed in section 2.9.2.

2.7.4 Pozzolanic cements

The addition of artificial or natural pozzolanic materials to cement produces some favorable effects, improving the resistance of cement mortars and concretes to some types of decay such as the alkali-silica reaction (ASR), the alkali-aggregate reactions (AAR), the delayed formation of ettringite (DEF), and the attack by sulfate-rich waters (see section 2.8.2.2).

2.7.5 Cement mortars

As cement shrinks upon setting, the addition of an inert material is required to prepare a mortar. The cement/sand ratio normally applied is close to 1:1, and so definitely higher than the binder/sand ratio in lime mortars; occasionally larger additions of sand are used.

At the worksite, cement mortars must be kept wet until the setting reaction is well under way.

The mechanical strength of the hardened mortars is influenced by the amount of water used for mixing, although in a less critical way than with lime mortars; water/cement ratios of 0.5:0.6 produce mortars with compressive strengths above 35 MPA, far above those of all the mortars used in traditional construction.

Lower water/cement ratios, which are possible if water reducers or superplasticizers are used, yield higher strengths.

2.7.6 Mortars for renderings

The porosity of cement mortars depends upon the amount of water used in mixing but, in general, is much lower than that of lime mortars. Pore distribution measurements show that it is mainly the larger pores that are missing; as a consequence, cement renderings tend to hinder the evaporation of water that may be present in the core of the walls and so to increase the water content of the masonry on which they are applied.

The use of cement renderings on old buildings is therefore not advisable.

This does not apply to a class of mortars called **macroporous** or **evaporating mortars**, which have been developed for the application over damp walls; these mortars contain admixtures, which cause the formation of gas bubbles during the hardening process.

Water can thus evaporate in a network of large pores while ample space is provided to allow the formation of salt crystals, thus mitigating the stresses that normally develop in this process (see section 3.2.4). The service life of these mortars when applied over damp masonry is thus longer than that of a normal lime mortar, while no hindrance is caused to the evaporation of moisture from the wall.

2.7.7 Structural grouts

Fluid cement mortars are frequently employed for the consolidation of old masonry by means of injections ("grouting" technique). Structural grouting is effective when the core of the masonry is composed of a rubble fill that is insufficiently cemented by a mortar, a defective construction, or a cohesion failure caused by mechanical stress (static loads or environmental dynamic impulses such as seismic movements or traffic vibrations).

The success of the consolidation depends upon the ability of the "grout" to penetrate even inside very fine cracks; therefore all components of the mixture must be very finely ground. The use of **micro-cements**, i.e., cements that have been ground down to a few micron particle size, is now gaining a wider acceptance in Italy (an example is the consolidation of the core of the walls of the Tower of Pisa).

Also special admixtures must be added:

- **superplasticizers** allow the required fluidity to be reached with a minimal addition of water and thus control the shrinkage of the fluid mix upon hardening.

- **water-retaining admixtures**, usually hydrophilic polymeric molecules, avoid the loss of water caused by the suction of the porous materials (**bleeding** of the grout) and allow the penetration of the mixture in the tiniest fissures.
- **shrinkage-compensating admixtures** produce a slight expansion in the course of the setting reaction, either by forming gas bubbles (e.g., aluminum powder) or by reacting with water and increasing in volume (e.g., quicklime).

2.8 Modern Concrete

2.8.1 Concrete mixes and properties

Cement concrete is composed of a cement mortar (cement/sand mixture) and rock fragments (or gravel), the **aggregate**, whose dimension according to European specifications is larger than 4.75 mm.

The amount and size of sand grains and aggregate pieces are calculated in such a way that they fill as much as possible the volume to be occupied by the concrete, leaving only very thin voids in which the cement will act as a binder for the whole mass.

Actually, it is a general rule, valid not only for all inorganic binders such as lime and cement but also for organic adhesives such as synthetic resins, that all binders provide their best mechanical performance when they are in the form of a thin layer between surfaces of hard inert materials.

The properties of the concrete after setting are determined not only by the types of cement and aggregate that are used but also by the ratios among the main components: the amount of cement per cubic meter and the water/cement ratio.

Composition of Cement Concrete	
amount of cement/cubic meter of concrete	150–300 kg/m^3
water/cement ratio	0.60–0.25

Increasing the amount of cement per cubic meter determines an increase in the strength of the concrete, while the reduction of the water/cement ratio results in both an increase of strength and an improved durability. The water/cement ratio may be brought down from 0.6 to 0.25 by adding a **superplasticizer**.

The compressive strength of cement concretes is always very high; minimum requirements range from 25 to 35 MPa according to the type of mix that is specified. Tensile strength, however, is its weak point, because the results of tensile tests show low strength and poor reproducibility.

Lightweight concrete may be produced by the addition of **air-entraining admixtures**, which in the mixing phase allow the introduction of air, forming tiny bubbles (less than 1 mm in diameter) that survive in the hardened concrete, creating an abundance of large pores normally lacking in cement mortars. This type of concrete shows an improved resistance to frost and salt attack besides good thermal insulation properties.

2.8.2 Concrete decay

2.8.2.1 Delayed ettringite formation (DEF)

In the normal course of the setting reaction of cement (see section 2.7.2), ettringite is formed by the reaction of gypsum with calcium aluminate, slowing down the exceedingly fast reaction of tri-calcium silicate with water.

In particular conditions, frequently when the temperature of the concrete mix becomes too high, ettringite is not formed immediately but may crystallize later when the concrete is already hard. This may happen because of the intentional heating of the concrete mix in cold climates or when large masses of concrete are poured.

Another possible cause of the DEF syndrome is the use of a form of calcium sulfate that dissolves too slowly (different calcium sulfate minerals are used in the cement industry).

The growth of the ettringite crystals in the pores of the hardened concrete gives rise to stresses large enough to cause considerable damage.

The addition of pozzolanic materials to the mix appears to reduce the risk of late ettringite formation.

2.8.2.2 Attack by sulfate-rich water

Water that contains **soluble sulfates** may cause the formation of crystals of **ettringite**, by reaction with hydrated calcium aluminate, or **thaumasite**, by reaction with hydrated calcium silicate. The growth of crystals inside the pores of the concrete results in stresses and damage. Also in this case, the addition of pozzolanic materials to the cement appears to mitigate the risk, or the consequences, of salt crystallization.

2.8.2.3 Alkali-silica reaction (ASR) and alkali-aggregate reaction (AAR)

It has been known for several years that when rocks that contain silica in an amorphous reactive form are used as concrete aggregate, serious damage may be caused by a reaction between the reactive silica and the alkaline materials present in the cement. The ASR reaction causes the formation of a swelling gel inside the concrete, which is particularly dangerous when large masses of concrete are poured, e.g., in the construction of dams.

More recently, it was discovered that other minerals present in the aggregate may produce a similar effect, in particular some reactive forms of alumina; the acronym AAR was used for this form of decay.

Special laboratory tests have been devised to evaluate the potential danger posed by the use of a given aggregate. When such a danger exists, a low-alkali cement should be used, a rather costly provision. It was also found that the effects of the reactions are mitigated by the addition of lithium salts or pozzolanic materials to the concrete mix.

2.9 Reinforced Concrete

2.9.1 Mechanical properties

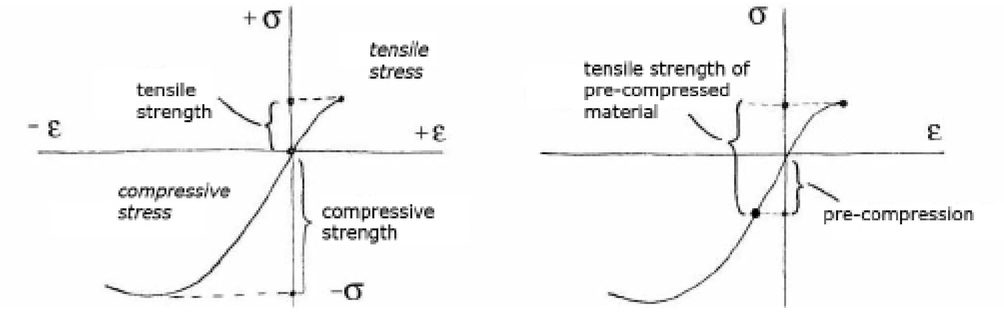
As was mentioned earlier (section 2.8.1), the very high compressive strength of cement concrete is not matched by a comparable tensile strength. Such a disparity is common to all rigid materials and the reasons are discussed in section 3.1.1.

The insertion of steel bars in the concrete provides the tensile strength that is required in modern construction, while the cement concrete provides the compressive strength and protects the steel from corrosion, thanks to the basic environment it creates around the metal (iron corrosion is discussed in section 5.1.6).

The thermal expansion coefficients of steel and cement concrete are rather close, so it is not to be expected that stresses would arise inside the concrete/metal composite because of the thermal cycles caused by the environment.

The tensile resistance of reinforced cement may be further increased by **pre-compression**; the principle underlying this technique is illustrated in figure 2.29.

Figure 2.29



theoretical principle of the pre-compression of brittle materials

The compression may be created by applying a tensile stress to the steel bars before the concrete is poured and releasing it when the concrete is hard (**pre-stressing**). In an alternative method, the steel bars are inserted in plastic tubes before the concrete is poured and are then subjected to a tensile pull after the concrete has hardened; at this point a fluid grout is injected in the tubes, and when the grout hardens, the tension on the bars is released and their contraction applies a stress on the concrete (**post-stressing**).

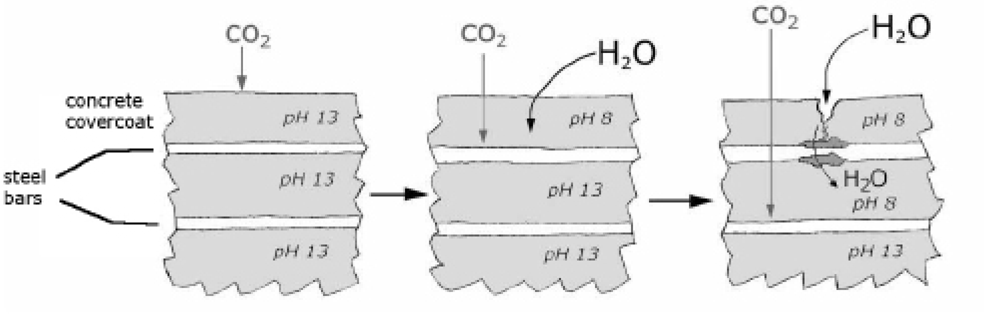
Steel bars are not the only way to improve the tensile resistance of concrete; on a smaller scale this may be achieved by inserting fibers in the mix. Many types of fibers have been used with success: metal, glass, synthetic resins. Recently (2007), very good results appear to have been obtained by the use of fibers made of polyvinyl alcohol, a synthetic resin that stands quite apart from others as it is definitely hydrophilic in character, a property that should determine a better adhesion to the cement mortar.

2.9.2 Corrosion of steel reinforcement

The basic environment created by cement around the steel bars is progressively neutralized by the carbonation process brought about by the slow penetration of carbon dioxide in the concrete. On average, the carbonation is believed to advance by 1 mm per year, but higher or lower rates are to be expected as a consequence of the variable porosity of the concrete; this in turn is influenced by the amount of water added to the mix when the concrete was poured and by the type of aggregate.

In fully carbonated concrete, at a pH around 8, the corrosion of steel is possible if water can reach its surface.

Figure 2.30



corrosion of steel bars in reinforced concrete

As iron corrosion determines an increase in volume, a stress is applied on the concrete that surrounds the corroded bar. The weak tensile strength of the concrete causes the cover layer over the outermost bar to fail easily when it is pushed from inside; air, carbon dioxide, and water can then penetrate further through the cracks and the process advances towards the core of the structure. The strength of a beam or pillar may be weakened to the point that it may lose most of its load-carrying ability.

The present European specification, EN 206, requires that reinforced concrete be designed according to the environment it will face in the course of its service life. The features that must be considered are:

- the **cement to aggregate ratio**, the amount of cement per cubic meter rising from 150 kg/m^3 to 300 kg/m^3 as the risk of corrosion increases;
- the **water/cement ratio** decreasing from 0.65 (low risk) to 0.25 (high risk);
- the **cover**, i.e., the layer of concrete protecting the most exposed steel bars, increasing from 20 mm, for internal walls, up to 50 mm when the corrosion risk is high, the maximum being required, e.g., for external walls at a seaside location.

The first two requirements aim to reduce the porosity and increase the strength of the concrete, while the third one aims to delay as much as possible the carbonation of the cement in contact with the outermost steel bar.

There are, however, other ways to prolong the service life of a reinforced concrete structure, namely:

- the application of a **hydrophobic paint** on the surface of the concrete;
- the application of a **polymer coating on the steel bars**, e.g., a thick layer of an epoxy resin (see section 6.5.3) applied in a powder form and baked;
- the **zinc coating of the steel bars**, zinc being applied by immersion of the bars in the molten metal;
- the **electrical protection** of the steel bars (see section 5.1.7.2);

- the use of **stainless steel bars** (quite expensive);
- the reinforcement of the concrete by **non-metallic fibers**, e.g., glass or synthetic resins.

2.10 Compatibility Problems Related to the Use of Cement in Architectural Conservation

2.10.1 The compatibility principle

The characteristics of cement-based concretes and mortars are quite attractive in the building trade because of the simplicity and reliability of the technology and the high strength of the hardened materials.

Problems may arise, however, when these materials are used in the consolidation of structures built with earlier technologies because of the significant differences in physical and mechanical properties between them and the traditional building materials and, also, because of some collateral effects related to the chemistry of cement.

Several cases are known in which the use of cement in conservation of ancient structures resulted in damage to the original materials; these examples led some architect-restorers to think that architectural conservation should use materials and techniques identical, if possible, to the original ones.

But even such a policy, based on a **principle of homogeneity**, would not be exempt from risks because consolidation carried out by traditional techniques involves important substitution of original materials and makes it difficult to distinguish the restored structures from the original ones at a later time.

Today, the majority of restoration experts in Europe let themselves be guided by a **principle of compatibility** stating that the materials used in restoration should be compatible with the original ones, i.e., should cause no damage to them while contributing to their conservation.

In other words, one can say that the original materials and those added in restoration should form a composite structure that shows a “satisfactory” behavior under the stress created by the environment that the composite will face.

By the term *satisfactory* it is intended that the inevitable onset of new deterioration processes should be delayed as long as possible and that the restoration material should be the first to fail.

Compatibility problems are better discussed if they are separated according to the type of deterioration process that is involved; this is done in the following sections when discussing the use of modern cement in architectural conservation.

2.10.2 Physical compatibility

- The low porosity of cement mortars and concretes may create problems by hindering the passage of water vapor, as already mentioned in the case of renderings, or by diverting rainwater the wrong way, e.g., discharging it on the adjoining original materials.
- The thermal expansion coefficient of standard cement concrete is frequently 50% to 80% larger than that of most stones or bricks. Possible contrasts due to thermal cycles would result in damage to the weaker material, normally the older one.

- The modulus of elasticity of modern concrete by far exceeds that of most traditional building materials; if both are included in a structure subject to a strain (deformation) imposed by the environment (e.g., because of subsidence or seismic activity or vibration), all of it is likely to be discharged onto the weaker material. The result is that the weaker material undergoes a damage that is larger than the damage it would have suffered if left alone, or if connected to a more deformable (i.e., lower modulus) one.

A rule widely followed in conservation is that if a new material is to be rigidly connected to an old one, it is desirable that their strength and modulus be suitably matched, i.e., not exceedingly different.

2.10.3 Chemical compatibility

Portland cement, in the course of its setting reaction, produces some soluble salts (mainly sodium sulfate, sodium carbonate, and sodium silicate), which are likely to migrate into the adjoining porous materials and cause efflorescence, subefflorescence, and incrustations (see section 3.2.4).

As an example, a typical case of an objectionable consolidation practice is the injection of cement-rich grouts inside masonry-bearing mural paintings or other decorations on its surface.

The damage that could be caused by these processes may be mitigated by the use of low alkali cements and by the addition of pozzolanic materials. Anytime cement is going to be used in contact with porous building materials, the conservator should consider provisions aimed at avoiding the penetration of water from fresh cement mortar into the pores of ancient stone, brick, or mortar.

Also, rainwater that flows over hardened cement mortar, or concrete, may cause damage when it is allowed to reach unprotected porous materials.

2.10.4 The specificity of compatibility problems

Compatibility in conservation is a notion that is always relative to both the original and the restoration material that is considered. There is no such thing as a modern material that is incompatible in general, i.e., with any sort of traditional building material.

In the case of cement, for instance, it is a well-established fact that the use of cement mortars to fill lacunae in soft stones, or traditional mortars, invariably resulted in damage of the porous material because of the crystallization of soluble salts produced by the filling mortar or of stresses caused by thermal expansion. This is not true, however, for all types of stone. It was observed in Rome that cement fills in the travertine façades of churches and palaces, which had been applied around 1900, had caused no damage to the surrounding stone ninety years later. In the present conservation practice, those fills are not removed (an operation that would be costly and cause considerable damage), but, if their color is objectionable, they are hidden by applying a silicate paint on their surface.

This is not a surprising fact if the characteristics of both materials are compared: travertine, sporting compressive strengths above 100 MPa, is stronger than any cement mortar and also has no microporosity to offer for salt crystallization (the holes left by the vegetal material trapped in the sediment are not pores and may even be useful to accommodate crystal growth). As a consequence, travertine should easily resist any thermal movement of the strong fill and should not be susceptible to deterioration by the salts coming from the cement mortar.

It is interesting to note that the same argument does not apply to white Carrara or Greek marbles, which are also quite strong but on aging become progressively microporous because thermal cycles and mechanical stresses result in the cleavage or the separation of their large calcite crystals; damage by salt crystallization becomes thus possible because a microporosity is created by this process (see section 3.2.4).

Part 3

Deterioration of Porous Building Materials

The decay of the porous building materials (stone, brick, concrete, mortar) is caused by mechanical, physical, chemical, and biological processes. Frequently, different processes act at the same time or in a sequence; as a consequence, when a material is deteriorating, the identification of the cause of decay is seldom easy and often requires an interdisciplinary study.

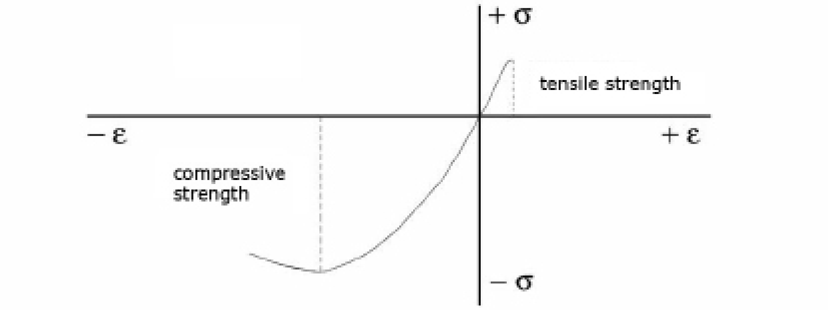
3.1 Mechanical Deterioration Processes

3.1.1 Mechanical properties of porous building materials

Porous building materials are composed of atoms connected by strong covalent bonds that have some ionic character (see section 1.2.3); the bonds are directional and do not allow for a plastic deformation of the crystals. Therefore, porous building materials are **hard, rigid, and brittle**.

As was already mentioned in section 1.3.2, the tensile strength of brittle materials is much inferior to their compressive strength and is normally considered to be unreliable because, when it is measured, the results show unpredictable variations in samples that are presumed to be more or less equal.

Figure 3.1

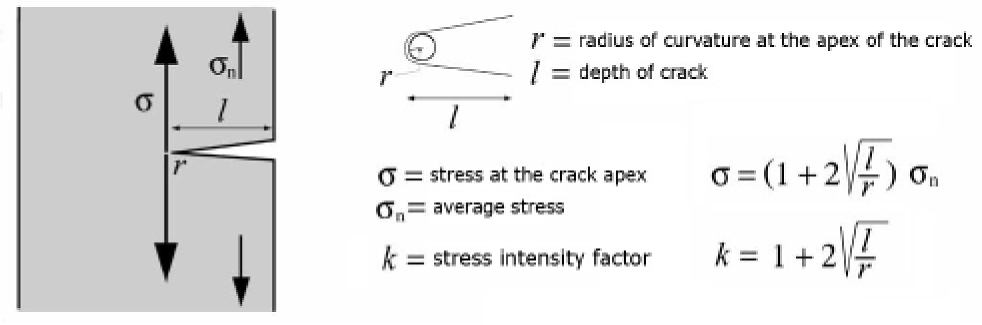


mechanical properties of brittle materials

The cause of this behavior is that in a tensile test or in real structures, the stress is never equally distributed across the sections of a block of material but is, rather, concentrated at some particular points. As stress cannot be redistributed through plastic deformation, the overstressed point fails and determines the failure of the whole block.

Under a tensile stress, the **stress concentration** is **located at the tip of any fissure** existing on the surface of the material, as shown in figure 3.2. The formula that allows the calculation of the stress intensification factor is accurate in the case of glass but only approximate for other brittle materials.

Figure 3.2



stress concentration under tensile stress

It is seen from the formula that the **stress intensity factor** increases as the length of the crack increases, so once the crack starts advancing it will not be stopped. Also, the stress increases as the radius at the tip becomes smaller, so the finest cracks are the most active.

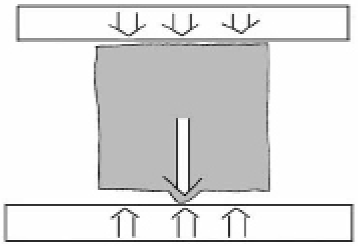
The erratic results of tensile strength tests on brittle materials are thus explained by the fact that the measurement is deeply influenced by the conditions of the surfaces of the test samples, which in turn depend upon the previous history of each individual piece.

Architectural conservation practices are or should be directly concerned by the consequences of this basic principle, because it leads to the conclusion that the surfaces of building materials should be dealt with very carefully in order to avoid adding new stress concentration points to the already existing ones.

Another important consequence of the stress concentration theory is that an improvement of the mechanical properties of a rigid material may be achieved by a systematic sealing of all cracks and other discontinuities existing on its surface.

Under compressive stresses the stress concentration points are not cracks or voids but rather **irregularities jutting out of the surface**.

Figure 3.3



stress concentration under compression

Stress concentration under compression may become quite dangerous in heavy stone construction, but this was well known to ancient builders who managed to minimize it in two different ways:

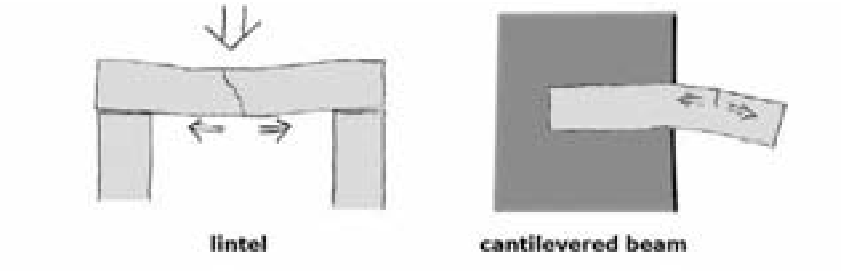
- introducing a mortar between uneven surfaces of stone blocks (e.g., the gypsum mortar between the stones of the Egyptian pyramids);
- smoothing very carefully the load-carrying surfaces of stone blocks and using no mortar between them (as in the Gothic cathedrals in Europe and the Inca walls in Peru).

3.1.2 Tensile stresses caused by static loads

Tensile stresses acting on a material frequently depend upon its position in the construction, all horizontal structures being unavoidably a source of such problems. A typical example is offered by **lintels**, in which the unsupported material bends under the weight and the inferior convex surface is under tension (while the concave upper surface is under compression); a condition in which even a tiny crack on the wrong side may create a dangerous situation.

An analogous case is that of **cantilevered beams**, where the surface subject to a tensile stress is the upper one.

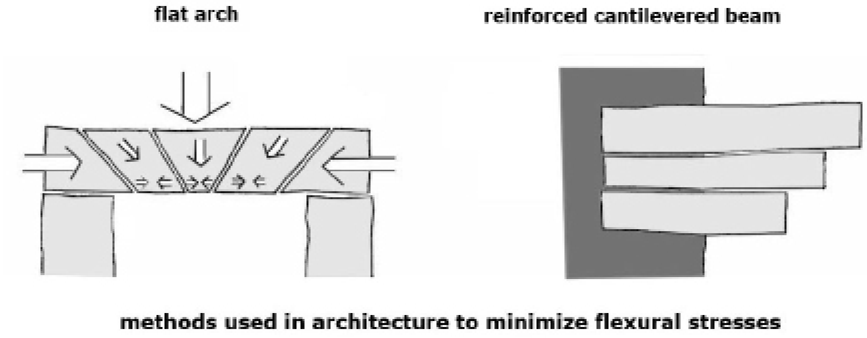
Figure 3.4



Special building techniques allowed builders in the past to mitigate the problems raised by these structures whose behavior is unpredictable. An example is the case of the **flat arch** (known since Roman times), built of wedge-shaped blocks or opportunely oriented bricks that, under the weight of the wall over them, create a compression on the lower surface of the lintel that tends to close the cracks and reduce the stress concentration at their tips.

Also, supported cantilevered beams are found in modern (e.g., eighteenth century) European construction.

Figure 3.5

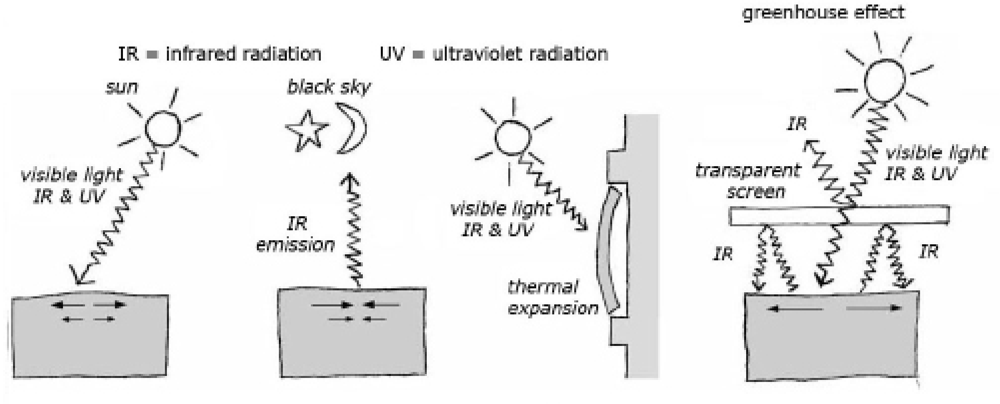


3.1.3 Thermal expansion

On the earth's surface, all materials **absorb energy in the course of the day** and **expand** under the impact of the **solar radiation** composed of visible light, ultraviolet (UV), and infrared (IR) radiation. **During the night**, all materials give off energy by **emitting infrared radiation (IR) towards the sky** and **contract.** Cooling is more efficient on clear nights because the intensity of the infrared emission depends upon the temperature of the visible target (the colder the target, the stronger the emission), and a **black night sky** is the coldest object that is visible from the earth's surface, much colder than the clouds.

Thermal cycles, diurnal (day-night) or annual (summer-winter), cause **periodical changes of dimensions** of the building materials and stresses arise in all constructions exposed to the earth's environment.

Figure 3.6



thermal effects

In blocks of materials that are not good conductors of heat (e.g., stone), a stress between the surface and the core (which is termed a **shear stress**) is originated both in the heating phase and in the cooling phase of the thermal cycle.

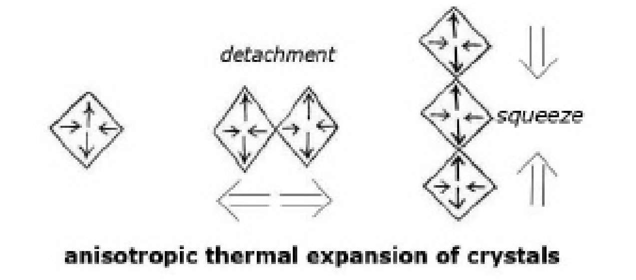
If the thermal expansion movement of a material is impeded by adjacent materials, a flexural stress arises that may be large enough to cause bending and cracking where the tensile stresses are concentrated. A typical case is that of stone veneer used for cladding façade walls, which bends towards the outside and cracks when suitable expansion joints are not provided. **Physical and chemical decay processes may then propagate from the damaged surface to the core**.

It is important to note that the interposition of a transparent screen, for instance as a protection against rain, results in the overheating of the surface because the screen hinders the transmission to the sky of the IR emitted by night, and so causes an accumulation of heat in the protected area (this is the well-known **greenhouse effect**).

The protection of works of art by means of transparent screens may well result in an increase of damage, particularly if the sunlight is allowed to shine on them.

Another type of stress arises inside some types of stone that are constituted of **large crystals** (e.g., granite, Carrara, or Greek marble); these undergo a progressive weakening of their structure on exposure to the thermal cycles because the crystals have an anomalous, **anisotropic**, **thermal behavior** since they expand upon heating in one direction (usually the main axis) and, at the same time, contract along other ones (usually perpendicular to the main axis).

Figure 3.7



The result is a progressive detachment of some crystals and the cleavage of others, an increase of porosity and a loss of cohesion.

Carrara marble, which shows a total porosity around 0.2% when extracted from the quarry, may reach a porosity of several percent points after some centuries of exposure to the terrestrial environment.

Differential thermal expansion

The thermal expansion coefficients of different materials used in construction or in architectural conservation may be quite different; this fact is bound to cause problems if the materials are connected to one another without an interposed expansion joint.

Thermal Expansion Coefficients Linear expansion per unit length per degree centigrade			
brick*	7×10^{-6}	carbon fibers	1.5×10^{-6}
stones	$6–9 \times 10^{-6}$	titanium	8×10^{-6}
cement concrete	$8–10 \times 10^{-6}$	iron	11×10^{-6}
wood, along fibers**	5×10^{-6}	copper, bronze	16×10^{-6}
wood, across fibers**	50×10^{-6}	stainless steel	16×10^{-6}
plastics, no filler	$60–100 \times 10^{-6}$	aluminum	24×10^{-6}
polyester/glass reinforced	$20–30 \times 10^{-6}$	lead	28×10^{-6}

* 7.2×10^{-6} is the thermal expansion coefficient of a modern brick façade to be considered in the calculation of the expansion joints, according to the American Concrete Institute (ACI); the thermal expansion of ancient bricks might be larger.

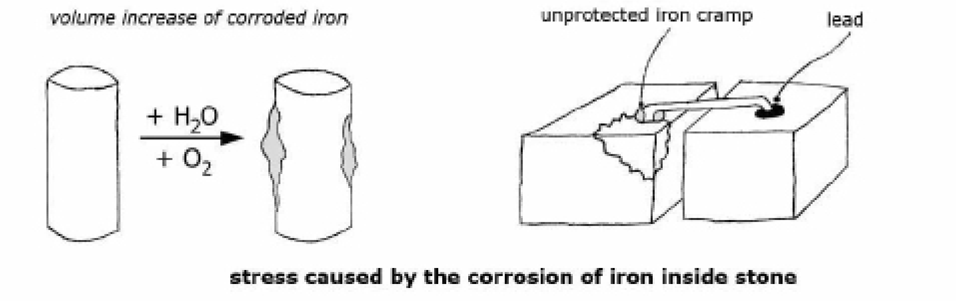
** The thermal expansion coefficients of different wood species are different; an average figure is presented here.

Expansion joints must be provided whenever large pieces of materials are connected, but particular attention must be given to the cases in which different materials are rigidly connected and the difference of the thermal expansion coefficients is large.

3.1.4 Iron and steel corrosion

The corrosion of iron entails an increase of volume (see section 5.1.6.2); if the metal is inserted inside a brittle material, such as stone or concrete, the tensile stress caused by its corrosion is large enough to break it, even if its thickness is considerable.

Figure 3.8

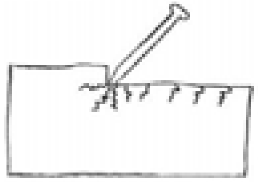


stress caused by the corrosion of iron inside stone

3.1.5 Human action

The work done to prepare a brittle material for its use in construction, or to clean it after a period of exposure to the environment, may cause damage to its surface that may impair its resistance to mechanical and physicochemical stresses.

Figure 3.9



cracking caused by chisel work

In the case of stones, damage to the surfaces may be easily inflicted in any of the following operations:

- extraction from the quarry (some techniques produce more defects than others);
- chisel work on surfaces;
- cleaning by sandblasting;
- cleaning with rotating discs or metal brushes.

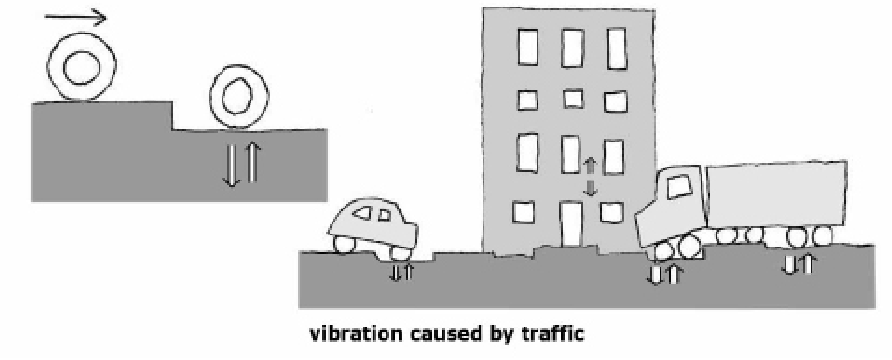
3.1.6 Traffic vibrations

3.1.6.1 Vibrations and resonance

Road traffic induces mechanical stresses in nearby buildings through vibrations that are caused by **the multiple impact of vehicle wheels over the irregularities of the pavement**. The intensity of the stress applied to the soil depends upon the height of the irregularity and the weight and speed of the vehicle.

Vibrations are transmitted through the soil to the nearby buildings, but their magnitude drops rapidly as they travel through the soil, attenuation being more than proportional to the distance from the source; as a consequence, only constructions that are very close to roads are affected.

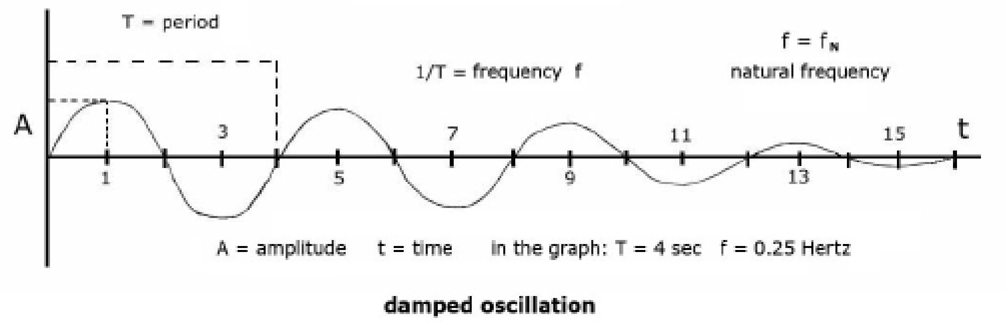
Figure 3.10



The damage that a structure may suffer due to vibration depends upon the phenomenon of **resonance**.

An object whose movement is restrained by at least one rigid connection (e.g., a pendulum affixed from its top or a building anchored in the ground) **oscillates** when it receives a single impact from an external force, but its movement is progressively reduced by friction and it finally goes back to its rest position. This is a **damped oscillation** that may be represented in a graph, as shown in figure 3.11.

Figure 3.11



The **frequency** (**f**) of oscillation is the number of complete cycles around the rest position that are performed in a second; it is measured in **Hertz** units (**Hz**). The time required for a complete cycle is called the **period** (**T**); therefore, according to these definitions, frequency and period are reciprocal numbers. The maximum distance reached by the object from the rest position is the **amplitude** (**A**).

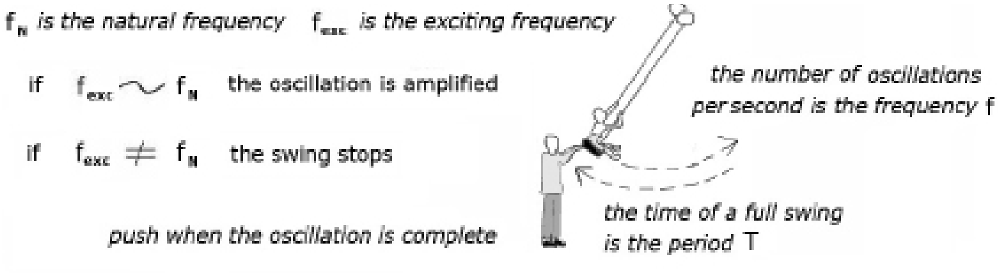
Oscillatory movements are called vibrations when the frequency involved is rather high; e.g., traffic vibrations show frequencies in the range of 10 to 30 Hz. Oscillatory movements caused by seismic phenomena show instead frequencies around a few Hertz units.

The frequency observed in a damped oscillation is called the **natural frequency** (f_N) of the object. When an object is compelled to oscillate by a series of impulses it receives from its environment, the result is a **forced oscillation** whose frequency must be that of the acting external forces (we call it the exciting frequency, f_{exc}).

If the exciting frequency is quite close to the natural frequency, the oscillation of the object is amplified and, as a consequence, the stresses caused by the movement are increased, a phenomenon called **resonance**.

If, on the contrary, the natural frequency is quite different from the exciting frequency, the object oscillates with a reduced amplitude or does not oscillate at all.

Figure 3.12



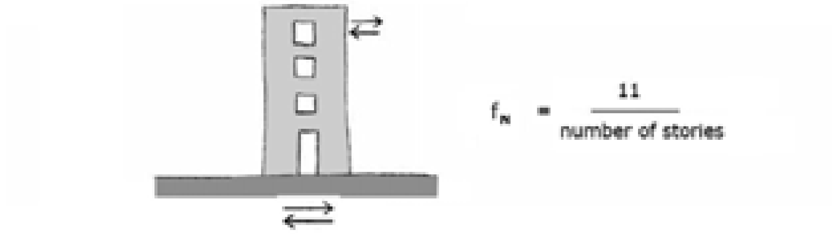
resonance

Resonance is best exemplified by a swing with a child sitting in it. In order to increase the amplitude of its oscillation and make the child happy (or afraid), his father must push it at the right time, when it has completed its cycle; that is, he must apply a force with a frequency near to the natural frequency of the swing/child system. If the push is not applied at the right moment the swing slows down, then stops.

3.1.6.2 The resonance of buildings or parts of buildings

The natural frequencies of buildings may be measured by applying some single impacts to their structure and measuring the frequency of the damped oscillation resulting from them. Approximate data may be obtained from a rule of thumb, which looks quite silly but actually is accurate enough to allow a general discussion of the possible damage caused by vibrations to buildings.

Figure 3.13

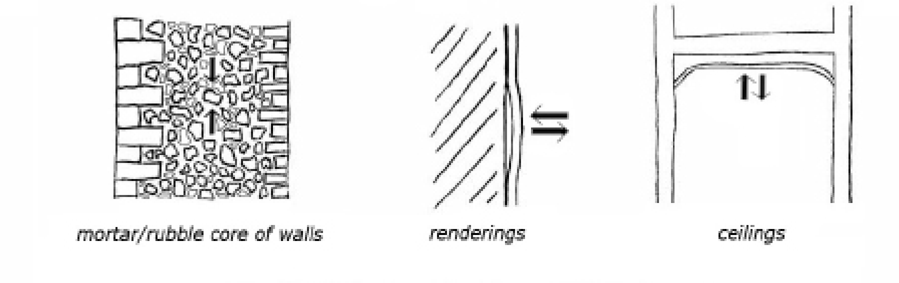


natural frequency of buildings

We see from this formula that the entire structure of a building should suffer from amplified movements (resonance) under the action of low-frequency oscillations (1–3 Hz) such as those imparted by seismic waves, while the action of traffic vibrations is unlikely to cause large movements.

Single parts of a construction, however, that are not tightly connected to the main structure may undergo resonance amplification in the range of 10 to 30 Hz. Examples of building parts that may potentially suffer damage or displacement because of traffic vibrations are ceilings, cores of walls made of weakly cemented rubble, renderings insufficiently adherent to walls, and roof tiles. As a consequence, traffic may cause serious damage to nearby historic buildings by affecting surface decoration, roof efficiency, or even masonry strength; it is also evident that the probability of damage is closely connected to the state of repair of a construction as the number of loose components increases with the progress of decay.

Figure 3.14



parts of buildings subject to vibration damage

3.1.6.3 Evaluation of vibration risk

The frequency and amplitude of vibrations are measured by applying accelerometers on the surface of an external wall, not too far from street level (frequently 1 m height is specified). The energy of the vibration, and so the risk of damage, is evaluated through the measurement of its **peak velocity** ($\mathbf{v_{max}}$), which is calculated from frequency and amplitude according to the formula shown in figure 3.15.

Figure 3.15

$$\text{peak velocity} \qquad v_{max} = 2 \pi A f$$

Vibrations with a peak velocity of 0.3 mm/second are barely noticeable, while at 2.5 mm/second they are decidedly annoying. Specification ISO TC 108 states that damage to buildings may be envisaged at peak velocities above 3 mm/second, i.e., in the case of very annoying vibrations.

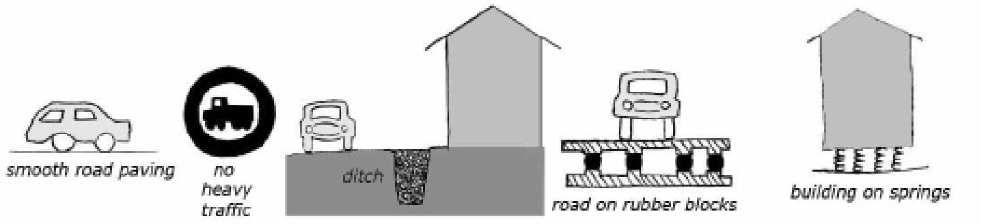
The limit allowed for historic buildings, however, should be lower, particularly if their state of repair is not good.

3.1.6.4 Mitigation of vibration damage

Five types of preventive action are listed in order of increasing costs for the community.

1. Make the road pavement near the building as smooth as possible.
2. Forbid the passage of heavy vehicles near the building. In serious cases, forbid all traffic.
3. Dig a trench between building and road, and fill it with loose material.
4. Mount the road pavement over rubber blocks (this was actually done in Rome on a heavy traffic road near the Villa Farnesina to protect mural paintings by Raphael and other sixteenth-century artists; and it works).
5. Mount the building structure over spring dampers (this may sound surprising, but is done in new construction, near highways, actually for the comfort of the inhabitants rather than for the safety of the building).

Figure 3.16



mitigation of vibration impact on buildings

3.2 Physical Processes of Deterioration of Porous Materials

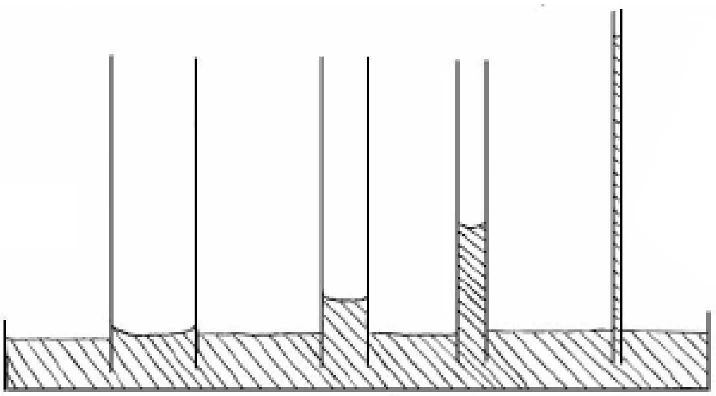
3.2.1 Capillarity

The majority of materials employed in traditional construction techniques—bricks, stones, mortars, concretes—are porous and hydrophilic.

Water, because of its polar nature, is attracted by hydrophilic surfaces (see section 1.7.1) and because of this attraction it is sucked into very small tubes or fine cracks whose walls are hydrophilic. Water can easily rise inside a vertical hydrophilic tube, overcoming gravity.

As the rise of water is greatest in tubes that are as thin as a hair (called **capillaries**, from *capillus*, "hair" in Latin), when it is observed inside glass tubes of various size (see figure 3.17), this phenomenon is called **capillary rise**.

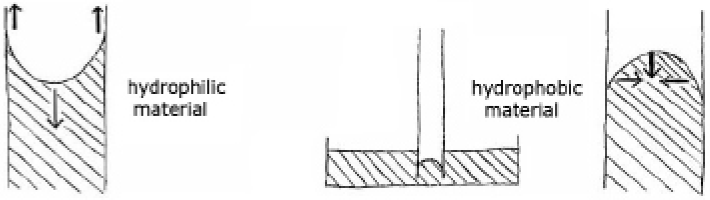
Figure 3.17



capillary rise

The surface of the water inside a capillary tube forms a **meniscus**, rising along the walls and being depressed at the center of the tube.

Figure 3.18



water meniscus inside capillaries

The meniscus makes it possible to visualize the forces acting on the water inside the tube; water molecules are attracted to the surfaces of the material and tend to climb along the walls, but they are partially restrained by the attraction towards the other water molecules; this attraction is most active at the center of the water column. Also, the gravity force tends to pull the water down but its effect is small in comparison with the electrical forces that act between the water molecules and the surface of the material.

In porous building materials, when the distance between the walls of the pores is of the order of magnitude of the micron (μm), the attraction to the walls prevails over the attraction between water molecules, allowing water to climb up to considerable heights.

In a hydrophobic tube (e.g., a tube made of a synthetic polymer), the meniscus is inverted, as shown in figure 3.18, because water molecules are not attracted to the walls and water shows no tendency to enter the tube.

3.2.2 Capillary rise in porous hydrophilic materials

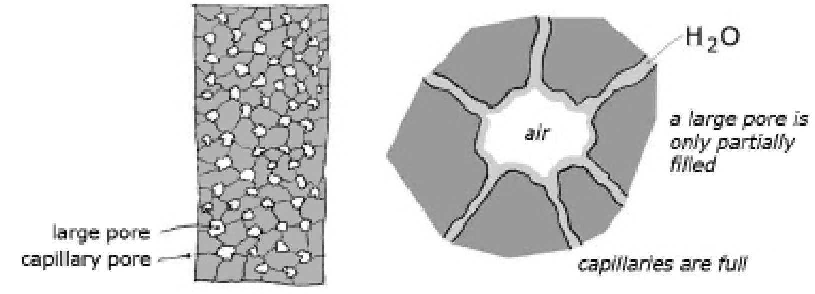
When the bottom of a brick is immersed in water, the capillary rise is easily observed because the wet surface is darker than the dry material (the optical effect is due to light-scattering phenomena, which are discussed in sections 3.3.5 and 4.4.2). In this situation, the rise is hindered not only by the forces discussed in the previous section but also, and mainly, by the evaporation of the water from the wet surfaces.

In the real case of a wall that is in contact with wet soil, water rises inside the pore system until an equilibrium is established when the amount evaporated from the surfaces (which keeps increasing as the wet surfaces are extended) balances the water uptake from the soil.

The pores in porous building materials have variable dimensions and various shapes; when the pores' dimensions are measured, however, this complex structure is normally represented in a simplified model in which the pores are assumed to be cylindrical tubes whose diameters ("equivalent diameters") can be calculated from the experimental data. It has been observed that the most frequent equivalent diameters lie normally within two intervals, which may be roughly designated as **large pores** (diameter **larger than 10 μm**) and microscopic or, better, **capillary pores** (diameter **between 1 and 0.1 μm**).

The total porosity and the ratio between these two categories of pores determine the behavior of building materials towards water and their vulnerability with respect to physical decay processes.

Figure 3.19



water distribution in the pores of a hydrophilic material

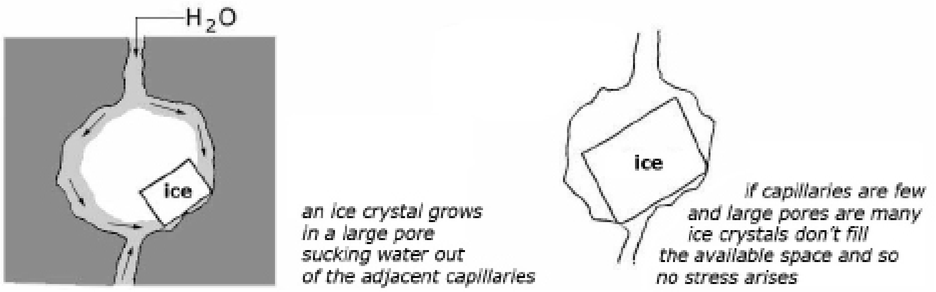
When a porous hydrophilic material is wet, it seldom happens that all the voids inside the solid are filled with water (water suction under vacuum is required to achieve that condition); the most frequent distribution is that in which all capillary pores are full of water, while in the large pores water is wetting the surfaces and air fills most of the internal volume.

3.2.3 Physical decay processes: Frost

When the temperature drops below 0°C, ice formation inside a wet porous solid may cause serious damage to some materials said to be **frost susceptible**, and not to other, **frost-resistant** ones. The difference in behavior of building materials with respect to frost damage is due in part to their mechanical properties as, other conditions being equal, stronger materials are obviously more resistant, but the most important factor is actually the pore size distribution.

The main cause of frost damage is the fact that crystals in general, and ice crystals in particular, grow easily in the large pores when the conditions for crystallization are reached, while inside capillaries the molecules of the liquid are so strongly attracted to the solid walls that it is difficult to form the seed of a crystal, tearing them out of their position. In large pores a thicker layer of water molecules would keep some of them attached in a relatively weak way so that they are more easily shifted to a new position in a crystal nucleus.

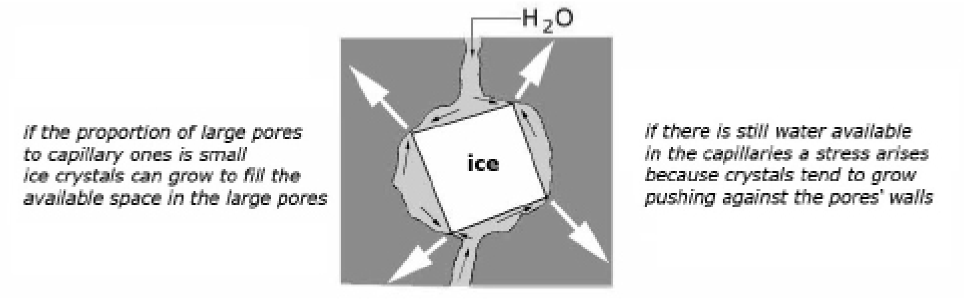
Figure 3.20



growth of ice crystals in a porous material

When the temperature drops below 0°C in a wet porous solid, the nuclei of the ice crystals start growing using the water available around them in the large pores, but when this becomes scarce they suck water out of the capillary pores. If the number of large pores is great and that of capillary pores small, at some point the water reserve is exhausted and the growth of ice crystals stops before they fill the large pores. In this situation no stress arises; the material is now completely dry and the ice crystals are located in the large pores only.

Figure 3.21



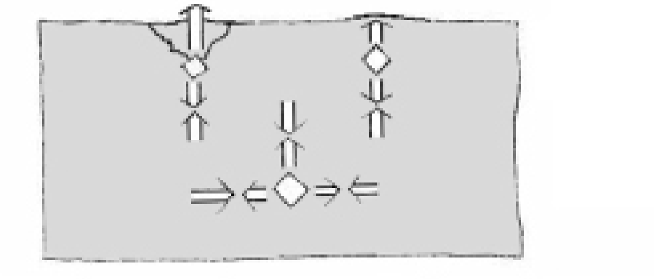
frost damage

If, on the contrary, a material has a large proportion of capillary pores, and so a great reserve of water stored in them when it is wet, upon freezing a stress arises because the number of large pores is insufficient to provide space for all the crystals of ice that the water can form.

A growing crystal, after filling the available space in a large pore, keeps attracting water by capillarity in the gap between its edges and the wall and so exerts a pressure on it. It must be noted, therefore, that the stress caused by the freezing of water inside a porous system is not basically due to the volume increase that is observed when liquid water is transformed into ice; in fact, substances that do not increase in volume upon solidification also can cause damage to porous materials when the temperature drops below their melting point. The increase of volume in ice formation contributes to the magnitude of stress, but it is not the deciding factor; it cannot explain why some materials resist frost and others don't, e.g., why lightweight concrete (see chapter 2.8) resists better than normal concrete, which, being stronger, should be more resistant.

When frost occurs, if an ice crystal is growing inside a material near its surface, the pressure it exerts is equivalent to a tensile stress acting on a thin layer of brittle material and is very likely to cause damage.

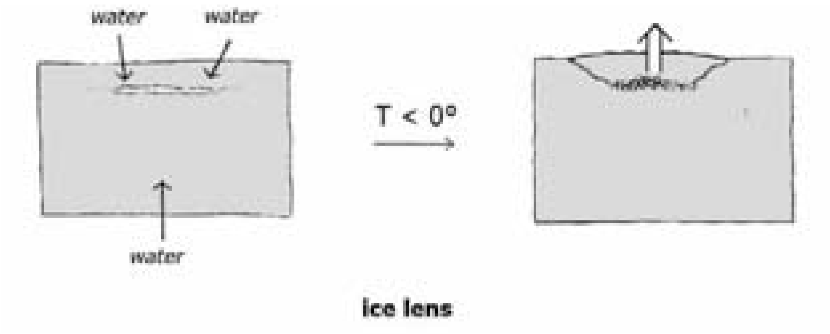
Figure 3.22



ice crystals cause damage near the surfaces

When a row of ice crystals grows in a crack near the surface, an "ice lens" is formed whose effects may be quite disruptive. This may happen in sedimentary stones when water accumulates at defective joints between layers.

Figure 3.23



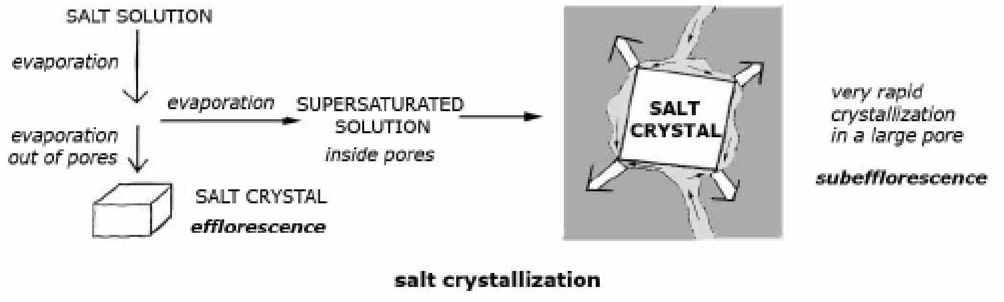
It must be noted that the mechanical damage caused by aging or rash mechanical treatment may affect frost-resistant materials, making them susceptible to frost damage by creating a network of fine cracks that act as capillary pores.

3.2.4 Physical decay processes: Salt crystallization

The evaporation of water from a wet porous material frequently causes damage to its surface because of the crystallization of the dissolved salts it contains.

As in the case of frost, the growth of crystals may take place only inside the large pores, while the capillary ones store the liquid and feed it to the growing crystals. Therefore, also in this case, a material with abundant capillary pores and a scarcity of large ones is more likely to undergo damage.

Figure 3.24



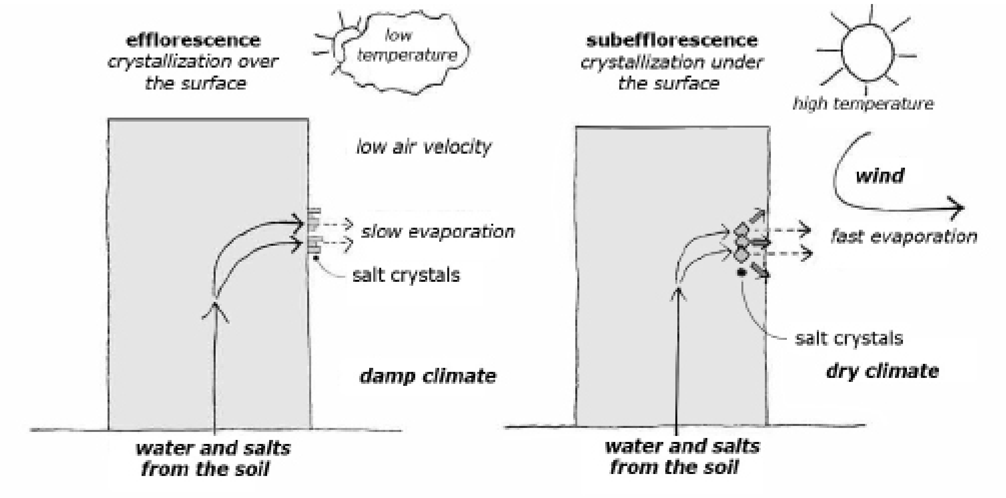
Inside a pore system, a salt solution that is losing water by evaporation would not crystallize immediately upon reaching the saturation concentration, because the ions attracted to the polar surfaces of the hydrophilic material tend to resist the shift to a new position to form a crystal nucleus.

A supersaturated solution would thus be created inside the pores; its crystallization may then be triggered by some random event and would take place very rapidly throughout the material, its velocity adding more power to the disruptive effect.

If crystallization takes place on the surface of the material, it follows its normal route and is not likely to cause stresses and damage; the visible salt crystals form an **efflorescence**.

The internal growth of crystals, which is the most damaging process, is termed a **subefflorescence**. Actually, both processes frequently take place in the structure of historic buildings and archaeological ruins, the prevalence of one process over the other being determined mainly by the environmental conditions around it.

Figure 3.25

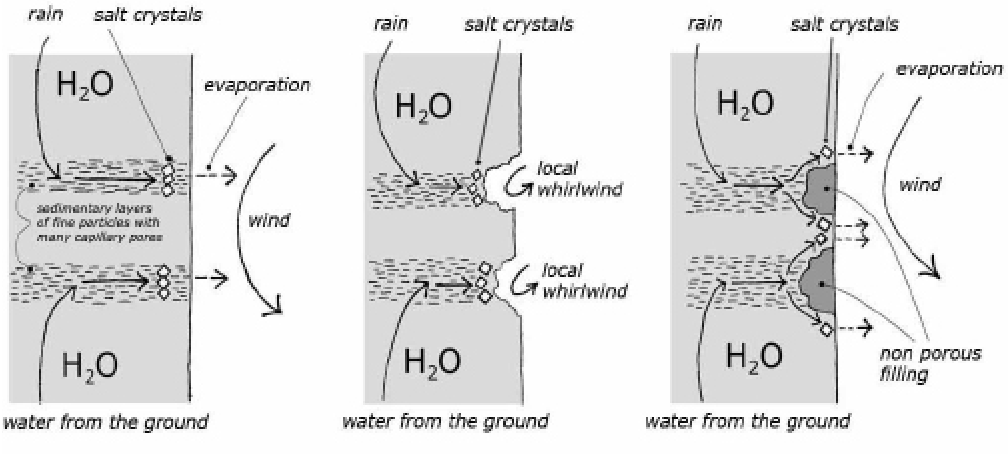


influence of climatic conditions on salt crystallization

Conditions favoring a slow evaporation from a damp porous structure (low to moderate temperature, medium to high relative humidity, low air velocity) lead to efflorescence. A warm, windy, dry climate favors subefflorescence and deeper damage. Very porous stones (e.g., tuffs, calcarenites) in warm, dry climates near the sea may undergo the formation of deep cavities (**alveolization**) because of salt subefflorescence. In stratified sedimentary stones, water is transmitted mostly through the layers that are richer in capillary pores; where these layers appear on the surface, crystallization occurs. Wind action accelerates evaporation and sets up the subefflorescence process that results in the formation of small cavities; further damage is then added by local whirlwinds that blast the inner surfaces of the cavities with stone debris.

The final result may well be a cavity large enough to threaten the stability of the structure above while nearby surfaces are still well preserved.

Figure 3.26



eolic erosion and improper consolidation

Filling such a cavity with a strong, low-porosity material would be the wrong move in the conservation game because water in the pores would be deflected to evaporate on the nearby surfaces and cause damage there, while the modern fill would be preserved.

Actually, the study of salt crystallization damage was one of the factors that led to understanding the importance of **compatibility** between the materials used in conservation and the original ones. In the treatment of deep corrosion of porous materials caused by salts, the filling material should be at least as rich in capillary pores as the adjoining original; it is even desirable that the future decay (which is unavoidable unless water circulation in the pores is controlled) should first affect the filling, which should sacrifice itself to preserve the original material.

The disruptive effect of crystallization is also influenced by the form and size of the crystals, and this in turn is determined not only by pore size distribution and weather conditions but also by the presence of extraneous substances, which may interfere with the growth of the crystals, e.g., by adhering to their surface when the first nuclei are formed.

It was recently proved in a research project that a **crystallization inhibitor** sharply reduces the damage caused by sodium chloride crystallization by favoring the formation of very small crystals and inhibiting their adhesion to other crystals or to the pore walls. Small separate crystals are apparently unable to cause damage in that particular case.

It appears that different substances act as inhibitors for different classes of salts; e.g., potassium ferrocyanide was found to be active versus sodium chloride, while organic derivatives of phosphoric acid showed some promise as inhibitors of sulfates.

Unfortunately, the encouraging results obtained in the laboratory have not been reproduced in actual field conditions up to the present time, a likely cause of problems being the difficulty of achieving a satisfactory distribution of the inhibitor in pores that are already full of water and salts.

3.3 Chemical Deterioration

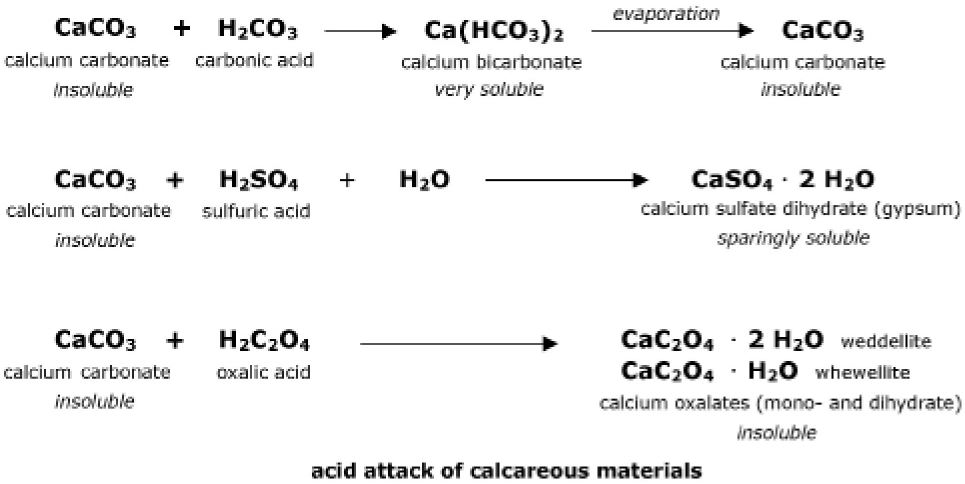
3.3.1 Acid corrosion of calcareous materials

Calcareous materials are defined as materials whose main component is calcium carbonate with or without magnesium carbonate. Under this heading we list calcareous stones (white marble, travertine, limestone, calcarenite, calcareous tuff) and lime-based mortars (renderings, stuccoes).

As was shown in section 1.5.1, calcium carbonate is attacked by the acids that are frequently present in atmospheric water (rain or dew), the final result of the process depending upon both the type of acid and the mechanisms of deposition of the acid water.

The chemical reactions involved are, in theory, the ones shown in the scheme in figure 3.27, but the real ones may be more complicated as the gases present in the air could be absorbed on the surface to react there with the help of some deposited particles that would act as catalysts.

Figure 3.27



If the compounds formed in the reaction are soluble, as is the case of calcium bicarbonate and calcium sulfate, they may be transported and deposited at some distance from the reaction site, or they may be re-deposited in the same place if the amount of water involved is small. Calcium bicarbonate forms the carbonate again when the water evaporates.

3.3.2 Oxalate "patina"

Among the compounds formed by the reactions of acids on the surface of calcareous materials, only calcium oxalates are insoluble. As a consequence, oxalates do not migrate under the action of water but remain where they have been formed, and the result is the development of surface layers, **patinas**, which are of interest in the conservation of historic architecture.

Oxalate patinas are frequently found on the surface of ancient stones (roman, medieval but occasionally also on more recent ones) exposed to urban atmospheres. Their color may vary from yellow to pink to red and brown; on north-facing surfaces and in polluted atmosphere, they may even be black.

Calcium oxalate is the dominant component (20% to 60%) but not the only one, and frequently the patina appears under the microscope to be constituted of several layers. The other principal components are calcium sulfate and various silico-aluminates whose provenance is probably atmospheric dust.

In some cases, oxalate layers appear to have exerted a protective action for the underlying stone, the reliefs of the Trajan Column in Rome being the best-known example; but this is not always true, as layers that are weakly adherent to the stone do not appear to have any positive effect from a conservation point of view.

The origin of these layers is still the subject of controversy as their main component, calcium oxalate, could be formed through at least three different processes:

1. the oxidation of organic materials applied on the surface of stone for a decorative, or protective, purpose;
2. the metabolism of microorganisms that colonized the surface in the past;
3. the reaction between carbon monoxide, the principal pollutant gas in the atmosphere of ancient cities, and calcium carbonate.

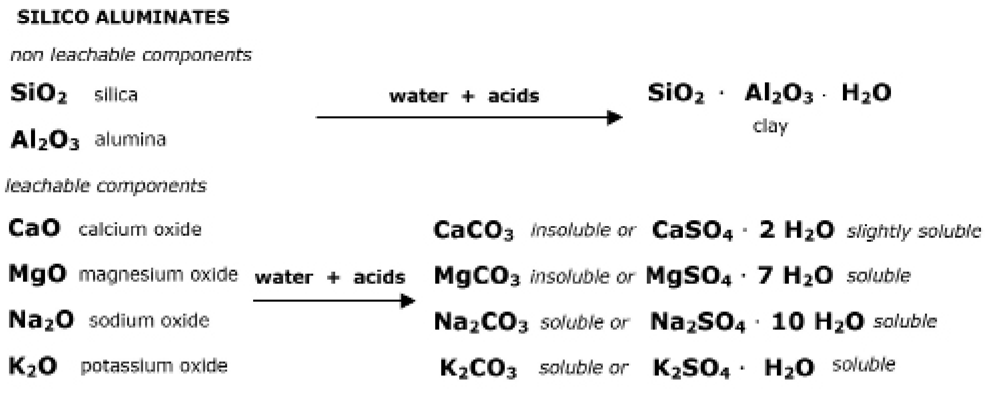
Attempts are being made presently to form protective layers of calcium oxalate by chemical reaction on the surface of stones, mosaics, or mural paintings, exposed outside.

3.3.3 Leaching of volcanic stones by water and acids

Granite, basalt, and other volcanic rocks contain crystalline silica (quartz), which is acid resistant, but also several types of silico-aluminate minerals in which silica and alumina are combined with various metal oxides (calcium, magnesium, sodium, potassium), which may be affected by chemical reactions when wet by atmospheric water.

The chemical reactions that are possible are summarized in figure 3.28 in an oversimplified scheme.

Figure 3.28



leaching of volcanic rocks by acid water

Silico-aluminates, such as feldspars, micas, and chlorites, are slowly transformed by contact with atmospheric water. In this process, called **leaching**, metal oxides are selectively attacked by the acids and transformed into more or less soluble compounds (carbonates or sulfates), which are removed from the stone and transported to a distance that depends upon the amount of water available and the solubility of the salt.

What is left over by a complete leaching process is clay, a combination of silica and alumina (see section 2.1.2 for the structure of clay minerals and their properties). In an intermediate phase of the process, the surface of the affected stones is enriched in clay, a material that impairs the strength of the original crystal texture; the surface layer also contains some more or less soluble salts leached from other stones or mortars at a higher level in the structure.

3.3.4 Sandstones and the leaching process

Sandstones are sedimentary stones formed by the transport and deposition of residues of the decomposition of volcanic rocks; the deposited materials have been compressed by other sediments and further consolidated (**diagenesis**) by the percolation of water that transported suspended (clay) or dissolved (calcium bicarbonate) material. Diagenesis creates a connective matrix among the volcanic rock fragments and the secondary minerals produced by the previous leaching processes.

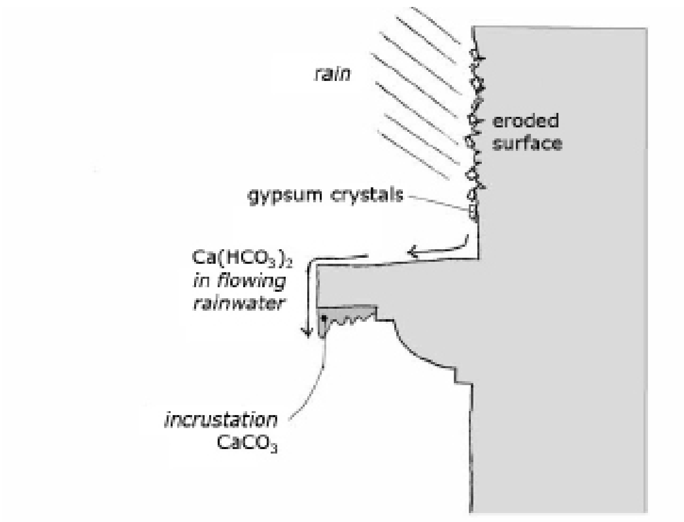
The composition of sandstones is therefore quite variable, and so is their behavior with respect to atmospheric water. If the matrix of sandstone is composed mainly of clay, the stone is easily damaged by water even if it is not acid.

A carbonate matrix is attacked by the acids that transform it into calcium bicarbonate (very soluble) or calcium sulfate (slightly soluble), which may be transported to other positions in the same stone or in the adjoining ones. Also, some leaching of the surviving fragments of volcanic rocks is possible, with further production of clay and salts. The result of this process, after a few centuries of exposure in a temperate climate, is a softening and slight swelling of the stone surface, which is enriched in clay, calcium carbonate, and calcium sulfate crystals in polluted urban atmospheres.

3.3.5 Wet deposition (rain) on calcareous materials

On calcareous surfaces, weakly acid rainwater brings about the dissolution of calcium carbonate, transforming it into soluble calcium bicarbonate and calcium sulfate (if sulfur dioxide is present in the air). These salts are then carried away by rainwater as it flows down the building surface and turn into solid substances (calcium carbonate and calcium sulfate di-hydrate, i.e., gypsum) when the water evaporates.

Figure 3.29

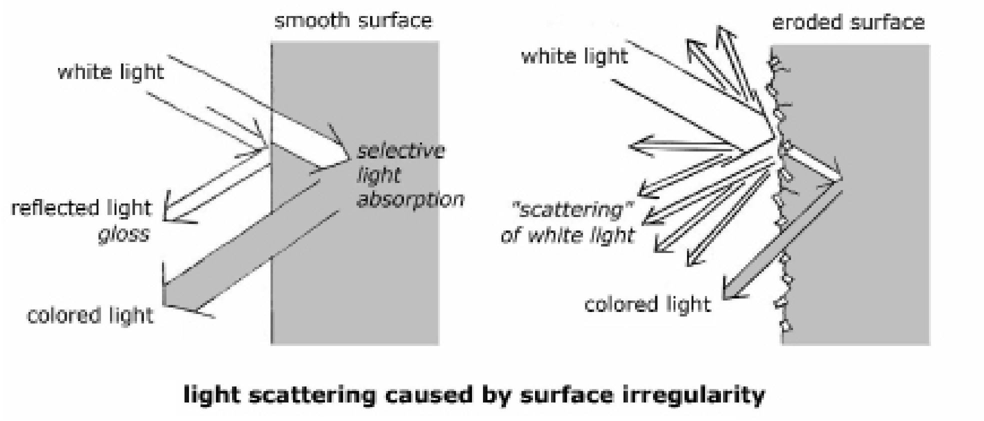


rain action on calcareous surfaces

The result of this transport of matter is usually the formation of **incrustations** (calcium carbonate, with some gypsum in polluted atmospheres), where the rainwater dwelled a longer time before evaporating, or even stalactites, where it dripped slowly from a cornice; these incrustations are quite hard and their removal may be quite difficult when façades are cleaned.

In the surfaces that are directly hit by the rain, the dissolved material is washed away, but they are left roughened by the corrosion process and some re-precipitated gypsum and calcite crystals are deposited in cracks and other irregularities. This condition results in an **eroded surface** and a drastic change in the optical properties of the material.

Figure 3.30



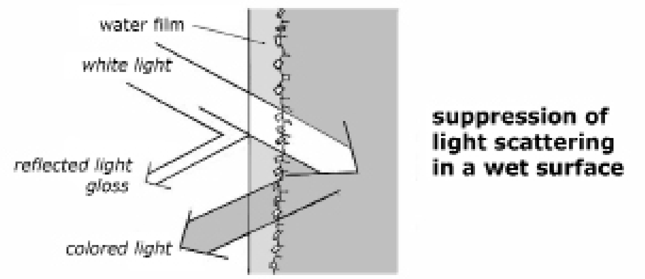
If the surface of a material is smooth, light is able to penetrate a few layers of atoms inside most materials, even in the apparently opaque ones, with the exception of metals, which reflect it completely because of the electric shield created by the moving electrons. Light penetration creates the color of all objects because some of the wavelengths included in the white sunlight spectrum are absorbed by the particular system of atoms and bonds existing in the material (the color seen is the one that is complementary to the color absorbed).

The roughening of surfaces gives rise to **light scattering**, that is, a dispersion of white light caused by the irregularities of the surface; the consequence of scattering is that part of the light is not allowed to penetrate inside the material and so the color fades, to disappear completely when light scattering is intense.

Roman travertine, as an example, has a light brown color when its surface is smooth, as it is when used inside a house with a smooth finish; but the surfaces of the Roman churches that are washed by the rain are completely white because of the scattering caused by the eroded surfaces and the tiny crystals of gypsum hidden in their irregularities.

Light scattering is reduced when the surfaces are wet and may be more permanently controlled by surface treatments, e.g., by polishing a surface or by applying a layer of a synthetic resin, as will be discussed in the next chapter (section 4.4.1) dealing with the conservation of architectural surfaces.

Figure 3.31



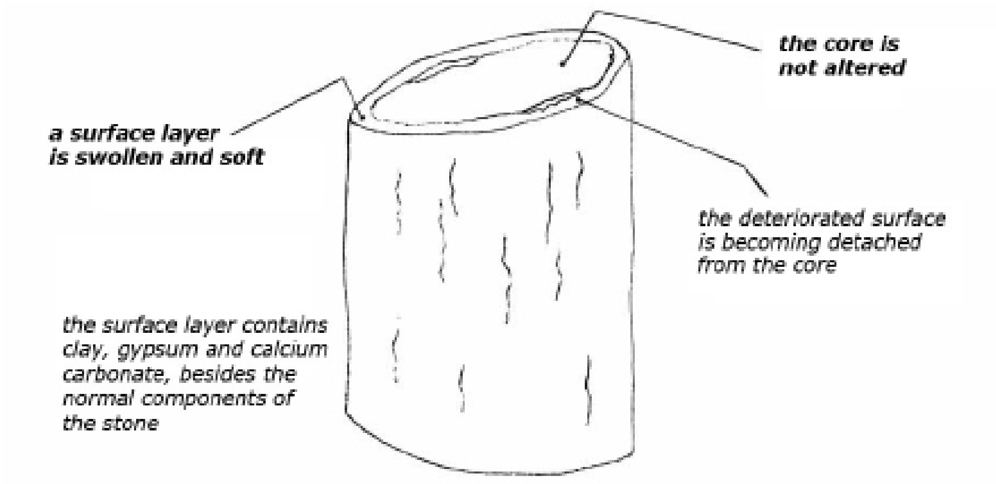
3.3.6 Wet deposition (rain) over volcanic stones and sandstones

Under the action of rainwater, stones whose composition is prevalently siliceous undergo the **leaching process of feldspars, micas, and chlorites**, which are in part transformed into clay and salts that are deposited downstream when the rainwater evaporates.

The surface of the stones is not dissolved—it even undergoes a slight increase in volume—but its strength is reduced and fissures appear on its surface; later in the process a transformed surface layer several millimeters thick shows a tendency to detach from the unchanged core.

Volcanic rocks show a far better resistance than clay-matrix sandstones, but in the long run thick, softened layers are formed also on their surfaces, and particularly so in the case of stones like granite, where the thermal movements of large crystals create fissures that facilitate water penetration.

Figure 3.32



decay induced by rain in siliceous stones

This process is slow but does produce significant damage in historic buildings and archaeological sites; weak crusts of 1 to 2 cm thickness and exfoliation have been observed in granite and sandstone exposed to urban atmospheres in buildings three to four centuries old.

3.3.7 Dry deposition (dew)

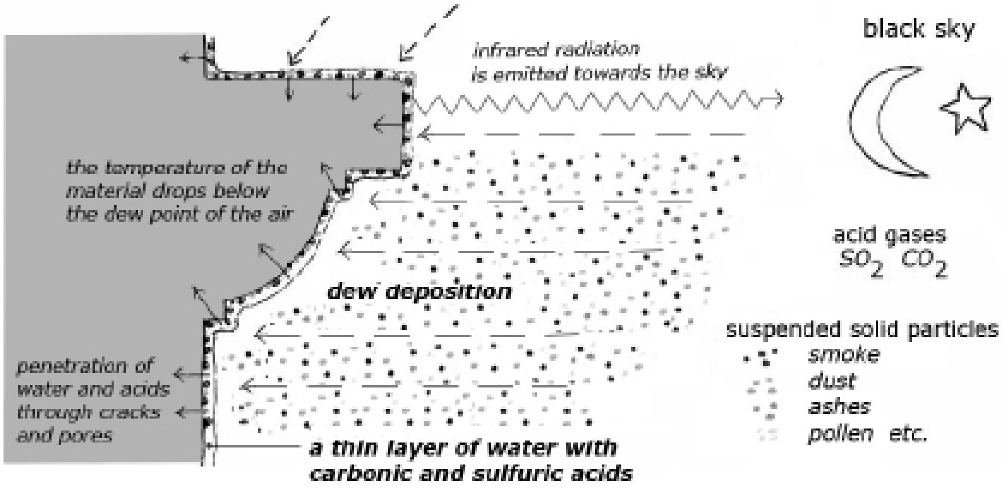
During the night, all external surfaces of buildings cool by radiating energy to the sky. If the relative humidity of the surrounding air is rather high, it may well happen that the temperature of the surface material drops below the dew point of the air (the temperature at which the relative humidity reaches 100%, i.e., saturation); a veil of water is then deposited on the cold surface, a phenomenon called **condensation**.

Physicists who study atmospheric processes named this phenomenon “dry deposition” somewhat improperly, because after all some water is involved, even if much less than in the case of rain. Normal people speak of “dew” and imagine pearly drops hanging from grass blades. Actually condensation in a city is a rather nasty thing because when water vapor condenses on a surface it sweeps away from the air all solid and gaseous impurities it contains, a dirty and dangerous material in a polluted urban atmosphere.

In a temperate climate not too close to the sea, condensation would occur at least half of the nights in winter and spring; in Venice, a very damp city surrounded by a lagoon, it has been said to occur about 80% of the nights throughout the year.

As the amount of water deposited is small, it doesn't run down the surface of a building like rain, but if pores or cracks are available, it penetrates a short distance inside the material.

Figure 3.33



nocturnal condensation

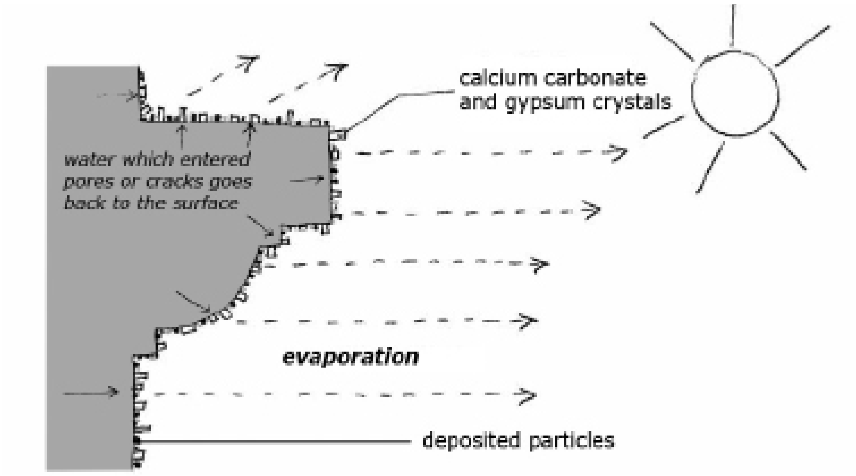
The condensed liquid contains particles of various nature that were suspended in the air; the prevailing color of the deposit in a polluted city is the black of carbon particles from heating systems, automobile exhaust, and other human activities. In the country, the dust of the surrounding soils and vegetal pollens would provide a lighter coloration.

Condensation may also sweep away the acids from the atmosphere or, alternatively, the gases may form the acids by reacting with oxygen on the wet solid surface with the help of catalysts provided by the deposited particles.

If some penetration is possible, the acid liquid may reach inside the surface materials in the millimeter range, to react there with the solids according to the schemes discussed earlier in this section.

In daytime the cycle is reversed because the dew evaporates when the temperature is higher and the air is drier, but only the water goes away while all the matter that was deposited during the previous night remains on the surface.

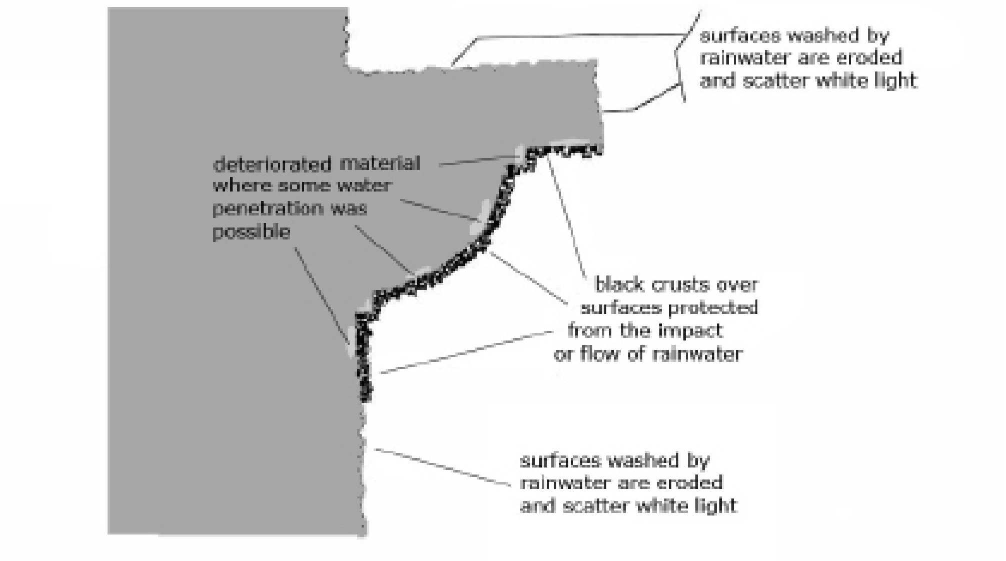
Figure 3.34



wetting - drying cycle, evaporation phase

The most common products of the reactions of the acids with the solid materials of the façades are calcium bicarbonate and calcium sulfate; in the drying phase they are brought to the surface by the evaporating liquid and deposited as calcium carbonate (called secondary calcium carbonate to distinguish it from the carbonate preexisting in the material) and gypsum. The result of this chemical process is some weakening of the internal material that was affected by the acids and some consolidation of the particles that were deposited on the surface by dew condensation.

Figure 3.35



final result of a great number of dew/rain cycles

The repetition of the wetting/drying cycle tends to increase the thickness of the dark layer formed on the surface and to consolidate it, but this is in part contrasted by the events of rainfall. Rainwater washes away all deposited material from the surfaces it impacts, or where it is allowed to run, causing the type of damage that was discussed earlier.

After some years of exposure to rain/dew cycles, the appearance of a historic building in a polluted atmosphere would be considerably changed because all surfaces protected by the cornices and other architectural details would be black, while those washed by the rain would be eroded and blanched by scattering. Furthermore, the penetration of acids might have affected some areas susceptible to deterioration because of defects, natural or induced by human activity (a typical example is relief work in which microscopic cracks are opened by prolonged chisel work); these might appear sound under the dark surface crust, but they may be on the verge of a collapse that could be precipitated by a random impact or periodical thermal expansion stresses.

The dark crusts rich in gypsum do not inhibit the prosecution of the acid attack to the underlying material because they allow the passage of water through tiny channels that can be detected by observation under a scanning electron microscope (SEM).

Part 4

Conservation of Architectural Surfaces

4.1 Basic Principles

The surfaces of brittle porous building materials (stone, plaster, stucco, concrete) that are exposed to the external environment undergo many types of decay processes that are conditioned by several factors, the most relevant ones being:

- the composition and porosity of the material;
- its previous history (works, restorations, accidents);
- the type of exposure (climatic and micro-climatic conditions);
- vegetal and/or microbiological colonization.

It is not surprising, therefore, to see that the symptoms and the velocity of decay processes are quite variable not only in different locations but even within the same building.

The present conservation technology was developed in the second half of the twentieth century; it is aimed at mitigating the decay factors, reconstituting the cohesion of the materials if compromised by the foregoing events, and delaying the onset of the unavoidable future decay processes.

Sometimes in the past, architects naively supposed that conservation technology was a single process applicable to all architectural surfaces, some sort of miraculous varnish or chemical that was supposed to consolidate any kind of material and to arrest indefinitely whatever type of decay.

What technology can offer today is instead **a sequence of operations, with several options available at each step**, whose results may be trusted only within the limits of a **service life** that, as things are now, is not exceedingly long.

Among the available options, the most suitable should be chosen according to the results of preliminary inquiries on the structure of materials and the causes of deterioration; the materials that will be used should be tested to evaluate their **durability** under the conditions they are going to face, and so to estimate the service life, at the end of which they will have to be repaired or substituted.

We think now that the aim of conservation technology should not be extreme durability, but rather a service life of twenty to twenty-five years, the task of the present generation of conservators being to hand over the "cultural property" in good condition to the next one, which, we hope, will have better means and better knowledge at its disposal.

Today, however, some of the materials we use do not allow foreseeing a service life longer than ten years or even less; as a consequence, a system of **periodic**

inspection and **maintenance** must be set up as the only possible guarantee for long-term conservation.

The main steps in the sequence of operations aimed at the conservation of architectural surfaces are:

- cleaning;
- consolidation;
- protection.

4.2 Cleaning of Architectural Surfaces

From a purely conservative point of view, the main reasons for cleaning an architectural surface of artistic or historic value are the following:

- **to remove potentially dangerous material** deposited by previous decay processes (e.g., soluble salts or gypsum-rich crusts);
- **to remove extraneous material adhering loosely to the surface** (e.g., dust or remains of earlier treatments) that would impair the adhesion of consolidating or protective materials that may be applied in the future. When the loose material is part of the original surface or has some historic importance, however, some consolidation that normally would be executed after the cleaning should be applied before it (**pre-consolidation**); this should be made in such a way as to interfere as little as possible with later cleaning operations.

Actually, in most cases the wish **to remove the disfiguring material** that hinders the “legibility” of the architecture is the main motive for cleaning; it is a legitimate one, but it does not coincide completely with the conservation requirements. Occasionally it may even oppose them, a typical example being the case of the dark oxalate “patinas” found over ancient stones, which are disfiguring but have a protective value if adherent to the surface (which, furthermore, can suffer damage when the “patinas” are removed because of their hardness and insolubility). Such situations call for a compromise between the opposing views that the architect and the conservator should be able to work out.

Cleaning is a necessary step before any conservative treatment, just as in the case of metals: rusted iron must be cleaned before painting because paint would not adhere on rust. But it must be kept always in mind that **cleaning can also cause damage** to the surface of brittle materials.

The main risks are:

- **removal of original material** and loss of detail in fine decoration work (as in capitals, reliefs, cornices);
- **creation of cracks** in the brittle materials by the use of unsuitable mechanical means (e.g., sandblasting, rotating tools);
- **production of soluble salts** as residues of chemical processes.

Actually, no cleaning process is completely exempt from the risk of damage, but these are minimized when cleaning is performed by professional operators specifically trained and accustomed to respecting conservation ethics.

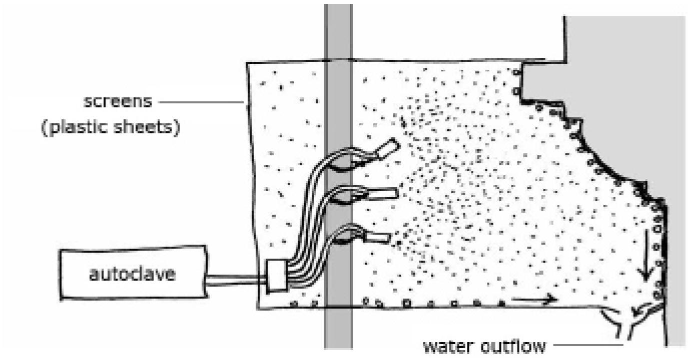
4.2.1 Water cleaning

Water is an efficient cleaning agent for architectural surfaces in polluted city atmospheres because it can dissolve the gypsum crystals that consolidate the dark crusts.

As the solvent action takes place at the interface between the liquid and the solid, increasing the surface of the liquid is a good way to improve its cleaning efficiency. Therefore 1 liter of sprayed water is a far more efficient cleaning agent than the same amount in bulk.

Water sprayed in very fine droplets is said to be "nebulized," and an even finer variety is called "atomized"; **nebulized water** is good enough for architectural cleaning.

Figure 4.1



cleaning by nebulized water

Another advantage of nebulization is that the amount of water that is being used is small, so the risk of impregnating the whole masonry structure with water is reduced.

The solvent action is normally slow and may require several days, but this does not result in an excessive cost because the process is fully automated and requires only periodical attention by the workforce. At the end, the remaining dirt is removed with soft brushes by the conservators.

Hard incrustations containing much calcium carbonate resist water cleaning and require more aggressive chemical or mechanical systems.

Another reason for looking for alternatives to water cleaning is that in some cases it is not desirable to leave the surface materials in contact with water for such a long period.

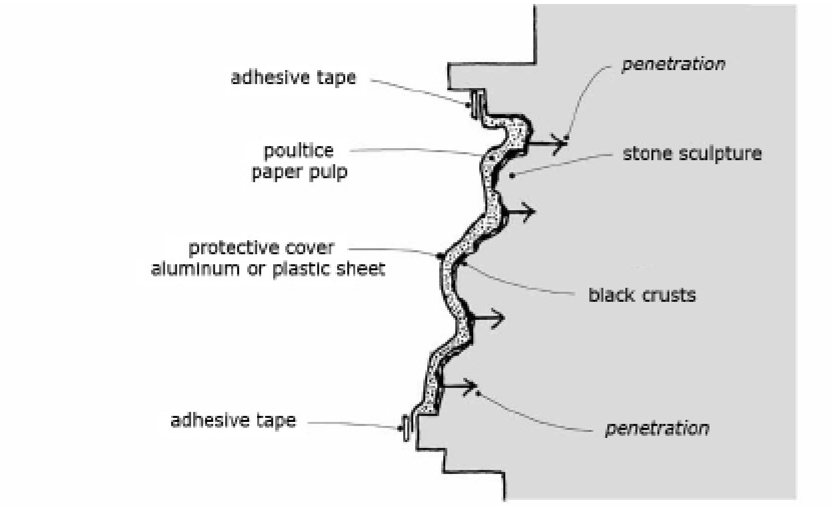
4.2.2 Cleaning by compresses or poultices

The use of substances that can dissolve incrustations by some sort of chemical reaction is the next option when water cleaning fails to produce an acceptable result in a reasonable time. The use of strong acids or strong bases, which was and still is a normal practice in the building industry, is not applicable to historic preservation, not only because of the possible damage to the original surface but also because salts are invariably formed as a by-product of the cleaning reactions and are a likely cause of future damage (it is not easy to eliminate them from a porous surface, even with a good final wash).

Less active agents reduce these dangers, but, as their action is slow, they must be kept in contact with the surface for longer times; this is achieved through the use of some **cellulosic material** applied as a poultice (e.g., paper pulp) or a compress (e.g., sheets of paper) impregnated with a solution of the chemical agent.

Poultices may be sprayed with special guns when large surfaces must be cleaned.

Figure 4.2



cleaning by poultice

The poultice or compress is usually covered with a plastic or aluminum sheet to avoid the evaporation of the water and is left in contact with the surface to be cleaned for a number of hours determined after a series of tests.

When the protective sheet is removed, poultices and compresses are left on the surface until they are dry, as this draws out of the pores the dissolved material, which may be dangerous or disfiguring (soluble salts or colored substances). After the water is gone, the dry material is carefully removed and disposed of.

When high-porosity materials are affected by soluble salts, special clays with high absorption capacity (**sepiolite** or **attapulgite**) are used in the poultice instead of cellulose as their absorbing power is much higher.

Clay poultices are also useful in removing spots of non-polar substances such as fuel oil, tar, or grease, but in this case a non-polar solvent (e.g., white spirit) must be used as the liquid phase.

The chemical most widely used today as the active agent in the water phase is **ammonium carbonate**, a mildly basic salt (see section 1.5.5) that decomposes slowly into ammonia and carbon dioxide, both gaseous substances; as a consequence it disappears after some time when it is left exposed to the air in a solid state. It is a quite useful property because the inevitable excess of reagent left in the pores evaporates, leaving no dangerous residue.

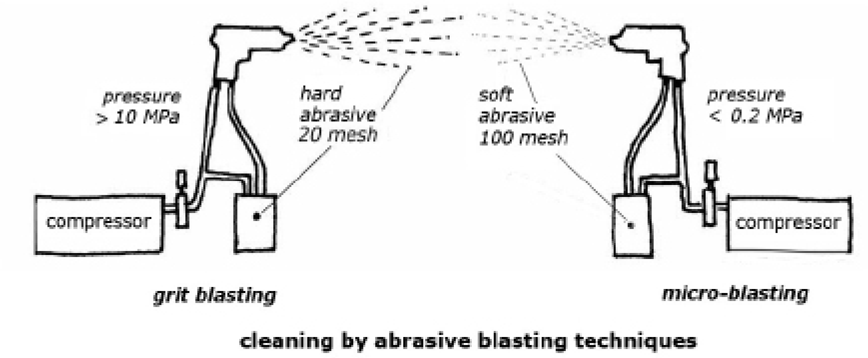
The addition of a chelating agent (e.g., **EDTA**, see section 1.5.6) to the liquid increases the efficiency of the method for the removal of calcareous incrustations and rust spots; a high EDTA concentration allows even the dark oxalate patinas to dissolve progressively and so controls their disfiguring effect.

4.2.3 Mechanical cleaning

When the wet cleaning methods are not efficient enough or not advisable, as in the presence of gypsum mortars or rusting iron cramps, mechanical methods are possible options provided the damage they inflict to the surface of brittle materials is mitigated as much as possible.

While the use of rotating abrasive discs or brushes is normally not advisable because they are both inefficient and damaging, grit blasting is frequently applied in the cleaning of historic architecture, although in a modified version called **micro-blasting** in Italy. In this technique, the abrasive used is not hard, ranging from calcium carbonate in microsphere form to glass microballoons and even to ground nut shells or fruit stones; also the air pressure is sharply reduced from more than 100 atmospheres, as normally is done in grit blasting, to less than 2.

Figure 4.3



But even with such precautions, micro-blasting is not suitable for the treatment of low-hardness materials (such as renderings, stuccoes, and soft sandstone or limestone) and also of hard stones containing large crystals (such as white marble or granite), which are easily cleaved under a mechanical impact.

Another limitation of this method is that the respect of the limits imposed on pressure and abrasive material is left to the goodwill of the operator or to the efficiency of quality control, as the same equipment may be used within wide limits of pressure and of type of abrasive.

The most suitable application is on hard microcrystalline calcareous stone (e.g., Roman travertine) that frequently forms on its surface thick, hard incrustations that are not easily removed by other means.

But even sandblasting is not sufficient to deal with centimeter-thick calcareous crusts formed by hard water in fountains; the bulk of such incrustations is normally removed by chisel work aided by gentle hammer blows aimed at impairing their adhesion to the underlying stone.

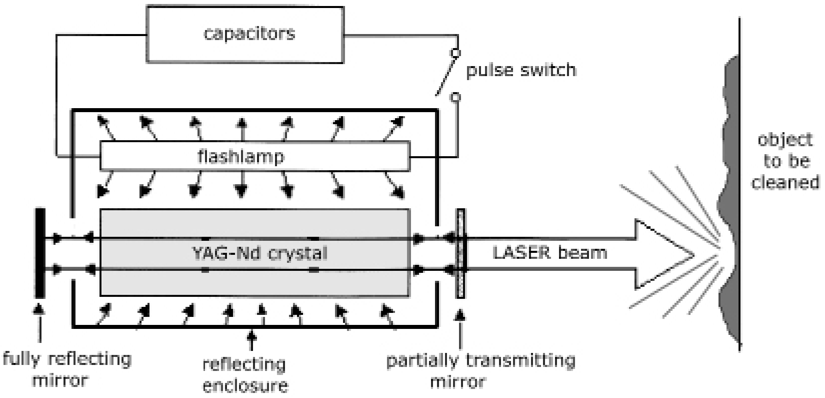
4.2.4 Laser cleaning

Powerful pulses of coherent light impacting on a surface are absorbed by the surface of the material, all the better if its color is dark, and transmit sufficient energy to the outermost layer of material to vaporize it without exerting any mechanical action.

Very fragile materials can be cleaned without a preliminary consolidation, which would reduce the efficiency of most cleaning methods.

The functional scheme of laser equipment is illustrated in figure 4.4.

Figure 4.4



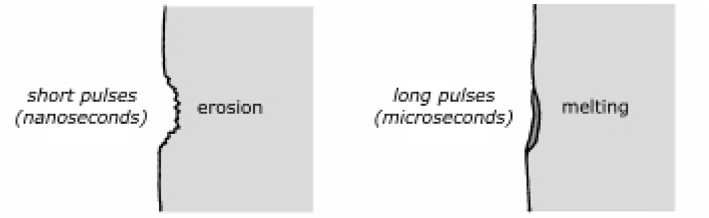
laser cleaning

The lasers most used in conservation today are of the **YAG-Nd** type, which are based on crystals of Yttrium-Aluminum Garnet, with Neodymium doping, and emit pulses of **infrared radiation** (1064 nm wavelength) that are not visible. In order to let the operator aim the beam properly, a low-power red laser is added to the instrument to mark the impact point.

A most important part of the instrument is the switch that regulates the duration of the pulses of light, because the effect of the laser beam on the impacted material varies according to the pulse duration and energy in a way that is relevant to conservation problems. A **Q-switch** laser provides pulses in the range of nanoseconds (10^{-9} seconds), while pulses in the range of microseconds (10^{-6} seconds) and milliseconds (10^{-3} seconds) are produced by a **free-running** device.

It should be kept in mind that the short Q-switch pulses may cause some mechanical damage to the surfaces of brittle materials, if an excessive number of pulses are applied, while the free-running type is more likely to cause the melting of an extremely thin layer.

Figure 4.5



laser-induced damage

Change of color is another of the possible negative effects that laser cleaning may produce; this has been experienced on white stone with the appearance of yellow or pink discoloration, and on some pigments in paintings. It appears that on white Carrara marble, the risk of discoloration is reduced by the use of longer pulses.

The use of laser cleaning on works of art is always preceded by accurate testing to assess the risk of unwanted side effects.

4.3 Consolidation of Architectural Surfaces

When the surface of a building material is at the point of losing cohesion, or adhesion to the masonry core, it must be consolidated not only for aesthetic reasons but also to ensure the correct conservation of the entire structure.

Stone consolidation processes have been widely used since the start of the nineteenth century; at the time, and still much later, the basic idea was that by the application of a single consolidation "treatment" all conservation problems would be solved. Also, surprisingly enough, while no maintenance was foreseen for the future, it was thought that the "treatment" would offer indefinite protection for the treated materials.

With such requirements any conservation treatment must necessarily fail, and so did some consolidation techniques that were actually efficient and came to be labeled as useless or dangerous. Another negative consequence was that the conservation of the surface materials of historic architecture was deemed to be impossible, substitution or ruin being the only available options.

In our present view, substitution should be accepted only when it is deemed to be necessary for conservation purposes (e.g., to restore the functionality of a cornice) because it frequently entails a substantial loss of information and aesthetic value.

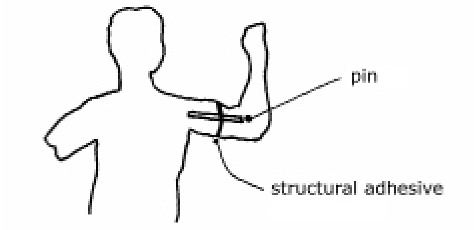
The consolidation technology we use today is based on the distinction among different types of damage and on the use of different techniques according to the type of damage. Furthermore, consolidation is aimed only at restoring cohesion to decayed materials, allowing them to face the environment with better chances of survival; **its function is mostly mechanical**, as the task to delay future deterioration is left to other practices that are classified under the label "protection" (discussed in chapter 4.4).

4.3.1 Adhesion of detached parts

In the conservation treatment of historic façades, it is frequently found that parts of architectural details are cracked and partially detached, e.g., because of the corrosion of iron cramps or when the adhesion of ancient repairs is at the point of failing. In such cases the complete detachment and reattachment of the loose element with a suitable adhesive is the simplest and most effective provision.

The choice of the adhesive depends upon the stress that the joint will have to bear in the future; unsupported parts, unless they are very small, require the use of a **structural adhesive** (see section 6.5.5.3), typically an **epoxy resin**; a suitable filler is added to the fluid resin if the fit of the broken surfaces is not very good and some gap must be filled. If the piece to be supported is heavy, a strong **pin** is inserted across the joint as a further guarantee against failure, even if the strength of the adhesive appears to be sufficient (the load-carrying capacity of a structural adhesive may be estimated at about half a kilogram per square millimeter of joint surface).

Figure 4.6



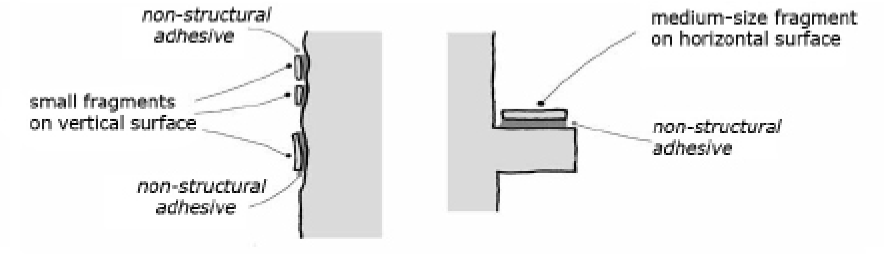
structural bonding

Since the pin must be corrosion resistant, it cannot be made of steel; **stainless steel** or **glass-reinforced polyester** are the most frequent choices, but care must be taken to avoid stresses caused by the thermal expansion of these materials whose coefficient is larger than that of normal steel and almost double that of many stones. **Brass** is another possible option, but with the same thermal expansion problem.

If cost is not a problem or few pins are needed, **titanium** is the best choice for the pin; besides being corrosion resistant, it has the smallest thermal expansion coefficient among the available metals, not much different from that of many stones (for thermal expansion coefficients, see section 3.1.3).

Unsupported small fragments or medium-size ones that are supported by a horizontal surface may be reattached more simply with a **non-structural adhesive**, normally a thermoplastic synthetic resin (see section 6.5.5.2), e.g., an **acrylic resin emulsion**.

Figure 4.7



non-structural bonding

4.3.2 Consolidation by surface grouting (non-structural surface injections)

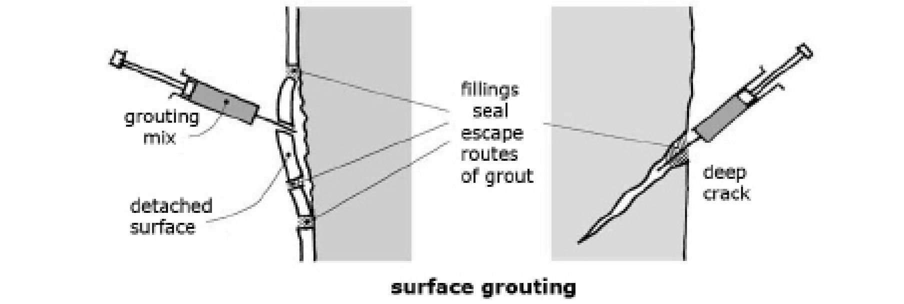
Deterioration processes frequently cause the detachment of surface layers from the inner structure in the façades of old buildings; typical examples are renderings stressed by vibrations caused by traffic, frost, or salt crystallization, or some types of building stone, like sandstone, tuff, or granite, in which chemical processes transform part of the surface minerals into clay and salts (see chapter 3.3).

One key point in the present preservation technology is that the loss of any original material that has become loosely attached to the surface must be avoided; this is not only because of its aesthetic or documentary value but also because the partly decayed but consolidated material will protect the one behind it from the action of the environment and so will delay the onset of a new sequence of deterioration processes.

Grouting is the name given to a rock consolidation technology based on the **injection of fluid materials** (grouts, normally cement-based mixtures or synthetic resins) that can harden inside the cracks.

In surface grouting, a hydraulic binder (usually hydraulic lime, see section 2.6.5) with suitable admixtures is injected by hand in surface cracks in stonework or masonry and behind renderings. The finest cracks into which hydraulic grouts can penetrate are a few tenths of a millimeter wide; to consolidate finer ones, a low-viscosity thermosetting resin such as an epoxy (see section 6.5.3) is required.

Figure 4.8



The injection of the grout is normally preceded by the injection of a liquid meant to “clean” the internal voids by removing dust and fine debris that would hinder the adhesion of the consolidant. In the case of hydraulic grouts, the injected liquid is just water initially, but frequently this is followed by a diluted suspension of a thermoplastic resin that is meant to make the surfaces more solid and somewhat “tacky.”

In the case of the injection of an epoxy resin, the cleaning liquid should be a solvent because the setting of the resin is hindered by the presence of water (alternatively, the material must be allowed to dry completely before the injection of the resin).

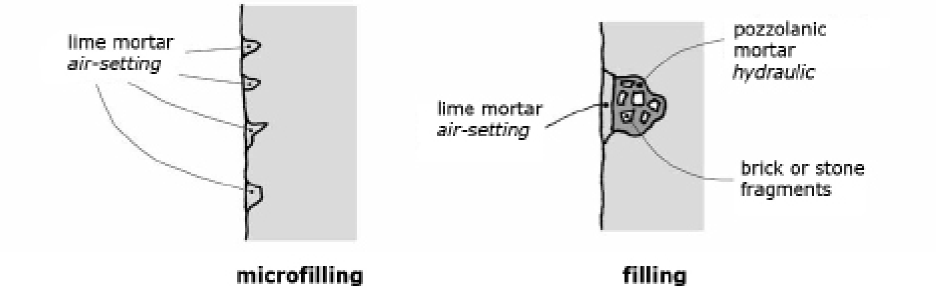
The preliminary injections are also useful to determine the points from which the grout might escape from the cracks and flow on the surface; this must be avoided not only for the soiling it causes but mainly because the diffusion of the grout inside the internal voids is unsatisfactory when the pressure (usually applied by hand) is released by the outflow of the fluid. Therefore, as soon as a point of escape is detected, it is carefully filled, normally with a lime mortar, and the injection of the grout is performed after the filling mortar has properly set (i.e., after several days).

4.3.3 Filling of cracks and voids

Filling all cracks and voids in the surface of deteriorated materials is a fundamental point in the present practice of conservation of architectural surfaces. The theoretical basis for the particular attention devoted to this step in the conservation process is the notion that any discontinuity of the surface of brittle materials is the prime cause of mechanical and chemical damage due to the concentration of stress and the penetration of acid water.

As a consequence, filling must be carried out with the utmost attention, down to barely visible imperfections, even in the case of the treatment of very large surfaces. The term *microfilling* (*microstuccatura*) is frequently employed in Italy to define this kind of work in treatment specifications.

Figure 4.9



Filling is normally done with a lime paste mortar, but in the case of medium to large cavities most of the void is filled first with pieces of an aggregate of suitable size (fragments of brick or stone) mixed with a hydraulic mortar (e.g., lime paste/pozzolan); then a final layer is made up with lime paste mixed with crushed stone. Colored stone powders are added to the filling mortar to adjust the color to match that of the adjacent material. Color matching is far more difficult if pigments are employed.

Color adjustment of the fill material is a step of capital importance and a time-consuming one, since filling is often extensive and the optical effect quite distressing in case of a mismatch.

4.3.4 Consolidation by impregnation

Since the first quarter of the nineteenth century attempts have been made to restore the cohesion to stones that had lost it, and two different lines of approach were taken that continue up to the present time. We can designate one of them as the "**organic**" approach, as organic materials possessing adhesive properties were used, and the second as the "**inorganic**," or "chemical," approach based on chemical reactions that cause the precipitation of inorganic compounds inside the deteriorated material.

The **organic** approach initially used various natural products, the most successful of which were hot linseed oil and molten paraffin wax, while the **inorganic**, chemical one produced several widespread methods of impregnation based on alkali silicates, fluosilicates (see section 7.1.3), barium hydroxide, or calcium hydroxide.

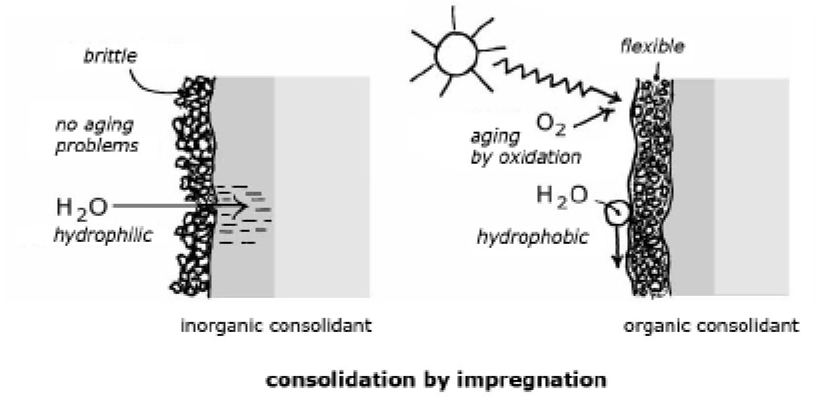
Actually, a majority of those processes were rather efficient, but some collateral effects prompted objections; the organic materials would tend to darken (linseed oil) or to attract dust (paraffin wax), while the chemical reactions, if not carefully executed, might produce salt efflorescence and surface crusts that exfoliated after some years.

The success of conservation treatments at that time was also prejudiced by their direct application on the stone as found, without previous cleaning and filling of cracks, and the misconception that their effect could last forever, no maintenance being foreseen.

In the twentieth century, the general progress of chemical technologies produced materials that made it possible to mitigate those defects, and both lines of work were continued: synthetic resins were used as organic adhesives, while ethyl silicate (see section 7.1.4) substituted inorganic silicates and fluosilicates as the most used inorganic consolidant.

The main characteristics of the organic and inorganic consolidation systems are shown in figure 4.10.

Figure 4.10



The product of consolidation by an inorganic chemical reaction is a material that is durable but does not change the main physical and mechanical characteristics of the treated materials, which still remain brittle and hydrophilic; therefore, their resistance to environmental decay processes is not improved (but this may well be taken care of in the final step of the conservation process).

Consolidation by organic materials has just the opposite characteristics: the brittleness is reduced and the surface becomes hydrophobic, but these properties are progressively modified by the aging process that affects all organic materials (see chapter 6.6).

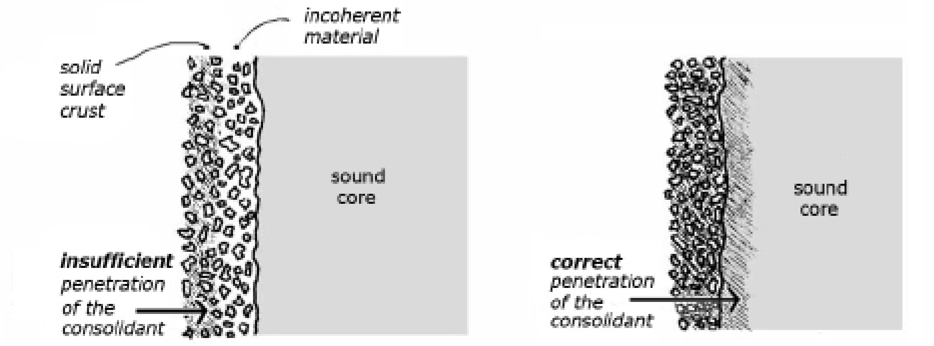
The optical properties are frequently impaired by a general darkening (which may become worse with time) and some unpleasant gloss from an excess of consolidant left on the surface (this, however, may be taken care of by an experienced conservator).

More recently, a new class of chemicals was developed, the silanes, that may be considered to be intermediate between the organic and inorganic materials; the silanes are monomers that form polymers, "silicones," with an inorganic backbone from which organic groups of atoms, carbon-hydrogen "radicals," branch out (see chapters 7.2 and 7.3).

It is too early to say whether this new, promising class of consolidants will supersede the established ones; it may well happen because nobody in the trade thinks that what we have now is perfect. In the meanwhile, in Italy, the preference is now given to ethyl silicate impregnation when such a step is required (see below); resistance to water penetration is then entrusted to the next step in the process, which is labeled "protection" and may or may not involve the application of a hydrophobic layer on the surface of the material after consolidation (see section 4.4.2).

In any case, whatever the consolidant chosen, the technique used to apply it must allow it to penetrate all deteriorated layers and to reach the sound core of the material, otherwise a solid crust would be formed over an incoherent base; this may look nice for a while, but the crust would soon spall off, causing damage worse than the one that might have been expected if no treatment had been performed.

Figure 4.11



depth of penetration of a consolidant

In present conservation technology, impregnation is not as important as it was in the past; it is just one of the available options, namely the one that is apt to deal with cases of decay in which the material tends to separate into very minute grains. When the fragments exceed a few millimeters in size, or when the cracks are wider than one-tenth of a millimeter, it is wiser to opt for microfilling, grouting, or the use of an adhesive.

4.4 Protection

4.4.1 Architectural protection

The decay of materials on the external surface of buildings depends in large part upon the action of rainwater flowing on them or of moisture migrating inside their pores.

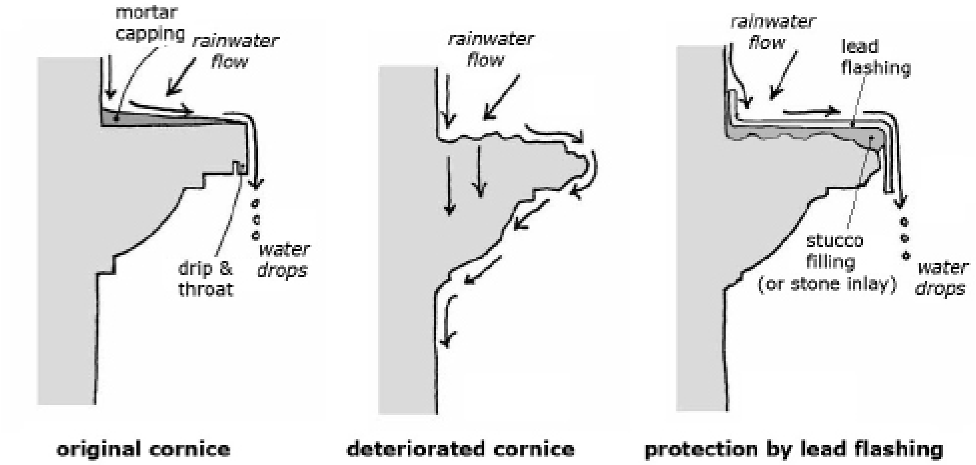
The study of the protection of the façades of architecture of artistic or historic importance should always start with a careful examination of the state of conservation of the entire building, with particular reference to those parts (roof, gutters, downpipes, cornices, windowsills, and all projecting elements, flashings, damp-proof courses, hydrophobic membranes, drains, etc.) that were designed with the purpose of protecting it against water and which may not be properly functioning because of their own deterioration or defective design (or execution).

A typical example concerns the architectural details projecting from the masonry in a traditional façade (e.g., cornices), which have an important protective function besides their decorative one; they should intercept the rainwater flow on the wall surface and shed it thanks to a drip, a narrow channel (“throat”) formed under their edges.

Frequently we find that the drip disappeared because of the deterioration of the material, while in other cases it was never made, and as a consequence a cornice lost most of its protective value for the surface below. This problem was often solved in the past by setting a slate plate on top of the cornice and letting it protrude a little beyond it so that water could drip away.

The durability of slate exposed to a temperate environment is in the range of 100 years; not bad, but lead can do better. Furthermore, lead may be bent around the edge of the cornice to form an efficient drip and may be painted the same color as the cornice material to make it disappear from the general view of the building.

Figure 4.12



4.4.2 Hydrophobic protective films

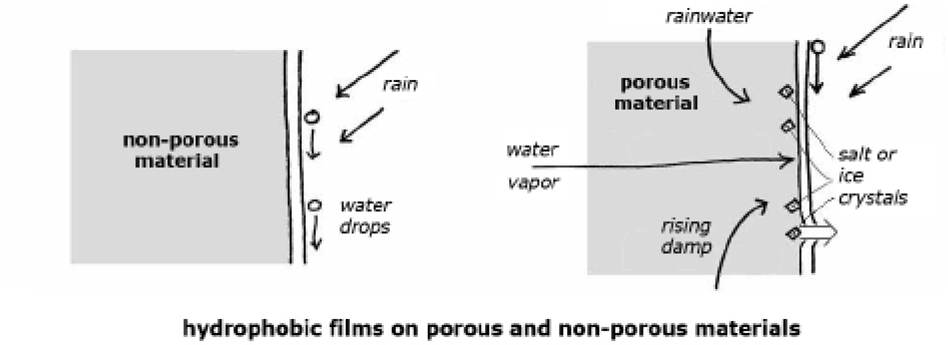
A water-repellent film on the surface of a building material should in principle exert an important protective action because the water impacting on its surface would not be allowed to penetrate into pores or cracks and would drip down without causing damage.

Actually, however, many unsolved problems still limit the efficiency of this type of protection.

In the first place, a surface film is well suited to the protection of low-porosity materials (the ideal case is that of metals) but not of very porous ones, because if water is able to gain access to the pore system from some unprotected surfaces or an inner source (e.g., a broken pipe), the film becomes a nuisance rather than an asset.

Besides the obvious cases of leaks from roofs or pipes and of capillary rise from damp soil, there is also the possibility of humidity condensation behind the film in cold climates (moisture being provided by the warm internal air) followed by possible frost damage, unless a vapor barrier is applied on the internal face of the wall (which may not be feasible in historic buildings).

Figure 4.13

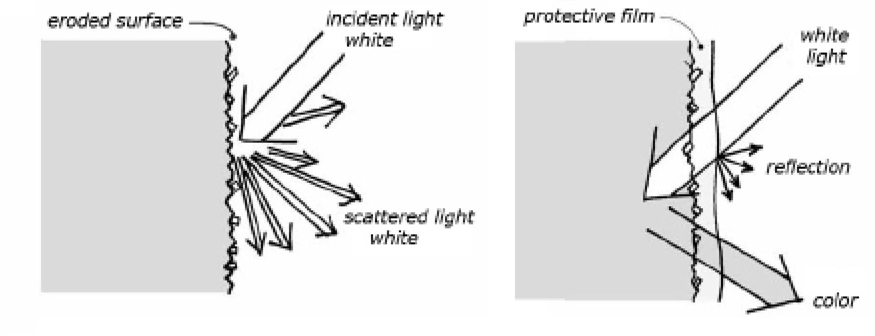


The application of protective films on low-porosity stone, like marble, granite, or travertine, would thus be quite useful, but other problems arise even in this case. One is durability: all hydrophobic materials undergo an oxidation process when exposed to oxygen and light (see chapter 6.6) and lose water repellency within a time span that is still too short (around five years for the best materials among those most frequently used) for a sustained maintenance cycle. Technology is progressing in this domain, however, and it is likely that more durable materials will be available soon.

Another problem is that the application of a transparent film on a stone, stucco, or rendering may cause some important optical effect by reducing the scattering of white light due to the irregularities of surfaces that are weathered or originally had a rough finish.

Such an effect is produced by most organic films, particularly if the refractive index is high (e.g., acrylic resins, see section 6.4.6), but much less by the silicones (see section 7.3.1) because of their partly inorganic structure. The ability to suppress scattering may be exploited in conservation work to reduce the blanching effect caused by a strong erosion of the surfaces, but on the other side protective films are frequently a cause of criticism because of the "plasticized" gloss they may confer if they are not properly applied.

Figure 4.14



suppression of scattering by a protective film

A stone that needs protection by a hydrophobic film is white marble, a material that was widely used in the past to carve fine architectural details and works of sculpture, which do deteriorate when exposed to the external environment and more severely in polluted atmospheres. Some cases of serious decay have been observed even in the interior of damp buildings.

Unfortunately, at the present moment all available protective materials show some defects that limit their utility. Linseed oil darkens upon aging, paraffin wax attracts dust, acrylic resins soon lose their hydrophobicity in an external environment, silicones lose their water repellency later than acrylics but still too soon and, furthermore, appear to offer little protection against acid gases. Finally, fluopolymers (see section 6.4.5), which resist oxidation better than the other polymers, attract so much dust that they can't be applied over white stones.

While these notes are being written, a new wave of potentially effective protective products is appearing on the market, and new testing programs are on the way; some improvement is certainly to be expected, but in the meantime the use of protective films is limited to details sculpted in low-porosity stone, while the most important artwork is removed from the historic façades, to be substituted by copies. On stones, stuccoes, and renderings of valuable façades, the use of films is aimed mostly at the correction of optical defects (e.g., blanching of corroded material) while protection is entrusted mainly to good maintenance of the protective features that are an essential part of the traditional architecture.

Part 5

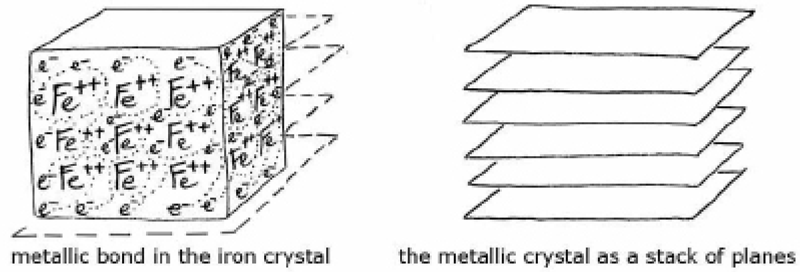
Metals

5.1 Ferrous Metals

5.1.1 Iron and iron-carbon alloys

Iron has a cubic crystalline structure in which the atoms are bound by an electronic cloud (or electronic glue) created by their outermost mobile electrons (see section 1.2.4).

Figure 5.1



metallic bond in the iron crystal

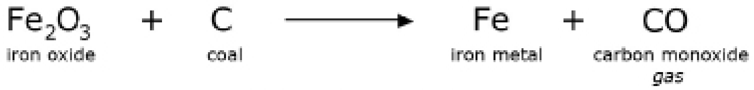
the metallic crystal as a stack of planes

atomic structure of iron metal

This type of bond, the **metallic bond**, determines the mechanical and physical properties of metals: plastic deformation, and electrical and thermal conductivity (see chapter 1.3).

The mechanical properties of iron, however, are also conditioned by the fact that unless it is purified by special techniques, some carbon atoms are always entrapped in the crystals; this happens because the method of production of the metal involves the removal of oxygen from the iron oxide ore by reaction with coal at a high temperature.

Figure 5.2



$$\underset{\text{iron oxide}}{Fe_2O_3} + \underset{\text{coal}}{C} \longrightarrow \underset{\text{iron metal}}{Fe} + \underset{\substack{\text{carbon monoxide}\\ \textit{gas}}}{CO}$$

iron production

As iron remains in contact with coal and carbon monoxide in the furnace, it absorbs carbon atoms that may be lodged in free spaces (**interstices**) in the crystal structure. In scientific language, carbon is “dissolved” in the iron and a “solid solution” is formed.

Fitting a carbon atom in an interstice involves, however, the displacement of some adjacent iron atoms and the creation of a local irregularity in the crystal structure, which is bound to hinder the slip of atomic planes that allows plastic deformation (see section 5.1.2).

The hardness of iron increases as the carbon content increases, but above a certain limit the metal becomes brittle because an excessive disorder of the crystal structure does not allow any plastic deformation.

Because of the high melting point of iron (1535°C), in the **"direct" method of iron production**, which was the only one used in Europe up to the thirteenth century, the metal is not obtained as a liquid, as are the other most common metals, but in a solid, spongy state (**bloom**).

In the **"indirect" method of production**, the blast furnace makes it possible to increase the amount of carbon dissolved in the metal so much that the melting point drops considerably (slightly above 1100°C) and the molten metal can flow out of the furnace, forming blocks of solid metal (**pig iron**). This is far less expensive, but the material so produced is always brittle and requires a laborious refinement to make it workable by mechanical means.

From the second millennium BCE up to recent times, iron technology developed slowly, aiming at the apparently impossible goal of obtaining a very hard but not brittle metal.

Ferrous metals today are classified in three main groups:

- **mild steel**, iron with very little carbon, not very hard, malleable;
- **steel**, carbon content up to 2% (usually 0.07% to 1.3%) and best mechanical properties;
- **cast iron**, carbon content above 2% (usually 3.5% to 4.5%), easily melted and cast but brittle (with the exception of special compositions or special heat treatment).

In the **modern** use, the term **steel** refers only to alloys that have been prepared in the liquid state, that is, at temperatures above the melting point of iron (1535°C), which could not be reached before the modern age.

In the course of the historic development of iron technology, however, alloys that fall within the composition limits of the modern steels have been produced since very ancient times, but the amount of carbon in the alloy was adjusted by working the metal in the solid state, a technique that did not permit an accurate control of the composition and produced metals of variable mechanical properties.

Some archaeologists use the term *steel* also in these cases; actually the term did exist in the past, but it was applied only to high-quality alloys, produced in small quantities by processes kept secret (and, in some cases, are not fully explained even today).

In these lectures the term *steel* will be applied only to low-carbon alloys of very good and strictly controlled mechanical properties, which in the case of architectural metals are only the modern ones (see section 5.1.5.4).

The modern definition of **cast iron** is applicable also to the ancient ferrous alloys that were prepared and used in the molten state (see section 5.1.5.2).

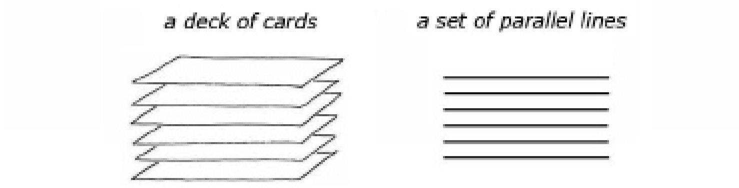
For all the historic alloys containing 0.1% to 2% carbon, which were prepared and worked entirely in the solid state, the term **wrought iron** will be used (see section 5.1.5.1).

In the case of the ferrous alloys produced after 1784 and up to the end of the nineteenth century refining cast iron by the “puddling” process, part in the liquid state and part in the solid state, the traditional name, **puddled iron**, is used (see section 5.1.5.3).

5.1.2 Plastic deformation and work hardening

A metallic crystal may be represented in an oversimplified way by a stack of planes of atoms, just like a deck of cards or, even more roughly, by a set of parallel lines.

Figure 5.3

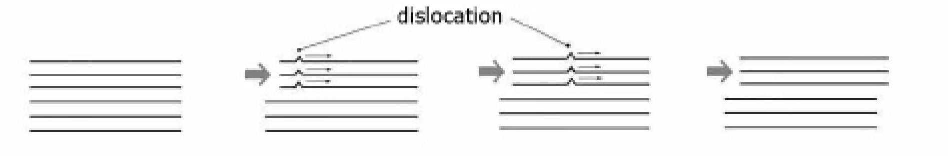


symbolic representation of a metallic crystal

The atomic planes may slide on top of one another in the crystal if a large enough stress is applied, because the metallic bond is not directional and no electrical potential barrier hinders their movement (see section 1.3.2.4). As soon as the stress ceases, the movement stops and the non-directional metallic bond freezes the atoms in their new positions; the result is a permanent, irreversible plastic deformation.

Sliding is made easier by the formation of a sort of fold, which is termed a **dislocation**, in the planes that are stressed.

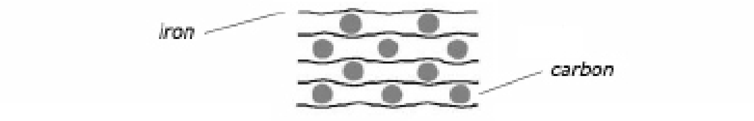
Figure 5.4



movement of a dislocation under stress inside a crystal

Moving across the crystal, a series of dislocations allows a part of the crystal to slide on top of another part under a stress that is highly inferior to the stress required to separate completely the two parts of the crystal and to reunite them in a new position. In all metallic crystals, the movement of the dislocations is relatively easy if the structure is regular, but it is hindered by any irregularity (**defects**), such as different atoms present in some positions or in its interstices (such as carbon atoms in the iron crystal).

Figure 5.5

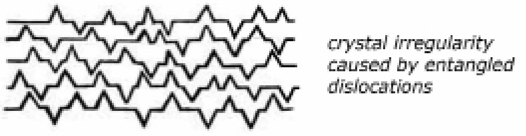


solid solution of carbon in iron

As a consequence, all metals become harder and less deformable when they are mixed with another metal, forming an **alloy**.

When a piece of metal is worked and its shape is being changed, a large number of dislocations are formed at the same time, and they move along different directions in the variously oriented crystal grains; this phase of easy movement, however, doesn't last forever because the dislocations tend to pile up around all irregularities until a sort of general traffic jam occurs and the sliding of atomic planes in the crystals is not possible anymore. In this condition a loss of plasticity and an increase of hardness is observed. This process is called **work hardening**.

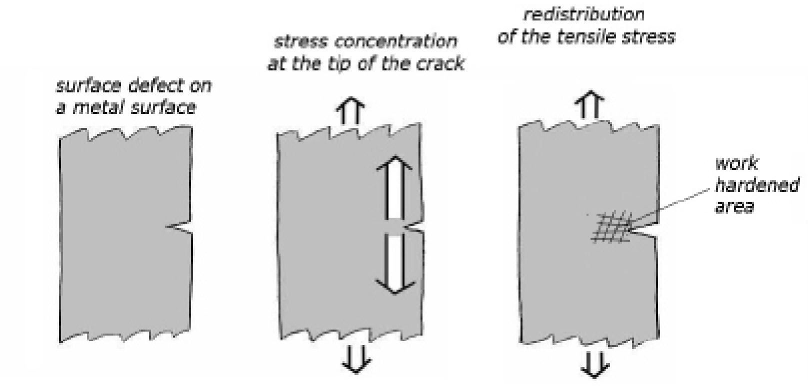
Figure 5.6



symbolic representation of work hardening

An important consequence of work hardening is that in a metal, the tensile strength is much less affected by superficial defects than it is in a brittle material like stone; in a metal, concentration of stress at the tip of a crack results in the deformation and work hardening of the affected area whose increased resistance hinders a further advancement of the crack and allows a more homogeneous distribution of the stress.

Figure 5.7



surface defects in metals don't affect the tensile strength as much as they do in brittle materials

There is an important exception, however. When a tensile stress is coupled with a corrosion process, the overstressed area at the tip of a crack is preferentially corroded by an electrochemical process and the fracture can advance quite rapidly (see **stress corrosion** in section 5.1.6.4).

5.1.3 Heat treatment of iron-carbon alloys

5.1.3.1 Quenching

The cubic crystal structure of iron, which is stable at temperatures above 700°C, is called **austenite**. It may lodge carbon atoms in its interstices up to a concentration of 2%; in high-carbon alloys (i.e., cast iron), carbon in excess of 2% combines with iron to form separate crystals of an iron carbide (formula Fe_3C), called **cementite**.

Crystals of austenite and cementite are different **phases** that coexist in cast iron when the molten metal solidifies, while only austenite exists inside just solidified steel.

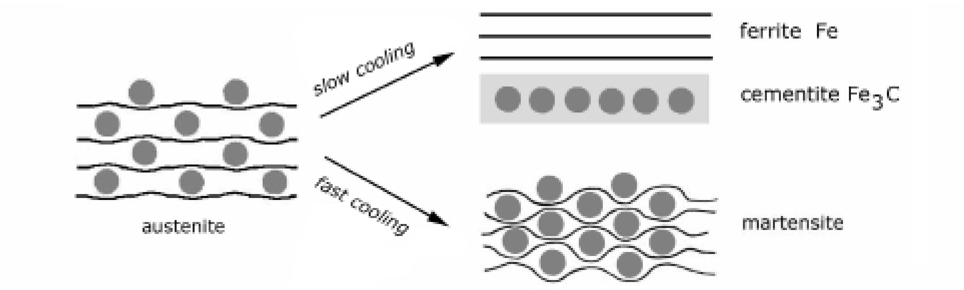
Austenite, however, is not stable below 700°C, so when the metal is allowed to cool, the crystal structure of iron changes into another type of cube. This phase is called **ferrite** and is almost pure iron; it offers smaller interstices that do not allow the access of carbon atoms at all.

When this transformation happens, the carbon should migrate out of the austenite crystals to form cementite, a process that is slow because it happens inside a solid material, while a still high temperature provides atoms with sufficient energy to reach their equilibrium positions.

So, when an iron-carbon alloy is cooled slowly, the austenite that is formed first is transformed into cementite and ferrite, but if the cooling is rapid (e.g., the red-hot metal is plunged into iced water) the carbon atoms are trapped in the modified iron structure, causing an extreme deformation.

The deformed, carbon-containing ferrite is called **martensite**. In martensite, no plastic deformation is allowed by the distorted crystal planes; the hardness is very high, but the metal is brittle.

Figure 5.8



quenching of ferrous metals

According to the evidence offered by archaeological finds, the hardening of ferrous metals by **quenching** appears to have been discovered around the year 1000 BCE.

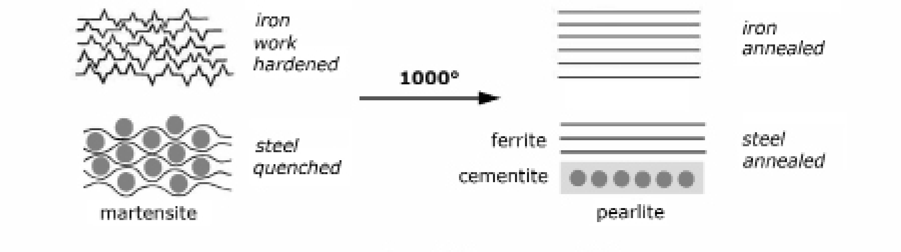
5.1.3.2 Annealing and tempering

The atoms in a crystal structure stay put in their proper positions only at the temperature of 0°K (zero degrees Kelvin, absolute zero, –273°C); at any higher temperature they vibrate around their equilibrium positions, the amplitude increasing as the temperature rises. At the melting point of a solid, the energy of the vibration is so high that the bonds that join the atoms break and the atoms gain complete freedom of movement.

If a crystal that was deformed by mechanical stress or a quenching process is heated at a sufficiently high temperature but below the melting point (around 1000°C for the iron-carbon alloys), the oscillations of the atoms are large enough to allow them to regain a correct alignment. This is the process of **re-crystallization**, through which the hardness and brittleness of a work-hardened, or quenched, metal is progressively reduced.

The technical name of the process is **annealing** if the heating is prolonged until the correct crystal structure is reestablished.

Figure 5.9



annealing of ferrous metals

When martensite is fully annealed, alternating layers of ferrite and cementite are observed under the microscope; this phase is called **pearlite**.

When an iron-carbon alloy is quenched, it is seldom desirable to go back to the initial condition, losing all the hardness that was gained. Normally, another heat treatment is applied, called **tempering**, which is meant to reduce brittleness while maintaining as much hardness as possible, a reasonable compromise that is achieved by an accurate choice of the temperature and the duration of the heating.

5.1.4 Creep

The plastic deformation of a metal should begin only under a stress that is greater than its yield strength (see section 1.3.2), but experience shows that a slow flow of a solid metal may actually happen if loads that are rather high but smaller than the yield strength are continuously applied for very long periods. This kind of progressive deformation under a continuous load is called **creep**.

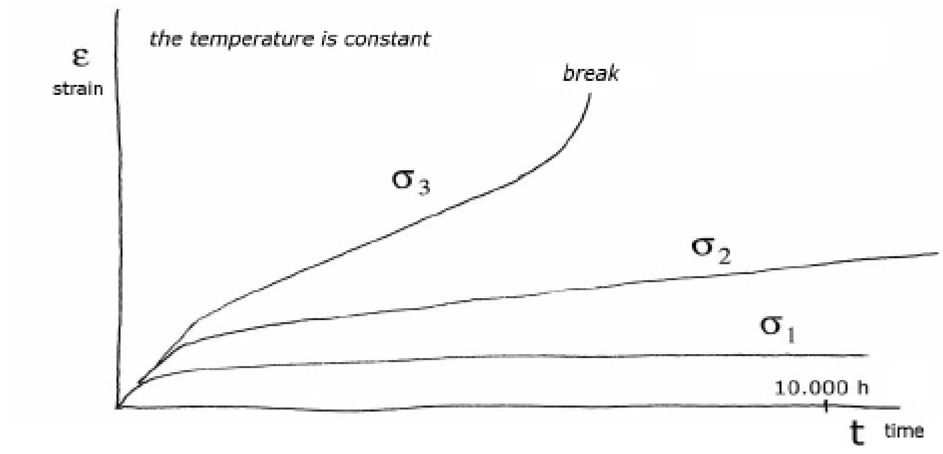
The velocity of creep flow increases as the stress applied and the temperature increase; under a combination of high load and high temperature, creep may cause the failure of metallic structures that should be stable according to normal static calculations.

The rate of flow is measured by applying a tensile stress to a test sample and measuring its elongation over a very long period of time (the duration of the standard test being 10,000 hours, i.e., over one year).

The results of the experiment are plotted in a graph that shows the strain (elongation) on the vertical (Y) axis, and the time on the horizontal (X) one. A typical graph shows an initial deformation that slows down rather rapidly and is followed by a straight line (indicating a constant rate of flow); if the slope of this part of the graph is small, the metal is likely to pass the test without failure, but if it is larger than a limiting value (which was established by previous experiments), the probability of a catastrophic outcome of the experiment is large.

If the test on a metal is repeated under increasing stresses, a series of graphs is obtained from which the critical stress that may lead to failure can be calculated.

Figure 5.10

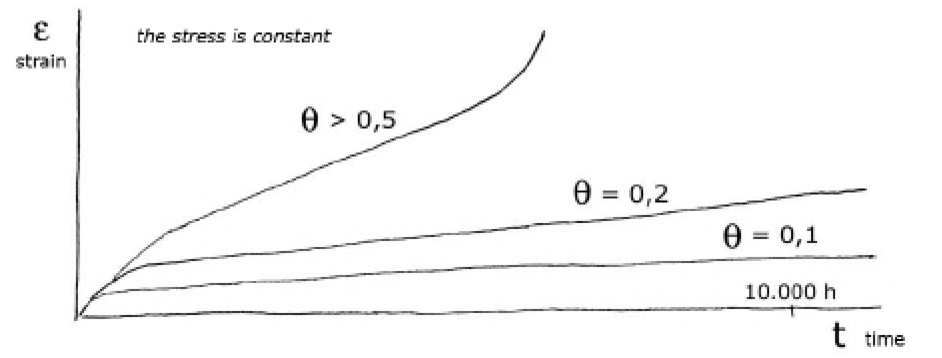


creep tested under increasing stress

The critical stress decreases when the temperature increases. If experiments are carried out applying always the same stress to the sample, rather high but lower than the critical one, and progressively increasing the temperature, another series of graphs is obtained; it looks similar to the previous one, but it is meant to evaluate a critical temperature above which failure by creep is possible.

When the creep behavior of various metals is studied and compared, the temperature is represented as the ratio of the temperature of the test to the melting temperature of the metal, both expressed as absolute temperatures, i.e., in Kelvin degrees. This ratio is designated by the Greek letter Θ (capital theta). It is observed that at equal values of Θ (theta) the graphs of all metals are similar and that the Θ value which is likely to cause failure under a high enough stress is not far from 0.5, i.e., failure is possible when the test temperature (in °K) is about half the melting temperature (in °K).

Figure 5.11



creep tested under increasing temperature

In the case of steels, whose melting point is around 1800°K, the critical temperature would be near 900°K (i.e., little above 600°C). Creep thus explains the insufficient resistance to fire of steel structures in high-rise buildings; even worse is the case for cast iron structures, as the melting point of cast iron (around 1400°K) is lower than that of steel.

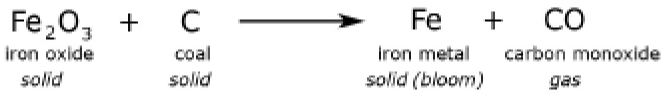
5.1.5 Ferrous metals used in architecture

5.1.5.1 Wrought iron

In the early phases of iron technology, the high melting point of iron (1535°C) did not allow the smelting of the metal from an iron oxide, or carbonate, ore. This explains why iron technology was developed much later than technology of other metals and alloys (lead, copper, and bronze) that could melt in a fire and flow into a crucible at the bottom of the furnace.

By blowing air into a charcoal fire using a manually operated bellows, it is possible to reach a temperature around 1000°C at which the reduction of the ore is possible.

Figure 5.12



$$Fe_2O_3 + C \longrightarrow Fe + CO$$

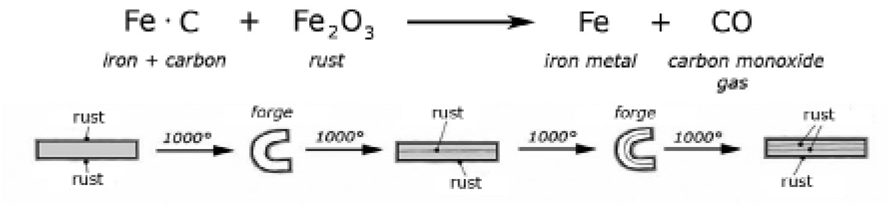
reduction of iron oxide for the production of iron metal

The metal is collected from the ashes as a spongy mass (**bloom**) that is compacted by hammering as it is kept red-hot over a fire. The iron that is obtained in this way contains a variable amount of carbon that must be adjusted according to the use intended for it.

If the metal is to be made more plastic, to be easily shaped, its carbon content may be reduced by hammering it flat over the fire, then folding it and hammering it flat again (**forging** the metal).

In contact with air at high temperature, a layer of rust (iron oxide) is formed over the surface.

Figure 5.13



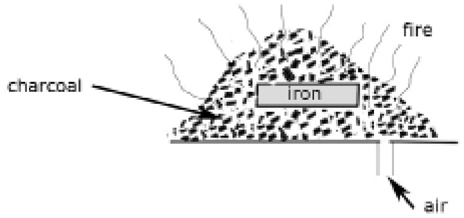
$$Fe \cdot C + Fe_2O_3 \longrightarrow Fe + CO$$

carbon content decreased by forging

Folding and hammering traps the rust into the hot metal so that the iron oxide can react with the carbon atoms embedded in the iron; the product is carbon monoxide, a gas that seeps out of the solid.

When, on the contrary, the carbon content must be increased to obtain a harder metal, a piece of metal is buried in the charcoal fire; here carbon monoxide is the prevailing gas and the process described above is reversed, as the gas seeps into the metal and is in part transformed into carbon dioxide, which seeps out again while some carbon atoms are left in the interstices of the iron crystals. The technical term for this process is *cementation*.

Figure 5.14



$$Fe + 2CO \longrightarrow Fe \cdot C + CO_2$$

Increasing carbon concentration in iron (cementation)

When the shaping of an iron piece on the forge is completed, the metal may be quenched, annealed, or tempered according to the need, as described in sections 5.1.3.1 and 5.1.3.2.

When the requirements of both hardness and flexibility are extreme (as in Japanese swords), very thin layers of low-carbon, malleable metal are alternated with high-carbon hard ones, and the whole pack is forged and quenched.

The use of wrought iron in architecture before the modern age was mainly to make metallic ties applied to stone construction; it is mentioned for the first time in the Propylaea of the Athens Acropolis and the Temple of Zeus in Agrigentum (fifth century BCE) and then continues up to modern times; iron ties are still widely used in the structural consolidation of masonry buildings.

Two important monuments entirely made of wrought iron are Indian columns: the Delhi Pillar (fifth century CE), 6 m long and 60 cm in diameter, and the Dhar Pillar (eleventh century CE), taller (12 m) but collapsed and broken into three pieces that now lie down after having been re-erected in various locations. The realization of such large pieces by forging iron is an almost incredible technological feat, and their resistance to corrosion is an interesting fact that has prompted several scientific studies.

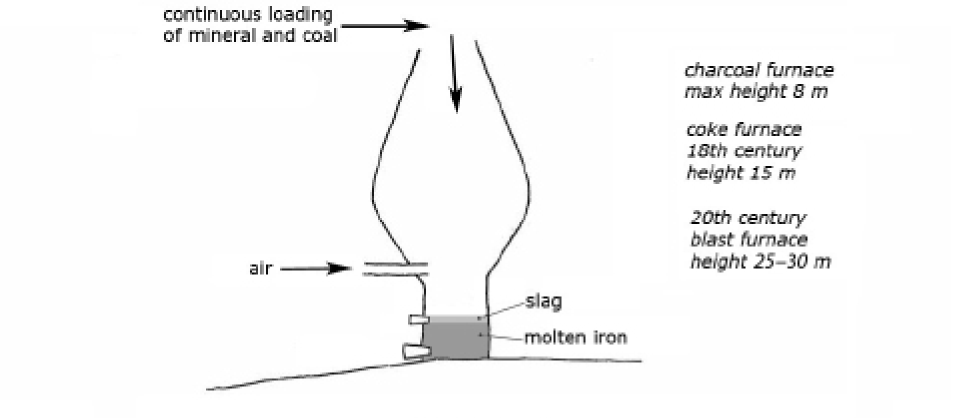
5.1.5.2 Cast iron

The melting point of iron-carbon alloys decreases as carbon content increases; a minimum melting temperature (**"eutectic point," 1150°C**) is reached when the concentration of carbon is 4.3%.

In a very tall furnace that is continuously loaded with carbon and iron ore, the iron bloom remains in contact with the burning coal for a long time and its carbon content may well rise up to 4.3%. So, if a hefty blast of air produced by hydraulic force pushes the temperature in the furnace above the eutectic point, somewhere around 1200°C, the metal melts and flows into the crucible at the bottom.

The impurities contained in the ores, mainly silicates, also melt, forming a liquid **slag** that floats on the molten metal and is collected separately. In the first phases of blast furnace technology, the slag contained a lot of iron that was lost and the yield of the process was low.

Figure 5.15



blast furnace

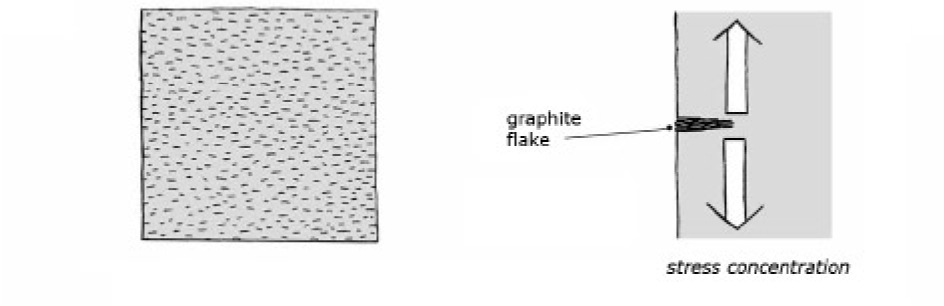
The **blast furnace**, according to recent archaeological finds, may have been invented in Europe as early as the thirteenth century in Sweden, the much earlier development in China (Han dynasty, from the second century BCE to the third century CE) apparently having had no influence on European technology.

The blast furnace propagated through central Europe in the fifteenth century, while in the Alps a differently built furnace (the "bergamasque" furnace) was developed independently from mainstream cast iron production.

As it is possible to collect the metal from the bottom of the furnace without stopping the fire, continuous production is possible, so the production of the metal is abundant and rather low cost.

Unfortunately, cast iron as obtained from the blast furnace contains 3% to 5% carbon and is brittle, not forgeable.

Figure 5.16



brittleness of cast iron

The **brittleness of cast iron** is due to the fact that when the carbon concentration in the iron is rather high (i.e., well above 2%), the cementite (Fe_3C) that is formed upon cooling the alloy is unstable and transformed into ferrite (Fe) and graphite (C). As the graphite crystals easily split along parallel planes (as was shown in section 1.4.6), the graphite flakes ("lamellae") on the surface of a cast iron piece act more or less like microscopic cracks, causing stress concentration and low tensile strength (as explained in section 3.1.1).

Compressive strength, however, is very good and the lubricating properties of graphite improve the machinability of the metal.

As cast iron could not be "wrought," it was designated by disparaging names in almost any language ("pig iron" in English; *gueuse*, i.e., "the miserable one" in French; *ferraccio*, i.e., "bad iron" in Italian) and its use, up to the sixteenth century, was limited to casting some household implements or tombstones for the "iron masters."

Things changed when, around 1550, iron cannons were cast in England at a cost of about one-third that of bronze cannons; blast furnaces were set up in great number all around Europe, and the production sharply increased. The process was also improved by adding lime (calcium oxide) to the charcoal/mineral mix, as this produced a low melting fluid slag, reduced the amount of iron dissolved in it, and removed some noxious impurities from the metal. Another improvement was the pre-heating of the air blast by means of the hot fumes escaping from the furnace.

As large amounts of the cast iron were now available at low cost, the efforts were multiplied to refine it; slow and tedious processes were developed that made it possible to work the metal on the forge, but a fully efficient process was realized only at the end of the eighteenth century (see the next section, 5.1.5.3).

In the meantime, the blast furnaces were becoming taller, passing from the 6 to 8 m of those that used **charcoal** as the source of heat and carbon, to the 15 m of the eighteenth-century ones, thanks to the high compressive strength of the **coke coal**, i.e., coal from which several noxious impurities had been distilled away. Present-day blast furnaces may be 30 m high.

The first successful structure built entirely of cast iron mentioned in the literature is the bridge on the river Severn (1779), which gave the name **Ironbridge** to the nearby town and is still extant, although open only to pedestrian traffic.

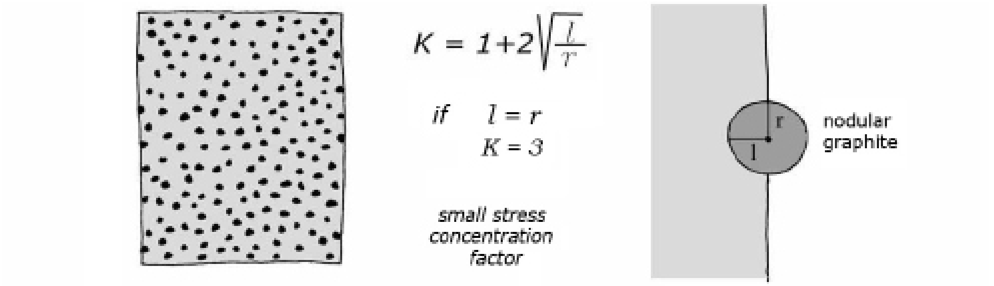
The Ironbridge is built just like a stone bridge, that is, in such a way that the metal is subject mainly to compression stresses. In the metal bridges of the nineteenth century, only the members of the structure that work under compression are made of cast iron.

Also, toward the end of the eighteenth century, one can date the first use of cast iron columns as structural members in buildings; the ceilings of very large rooms in textile mills were supported by cast iron columns (Shrewsbury, 1790). Decorative and structural elements in cast iron (e.g., columns and capitals) were used in architecture in the United States around 1850.

Parallel to the quest for the production of wrought iron from cast iron, further research aiming to obtaining **non-brittle iron castings** went on for over two centuries, e.g., trying to burn out the carbon from the surface of cast pieces ("white cast iron with a black core").

A satisfactory result was finally achieved around 1950 by the addition of a small amount of an alkaline metal (cesium or magnesium). The atoms of the alkaline metals slow down the crystallization of the graphite, and in this condition the graphite forms round nodules instead of "lamellae"; as it is easily seen from the stress concentration formula (see section 3.1.1), a spherical shape of a surface anomaly would sharply reduce the concentration factor, besides the fact that the nodules probably no longer present a preferential splitting direction.

Figure 5.17



spheroidal cast iron

Spheroidal cast iron shows a high tensile strength and is not brittle.

Malleable cast iron is now produced, but only in small sections by quenching the cast objects and then tempering them at 900°C; also in this case the formation of graphite is slower and results in nodular particles.

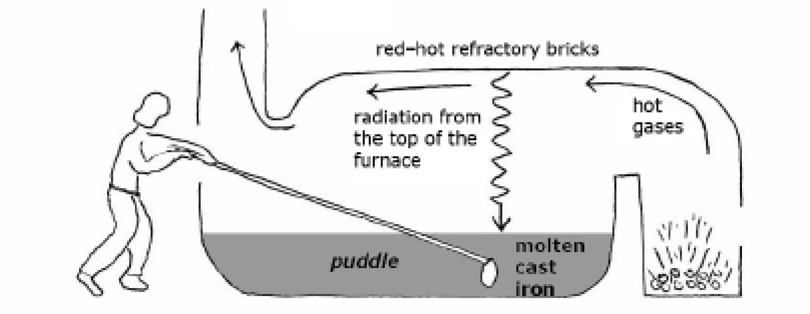
5.1.5.3 Puddled iron

The puddling process, patented in 1787, solved the problem of producing large quantities of forgeable iron from cast iron at low cost.

The name of the process derives from the peculiar form of the floor of the furnace, in which cast iron from the blast furnace was re-melted, forming a "puddle" that was continuously mixed by a worker operating a long tool through an opening in the side wall.

Another important characteristic of the puddling furnace was that the molten metal was kept separated from the coal that was burned to keep the metal in the liquid state; this avoided the re-dissolution of carbon atoms in the iron, which was the main cause of the inefficiency of the previous processes.

Figure 5.18



the puddling process

The hot gases from the fire were led along the top of the furnace, which reverberated the heat by emitting visible and infrared radiation towards the puddle. The mixing action was conducted in such a way as to mix as much air as possible with the liquid, the oxygen in the air progressively "burning" the carbon atoms away from the iron, purifying the metal and contributing extra heat to the operation of the furnace.

Figure 5.19

$$Fe \cdot C + O \longrightarrow Fe + CO$$

removal of carbon from cast iron in the puddling process

As the carbon content of the metal was reduced, its melting point increased until, at about 1% carbon, the temperature that the furnace could reach was not sufficient to avoid solidification. An able operator was required at this point to roll the solidifying paste into a ball that could be extracted from the furnace to be brought to the forge. By this time the forge was powered by steam, which allowed the shaping of very large objects and a fast pace of production.

The final carbon concentration could be adjusted at the forge by the traditional methods which, however, could not guarantee the accuracy that is possible today when the composition of the steels is brought within the specified limits in the liquid state.

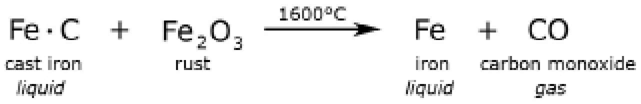
Anyway, puddled iron could offer a reliable tensile strength, which allowed its use in the production of **railroad tracks** and in the construction of bridges (the **Menai Bridge** was built by Telford in 1826).

Famous examples of iron structures built with puddled iron in the nineteenth century are **Les Halles** (Paris, Baltard, 1854) and the **Tour Eiffel** (Paris, Eiffel, 1889). At the time of the construction of the Eiffel Tower, modern steel was already available but puddled iron was preferred because it was less expensive.

5.1.5.4 Steel

In order to remove the excess carbon from cast iron in the liquid state in one step, a temperature above the melting point of pure iron (1535°C) is required. In the eighteenth century, such high temperatures were reached only in the Sheffield ironworks and made it possible to produce small amounts of high-quality steel for military uses by adding rust to molten cast iron held in crucibles. At the time, the process was kept secret.

Figure 5.20

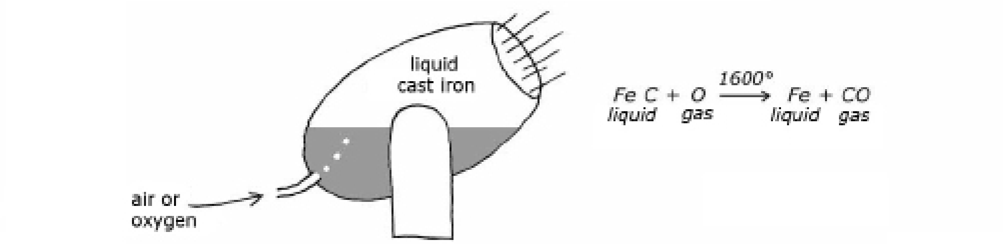


$$Fe \cdot C + Fe_2O_3 \xrightarrow{1600°C} Fe + CO$$

steel production in the crucible process

A large-scale production of steel was made possible only by the Bessemer converter (1856).

Figure 5.21



the Bessemer converter

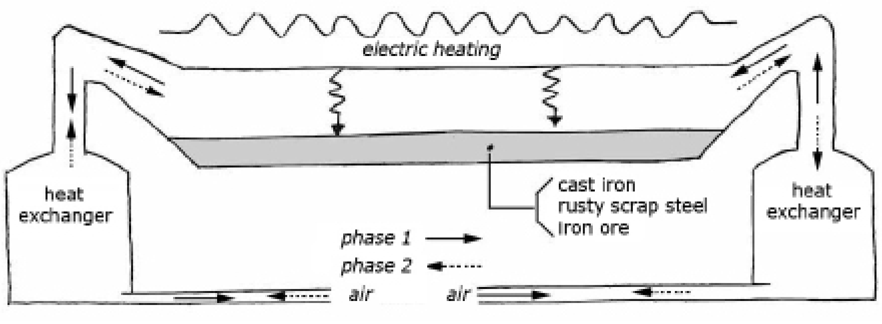
The converter is a surprising furnace because it has no heating system; the energy that keeps the metal in the molten state is provided only by the carbon present in the cast iron, which is burned off by air or pure oxygen blown in from the bottom of the pear-shaped container. Oxygen removes not only carbon but also other undesirable impurities such as sulfur that impair the workability of the metal.

The color of the flame at the top of the converter allowed the operator to detect the moment when the process was complete and the “pear” was to be tilted, pouring the liquid onto the floor of the shop into a channel system that led to the ingot molds.

Scrap-metal recycling soon became a significant problem, however, because steel does not contain enough carbon to provide sufficient energy for the converter; today, the converters can accept only one-quarter of their charge (over 300 tons) as scrap metal. The Bessemer converter risked being “killed by its own success” (as one historian wrote).

The problem was solved by the Martin furnace (1865), which was transformed later by Siemens into an electrical furnace. The basic process is similar to the crucible process of the eighteenth century, but the new equipment allows for a much larger production; if the cast iron is melted without direct contact with a fuel and is mixed with rusty metal and iron ore, the oxygen of the iron oxides transforms the carbon contained in the molten metal into carbon monoxide, a gas that burns to carbon dioxide in the air, adding energy to the system. What is completely new in the Martin-Siemens process is the efficient system of energy recovery, based on a couple of heat exchangers and a periodical inversion of the air flow that preheats the air entering the furnace.

Figure 5.22



the Martin - Siemens furnace

In present-day furnaces, heat is provided by an electric arc struck between graphite electrodes.

Modern steel has been available on a large scale since 1866; good and reliable mechanical properties favored its widespread use as a structural material in architecture, in particular in high-rise buildings.

Initially, however, when its low resistance to corrosion was assessed (see section 5.1.6.3), some resistance was met. The British Board of Trade prohibited the use of steel in the construction of bridges, a ban that was lifted in 1877. The first steel bridge, Baker Bridge in Edinburgh, was built in 1890. Corrosion, actually, is still a problem, but Baker Bridge, a railroad bridge that is still in use today, demonstrates that a well-organized maintenance system can ensure a long service life to steel structures even in an aggressive environment.

Creep under high loads and high temperatures (see section 5.1.4) is another serious problem of steel structures, as large buildings may not resist fire long enough to allow a complete evacuation of the residents, unless special provisions are introduced in the design to delay the rise of temperature inside the metal as long as possible.

5.1.5.5 Stainless steel

The addition of a considerable quantity of chromium to iron-carbon alloys (at least 12%) results in the **passivation** of the metal, i.e., resistance to corrosion, in both dry and wet conditions (see the discussion of corrosion processes in sections 5.1.6.1 and 5.1.6.2).

Passivation is thought to be caused by the formation of a thin, invisible layer of chromium oxide on the surface of the metal.

If the addition of chromium is kept below 15% and enough carbon is present, austenite is formed first when the liquid alloy solidifies and is transformed into ferrite and cementite on further cooling, as in the case of normal steel. It is possible, therefore, to quench these alloys, which are called **martensitic stainless steels.** These are the strongest stainless steels but exhibit a corrosion resistance inferior to that of the other types.

The normal use of this type of steel is in objects that require both hardness and corrosion resistance, e.g., pumps, cutlery, and scissors. A recent use in architectural conservation is in metal ties in the consolidation of stone or masonry structures (e.g., the façade of St. Peter's Basilica in Rome and the Tower of Pisa). Their high mechanical strength and relatively low thermal expansion coefficient (close to that of normal steel) are favorable factors for their use in architecture, where the low corrosion resistance of normal steel is not acceptable.

420 Martensitic Stainless Steel

ASTM/AISI number	EN (European name)	Thermal expansion coefficient	Carbon (C) content	Chromium (Cr) content
420	X10C13	11×10^{-6}	0.15% min	12–14%

Martensitic stainless steels are magnetic, as normal steels are; this makes it possible to distinguish them from austenitic stainless steels, which are not magnetic.

The welding of stainless steel in general requires particular attention as the heated metal around the welded area may become "sensitized" and lose its corrosion resistance because part of its chromium content combines with carbon, forming chromium carbides and so is lost for corrosion resistance. A heat treatment is normally applied after the welding to "dissolve" the carbides that might have been formed again into the alloy.

Austenitic stainless steel is the stainless steel most used in architecture. Its composition includes chromium, in a higher concentration with respect to the martensitic stainless steels, and nickel in an amount that is sufficient to stabilize the austenite structure, avoiding its decomposition upon cooling. Because the transformation of austenite into ferrite and cementite is not possible, quenching also is not possible, and as a consequence hardness and mechanical strength cannot reach high values.

Corrosion resistance is, however, superior to that of martensitic stainless steels.

As the austenite phase of iron alloys is not magnetic, these stainless steels are easily recognized because they lack the magnetism of normal steels.

In architecture, two alloys are mainly used, designated by AISI numbers 304 and 316.

304 and 316 Austenitic Stainless Steels

ASTM/AISI Number	EN - Spec European steel name	Thermal expansion coefficient	Carbon (C) content	Chromium (Cr) content	Nickel (Ni) content	Molybdenum (Mo) content
304	X5CrNi 18-10	16 x 10^{-6}	0.04–0.1%	18–20%	8–12%	—
316	X5CrNiMo 17-12-2	16 x 10^{-6}	0.06% max	16–18%	10–14%	2–3%

The use of these steels in architecture is non-structural: roofing, cladding, interior or exterior trim, pipes, bolts, cavity wall ties, etc.

Alloy 316 is preferred to 304 whenever welding is required, as the presence of molybdenum and low carbon content restrains the precipitation of chromium carbides and reduces the danger of the "sensitization" to corrosion. Examples of the use of alloy 316 in contemporary architecture are the spherical surface of La Géode in La Villette Park in Paris, the roofing of Frank Gehry's Peter B. Lewis Building at Case Western Reserve University in Cleveland, and Gehry's Walt Disney Concert Hall in Los Angeles.

Bars of 304 steel are used as reinforcing ties in the restoration of metal (e.g., the angel statue on top of Castel Sant'Angelo in Rome) or stone sculpture, and of façade decoration in general. When stainless steel is used in contact with stone, care must be taken of the stresses that may arise because of differential thermal expansion, since the thermal expansion coefficient of austenitic stainless steel is about 50% higher than that of normal steel and about 100% higher than that of most stones.

5.1.5.6 Weathering steel (Corten)

Weathering steels, also known as **Corten**, or **Cor-ten** (U.S. Steel trademark), **steels**, are not real stainless steels because the metal is not inherently resistant to corrosion; rather, they owe their good weathering properties to the patina that forms spontaneously on their surfaces when they are exposed to air and makes it possible to use them without the protection of a paint.

The peculiar compactness and adhesion to the metal of the orange to reddish brown patina is due to the small amounts of copper, chromium, and phosphor (and also other metals in some cases) included in the composition of the alloy.

Corten steel has been used successfully in buildings, bridges, and outdoor works of art, but experience shows that their corrosion resistance may fail under particular conditions of exposure, in particular:

- when water is allowed to remain in contact with the metal for a long period of time;
- in salt-laden atmospheres;
- in air polluted by acid gases.

A drawback of their use in architectural conservation is that their runoff under heavy rains produces rust stains on the underlying materials.

5.1.6 Corrosion

5.1.6.1 Dry corrosion

Iron in contact with air in a dry environment reacts with oxygen, forming iron oxides whose composition depends upon the concentration of oxygen in the air surrounding the metallic surface.

When the concentration of oxygen is normal (i.e., around 20%), the oxide formed is the mineral **hematite**, which has a red color. A **red oxide** patina is formed very rapidly on the surface of red-hot iron (900° to 1000°C) when it is worked on the forge.

Figure 5.23

$$2\ \mathrm{Fe} + 3\ \mathrm{O} \longrightarrow \mathrm{Fe_2O_3} \quad \textbf{\textit{red oxide}}$$

iron oxidation at high oxygen concentration

The process affects the metal only on its surface, and so it would impair only the appearance of an object rather than its function, but the red oxide layer is rather porous and does not offer much protection when the metal comes into contact with water, and a more dangerous corrosion process may begin.

If iron is kept on the forge while the air blast is reduced (so the temperature is lower and there is less oxygen present), a compact layer of a **black oxide** (**magnetite**) is formed.

Figure 5.24

$$3\ \mathrm{Fe} + 4\ \mathrm{O} \longrightarrow \mathrm{Fe_3O_4} \quad \textbf{\textit{black oxide}}$$

iron oxidation at low oxygen concentration

This was the normal finish that was applied to decorative wrought iron objects by the blacksmiths; it had a definite protective value that could be increased by applying a film of hydrophobic material on it (mainly mineral oils).

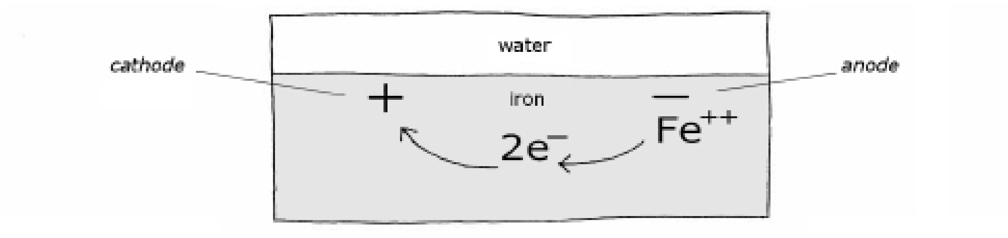
A good example of the durability of wrought iron coated by a black oxide is the Delhi Pillar (see section 5.1.5.1), which is in good condition after over fifteen hundred years of exposure. In that case the shape of the object also contributes to its good conservation by allowing for a rapid drying of its surface after each wetting phase.

5.1.6.2 Wet corrosion

When a film of water is deposited on an iron surface and is allowed to stay there for some time, an electrochemical process is set up that can cause damage in depth and even destroy the functionality of a metal object. This destructive process is electrochemical in nature, as it involves a movement of electrical charges and the development of chemical reactions.

A **galvanic cell** is formed that produces an electrical current (the conditions that determine the formation of electrical cells on metallic surfaces are discussed in the next section, 5.1.6.3) and causes the transformation of part of the metal into rust.

Figure 5.25



anodic reaction: electrons shift from anode to cathode

The iron atoms at the negative pole of the cell (**anode**) lose the outermost electrons, which are attracted by the positive pole (**anodic reaction**); since those electrons are the ones that create the bond between the atoms (see section 1.2.4), the affected iron atoms lose their bond to the other ones. Having each lost two electrons, they get a double positive charge that causes them to repel each other and to migrate into the water layer.

The metal surface is thus etched at the anode of the cell, but the process would stop soon because the migrating electrons on reaching the positive pole would neutralize the positive charge, unless they are absorbed by some other process.

The **cathodic reaction** at the positive pole of the cell (**cathode**) takes care of that using hydrogen ions, which are always present in water because of its partial dissociation (see section 1.5.3).

Figure 5.26

$$H_2O \rightleftarrows H^+ + OH^- \quad \textit{water dissociation}$$

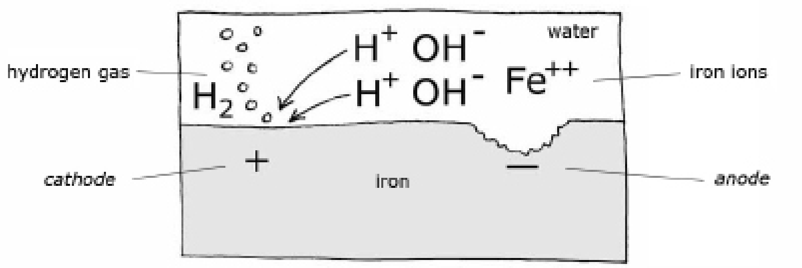
$$\textit{hydrogen ions} \quad 2H^+ + 2e^- \longrightarrow H_2 \quad \textit{gas}$$

cathodic reaction: electrons and hydrogen ions form hydrogen gas

Bubbles of hydrogen gas are developed at the positive pole and the excess of electrons is consumed. The cell can thus keep functioning; an electric current flows inside the metal from the negative pole to the positive one while the etching of the metal continues and a cavity is formed at the anode.

It is important to underline that a sizeable concentration of hydrogen ions is required to keep the galvanic cell working at a fast pace; as a consequence, in a very basic solution, when the concentration of hydrogen atoms is extremely low (see sections 1.5.1, 1.5.2, and 1.5.3), the wet corrosion of iron is not possible.

Figure 5.27



the galvanic cell in action: the anode is corroded

The last phase of the electrochemical corrosion process is **rust formation**, a set of reactions that is presented in an oversimplified form in figure 5.28.

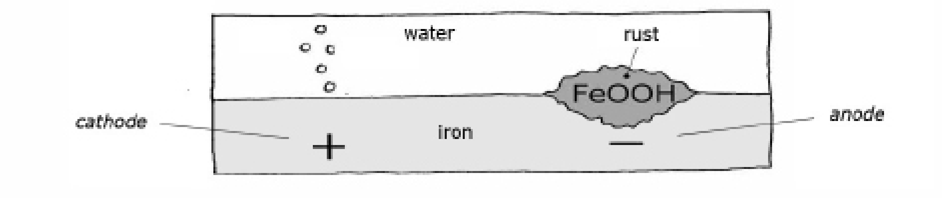
Figure 5.28

$$2\,Fe^{++} + O + 4\,OH^- \longrightarrow 2\,FeOOH + H_2O$$

rust formation (a simplified reaction)

It is important to note that rust formation involves an increase of volume relative to the volume occupied by the metal; as was shown in section 3.1.4, this results in destructive stress when the metal is inserted into a rigid material like stone or concrete.

Figure 5.29



the volume of the rust is larger than that of the metal that was corroded

If the liquid surrounding the metal is strongly basic, the hydrated iron oxide (FeOOH) is formed slowly and is deposited as crystals of **lepidocrocite**, the compact γ-(gamma) form of hydrated iron oxide, which protect the metal against contact with the liquid phase; corrosion stops, and the metal is said to be **passivated**.

If the liquid environment is almost neutral or (worse) acid, the electric cell works efficiently and the hydrated oxide is deposited rapidly in the α-(alpha) form (**goethite**), which is porous and allows in-depth penetration of the corrosion process.

Some soluble salts, e.g., **chlorides**, interfere with the deposition of the hydrated iron oxide and **inhibit passivation**; this explains why de-icing salts accelerate the corrosion of vehicles and the deterioration of reinforced concrete. The porous β-(beta) form of hydrated iron oxide (**akaganéite**) is frequently found on corroding iron when chlorides are present.

5.1.6.3 Galvanic cells

Positive and negative poles active in the wet corrosion process may form on a wet metal surface for various reasons; the main ones are discussed below.

a. Contact between different metals

The tendency to release their outermost electrons is not the same for all metals; **noble metals** (like gold, platinum, and silver) do not release them easily, while **base metals** have a tendency to lose them. These tendencies can be evaluated by measuring the potential of a pile formed by the metal under study as one of the electric poles (electrode), while the other pole is a standard reference electrode. All metals can thus be arranged in a **scale of standard potentials** from which it is possible to evaluate their tendency to lose or retain electrons, and thus to undergo corrosion processes.

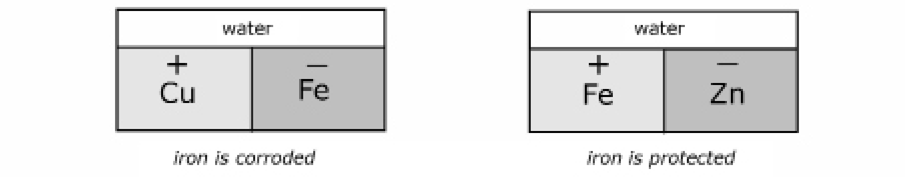
Standard Galvanic Potentials

Metal	Symbol	Potential	Notes
Gold	Au	+1.50	most noble
Platinum	Pt	+1.12	
Silver	Ag	+0.80	
Copper	Cu	+0.34	
Hydrogen	H	0	***reference electrode***
Lead	Pb	–0.13	
Tin	Sn	–0.14	
Nickel	Ni	–0.25	compact oxide
Cadmium	Cd	–0.40	
Chromium	Cr	–0.42	compact oxide
Iron	Fe	–0.45	
Zinc	Zn	–0.76	
Titanium	Ti	–1.63	compact oxide
Aluminum	Al	–1.66	compact oxide
Magnesium	Mg	–2.37	reactive metal
Sodium	Na	–2.71	reactive metal
Potassium	K	–2.93	reactive metal

The position in the scale of potentials, however, is not the sole factor that determines the resistance of a metal to atmospheric corrosion, because this is also influenced by the physical properties of the compounds formed on its surface under the action of oxygen or other gases present in the air. Because of this, some metals that show a negative standard potential (like nickel, chromium, aluminum, and titanium) are quite resistant under normal atmospheric conditions because when they are in contact with air, they form an impervious layer of metal oxide that inhibits further reaction.

Such resistant layers are overcome, however, when two metals are put in contact and both are covered by a film of electrical conductive water (i.e., water that contains some ions formed by dissolved substances, “electrolytes”). A galvanic cell is formed, with the nobler metal at the positive pole (cathode) and the less noble one at the negative pole (anode).

Figure 5.30



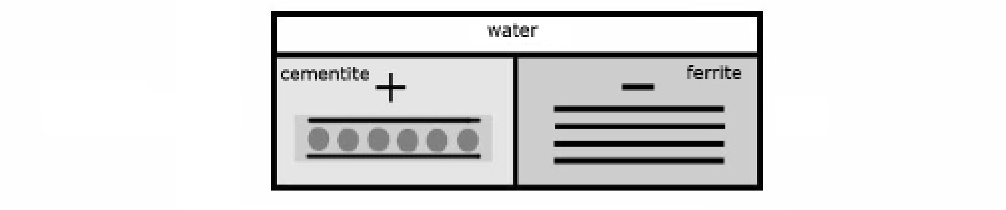
galvanic cell produced by the contact of different metals

The base metal is corroded while the nobler one not only is unaffected but its resistance to corrosion is even improved.

b. Different crystals in a metallic alloy

Alloys are frequently composed of crystals, which have a different chemical composition and a different structure; a typical example is steel, which is a mixture of ferrite (Fe) and cementite (Fe_3C) crystals (see section 5.1.3).

Figure 5.31



galvanic cell in steel due to the contact between different crystals

Cementite is the positive pole of the galvanic cell when the metal is wet, so ferrite is preferentially corroded.

One may be tempted to say that pure metals resist corrosion better than alloys, and this is often true, but there are important exceptions in cases in which the added metals introduce properties that improve resistance to corrosion.

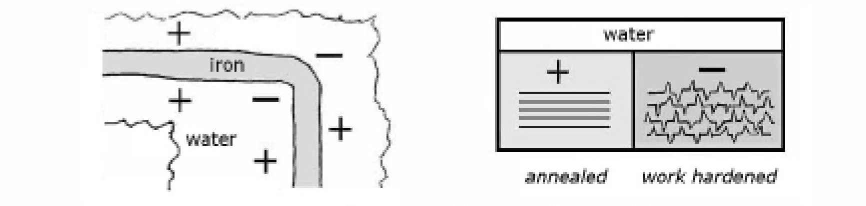
An example is the addition of chromium to iron in stainless steel, which results in the passivation of the surface (see section 5.1.5.5), and another is the addition of small amounts of copper and other elements to iron in Corten steel, which improves the compactness and adhesion of the oxide formed on the metal (see section 5.1.5.6).

Also, bronze, an alloy of copper and tin (see section 5.2.4), and brass, an alloy of copper and zinc (see section 5.2.5), show remarkable resistance to atmospheric corrosion.

c. Deformation of the crystal structure

When a piece of metal is shaped by forging or stamping, usually only part of it undergoes plastic deformation; the metallic crystals in that area are work hardened, while the crystals in the adjoining areas are unaffected. When water wets the surface, the work-hardened parts get a negative charge, become “anodic” with respect to the other ones, and are preferentially corroded.

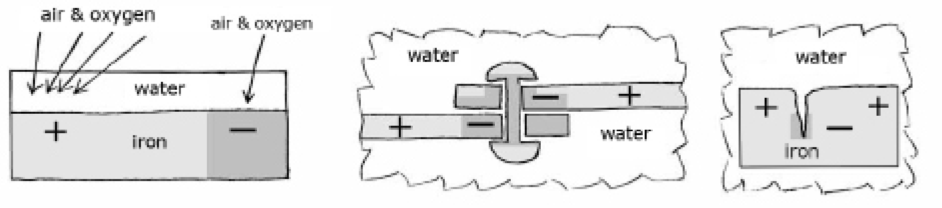
Figure 5.32



galvanic cell produced by work hardening

d. Different oxygen concentrations in the water phase ("differential aeration")
Even in the case of a perfectly homogeneous metal, galvanic cells may be formed on the surface of a metal when the water wetting one part of it is less exposed to contact with air than the water over other surfaces. As the oxygen concentration in the hidden parts of the water film is reduced by the reaction with the metal atoms and not enough air is provided to restore the initial level ("oxygen depletion") the metal surface in this area becomes "anodic" (negative) with respect to the more exposed ones.

Figure 5.33



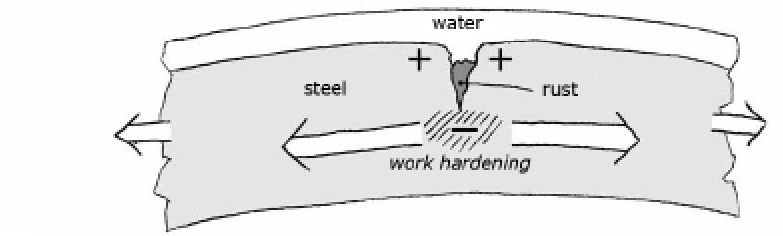
galvanic cells produced by differential aeration

This is a most insidious corrosion process, as it affects the least visible parts of a metal structure and then advances in depth because the corroded parts become covered by porous rust and so are even less aerated than they were at the start.

5.1.6.4 Stress corrosion

The combined action of a wet corrosion process, a tensile stress, a surface defect, and/or a difference in aeration may cause a rapid progress of decay in depth and the complete loss of resistance of a metal section in a short time.

Figure 5.34



stress corrosion

When the surface is wet, the electrochemical process is doubly active at the tip of a crevice subject to a tensile stress, because the metal at the tip of the crack is both work hardened by stress concentration and less aerated; furthermore, conditions get worse once some rust has been deposited in the crack.

5.1.6.5 Corrosion resistance of the ferrous metals

Ferrous metals show vast differences in corrosion resistance that are explained in part by the concentration of carbon in the alloy, but often depend upon other factors such as the presence of impurities, e.g., phosphor or siliceous slag, or the separation of carbon as graphite flakes dispersed in the metal.

Wrought iron normally has a low carbon content, so few crystals of cementite are available to form galvanic cells when the surface is wet. Another protective factor is the formation of a black finish produced in the final phase of the work on the forge; the black oxide layer has low porosity and adheres well to the surface of the metal.

In the case of ancient wrought iron, it is also believed that phosphor impurities promote corrosion resistance by forming iron phosphates, while traces of siliceous slag improve the adhesion of the oxide layer.

Not all ancient wrought iron shows corrosion resistance, however. Iron objects such as tools, weapons, or reinforcing ties that were treated in the forge to produce an elevated carbon content are frequently found in an advanced state of corrosion in archaeological excavations or in outdoor exposure.

The low corrosion resistance of **modern steel** has been well known from the start of its mass production; it may be ascribed to the larger amount of cementite crystals in the alloy, with respect to wrought iron, and to the absence of impurities such as phosphor or siliceous slag.

Cast iron, containing far more carbon than steel, should show low corrosion resistance but actually behaves in general much better. This may be due both to its silicon content (added on purpose to influence the segregation of carbon in the cooling phase) and to the fact that when a cast piece is machined, the graphite it contains is spread as tiny flakes on the surface of the metal.

The resistance to corrosion of stainless steels and Corten steels was discussed in sections 5.1.5.5 and 5.1.5.6.

5.1.7 Protection of ferrous metals against corrosion

Wet corrosion can advance in depth in the body of iron alloys and so is far more dangerous than dry corrosion, which affects only the surface of the metal.

The techniques used to fight corrosion are based on two basic principles:

1. avoid the formation of a water film in contact with the metal, or at least reduce the wetting time of the metallic surface;
2. feed electrons into the metal to replace the ones that are lost through the activity of the galvanic cells.

Up to recent times, the first approach was the one universally used, but the second one is now being applied with success in new construction and may turn out to be useful also in the conservation of historic architecture.

5.1.7.1 Environmental protection

It is a well-established fact that the amount of damage suffered by metallic structures exposed outdoors is proportional to the **wetting time** of the surface; therefore, the **design of steel structures** must aim to ensure the rapid flow of water and the fast drying of all surfaces, avoiding all features in which water may remain trapped, forming small pools.

It is important to note that the same principle should also govern the **design of reinforced concrete structures** as the corrosion of the steel reinforcement (see section 2.9.2) is also influenced by the wetting time of the concrete surfaces.

Actually, wetting time, a term used mainly in metal corrosion studies, is a factor that should be considered for all types of building materials exposed outdoors because it affects the service life of all of them, even if through different chemical or physical mechanisms. In both new construction and conservation of existing structures, **good design** is a capital factor in determining the corrosion resistance of objects exposed to an aggressive environment in order **to ensure a satisfactory service life** of all materials involved.

Important points in the design of metallic structures are:

- control the rainwater flow on the surface, avoid the creation of accessible cavities and recesses that escape inspection and in which water is likely to remain for some time with little contact with air;
- avoid direct contact between metals of different standard potential;
- use, if possible, metals of proven resistance to the environment in which they will work or specify the **correct treatment and maintenance** of the metals that are not corrosion resistant (e.g., steel).

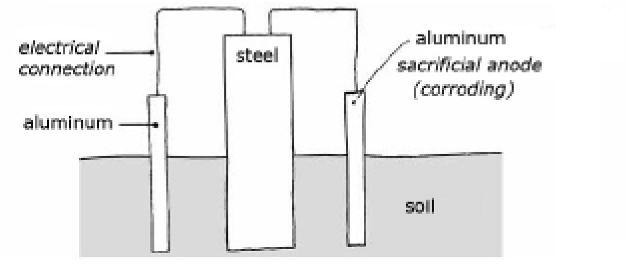
5.1.7.2 Electrical protection

If a flow of electrons is provided into a metal surface that risks corrosion, they can substitute for the ones that are being lost in the galvanic cells and so avoid the transformation of metal atoms into positive ions.

This can be realized in a **passive** way by creating an electrical connection between the metal to be protected and a baser one, i.e., a metal that comes below it in the standard potentials scale. In this situation the base metal releases electrons into the nobler one and is corroded in place of it.

The base metal is called a **sacrificial anode**; its protective action lasts as long as there is still enough uncorroded metal to provide a decent flux of electrons.

Figure 5.35

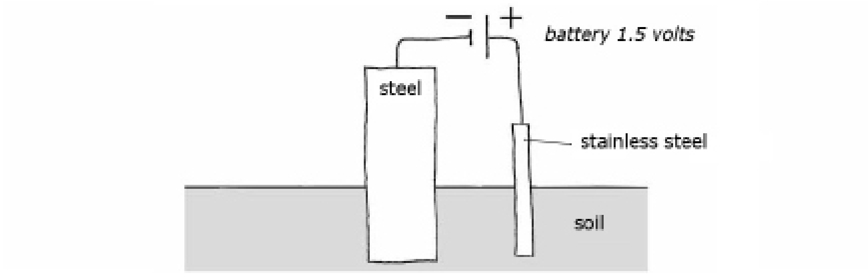


passive electrical protection by sacrificial anodes

In the case of iron alloys, the most frequently used sacrificial anodes are made of zinc or aluminum. Such a protection system is used mainly for steel-frame structures that are partially immersed into the ground (e.g., power transmission towers). It is important to note that the total surface of the sacrificial anodes must be of the same order of magnitude as the surface to be protected and, obviously, that the anodes must be periodically substituted.

In an **active** system of electrical protection, a battery (or a rectifier if an alternated current connection is available) is used to provide electrons to the protected metal.

Figure 5.36



active electrical protection

The potential involved is not high (about 1.5 volts); the metal is connected to the negative pole of the battery, while the positive one connects to a non-corrodible metal (e.g., stainless steel).

Active electrical protection is widely applied in the protection of steel reinforcement in important structures built of reinforced concrete (mainly bridges) by inserting the positive electrical poles in such a way that they face all reinforcement bars and that their surface is comparable to the extension of the surface to be protected. This does not pose problems in new construction projects, as the positioning of the electrical system is done before the concrete is poured, but obviously this is not so if the system should be applied to an existing structure. Still, at least one case is known in which active electrical protection was applied to a nineteenth-century floor, inserting special titanium electrodes near the partly corroded iron joists (a villa near Palermo, Italy).

5.1.7.3 Surface treatment and coatings

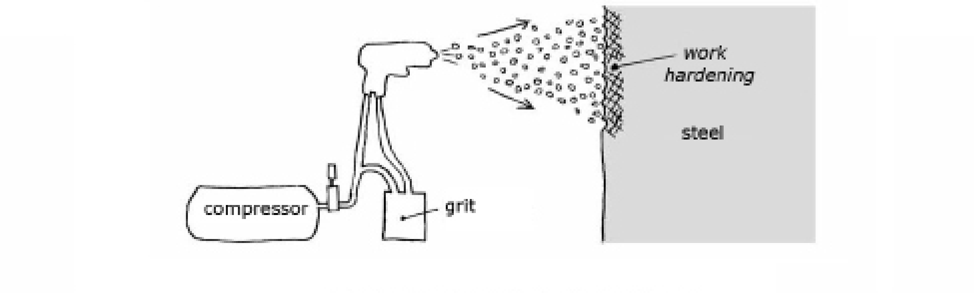
a. Cleaning

The surfaces of ferrous metals must be cleaned before any protective treatment is applied in order to remove rust and all other extraneous matter that might inhibit the proper adhesion of the protective layers that will be applied on them.

Degreasing by solvents and a dip in very acid or basic solutions is the normal industrial practice when dealing with objects of limited dimensions, but this is not applicable to the metals that are treated in architectural conservation.

Grit blasting is the cleaning technique that is generally applied to large metallic surfaces; while such a practice is considered unacceptable for the cleaning of brittle materials (with the exception of the “micro-blasting” technique applicable to hard, finely crystallized stone; see section 4.2.3), in the case of metals the risk of damage is greatly reduced because, under the impact of grit particles, the surface undergoes plastic deformation and its strength is improved by work hardening.

Figure 5.37



blast cleaning of steel structures

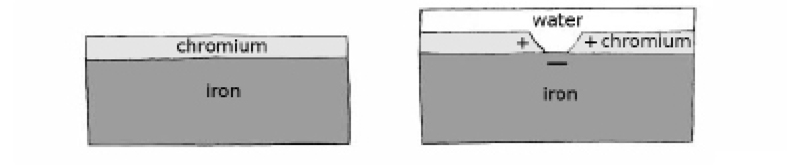
b. Plating and galvanizing

A thin layer of another metal can be applied on iron to protect it against corrosion. It may appear that the best way of achieving an efficient protection (aside from cost) would be to apply a metal that is nobler than iron and provides a good resistance to both dry and wet corrosion. Such a treatment is termed a **cathodic protection**.

Following this line of reasoning, the metal most used in the past to protect iron was **chromium**; it could be applied on objects not exceedingly large by **electroplating**, i.e., immersing them in large tanks containing a solution of chromium salt and connecting them to the negative pole of a rectifier (the positive one being connected to a non-corrodible metal, e.g., platinum, also immersed in the tank).

Experience proved that this system works only if the chromium layer never leaves any tiny part of the surface unprotected, otherwise a galvanic cell operates very efficiently to destroy the iron under the chromium whenever the surface is wet.

Figure 5.38



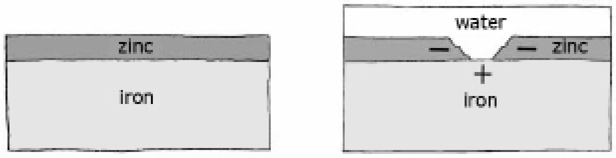
cathodic protection - chromium plating on iron

A typical problem in the past was that of car bumpers, which started corroding as soon as a mechanical impact created a flaw in the chromium surface. A good service life could be obtained only if a very thick layer of chromium was applied over thick undercoats of copper and nickel, but the cost of such a plating treatment was very high; so, in the end, chromium-plated bumpers were replaced with reinforced synthetic resin ones, which are used today.

Protecting iron with a baser metal may not appear to be a very bright idea, but it is in fact the one that works in the long run; the technical definition of such a treatment is **anodic protection**.

Zinc may be applied over iron either by electroplating or by **galvanizing**, i.e., immersing the iron objects in a tank of molten zinc.

Figure 5.39



anodic protection, galvanized iron

In this case, an interruption of the protective layer does not cause much harm as iron finds itself on the right side of the cell, i.e., at the positive pole, and is protected while the zinc layer is consumed by corrosion. It is a case of **sacrificial protection**, which is effective only as long as metallic zinc is available; the protective value of the treatment, therefore, depends upon the thickness of the zinc layer.

A drawback of anodic protection is that it doesn't look nearly as good as chromium plating, which is shiny up to its final collapse; corrosion of zinc outdoors results in white zinc oxide or zinc salts which mix with atmospheric dirt to produce whitish gray stains. It was found, however, that a further treatment with a solution of a yellow chromate yields a golden-iridescent finish (**chromate conversion coating**) that shows an improved weathering resistance or, as an alternative, constitutes a good base for a paint.

c. Phosphate coating

Phosphoric acid solutions on iron surfaces remove all residues of rust and create a layer of iron phosphate crystals that improves the resistance of the metal to corrosion. The application of a transparent wax or oil finish on top of the phosphate may further improve weather resistance, or, alternatively, the phosphate layer may constitute a good preparation for painting, e.g., with a polyurethane paint.

The phosphate conversion treatment may be applied by brush, spray, or immersion and is today the preferred way to deal with exposed iron ties or cramps in masonry structures.

It is interesting to note that the resistance of the Indian wrought iron pillars to corrosion (see section 5.1.5.1) is explained today by the spontaneous formation of iron phosphate on their surfaces, due to the phosphor impurities present in the ancient metal.

d. Painting

Paint is the most common protective treatment of ferrous metals and the most efficient one. The hardest, most resistant coatings are produced by paints that harden at high temperature, e.g., 180°C (oven-drying paints) or when exposed to intense ultraviolet radiation, but only objects of limited dimensions (e.g., the metal parts of window assemblies) can be thus treated.

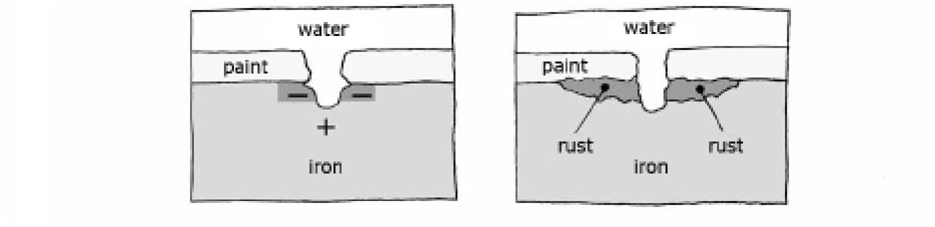
Air-drying paints are therefore the standard coating for iron and steel in architecture, unless the metal parts can be disassembled and brought to a shop for a new treatment.

Until the twentieth century, **linseed oil** paints were universally used, to be later replaced with **alkyd** paints, based on mixtures of natural drying oils and synthetic resins (glycerophtalic resins). Today, **polyurethane** paints and **acrylic** paints (or a mix of them) substitute for the alkyds when a superior weather resistance is required.

Epoxy resins are less well suited for outdoor use because of their inferior resistance to oxidation when exposed to air and radiation; they are frequently employed in undercoats, protected against oxygen and light by the top layers, to exploit their strong adhesion to metal surfaces.

A **scratch** in a paint film may open the way to a corrosion process that may propagate under the coating because, when the surface is wet, a galvanic cell operates between the metal under the paint (less exposed to oxygen, negative pole) and the surface laid open by the scratch (more oxygen, positive pole).

Figure 5.40



galvanic cell and corrosion caused by a scratch in the paint

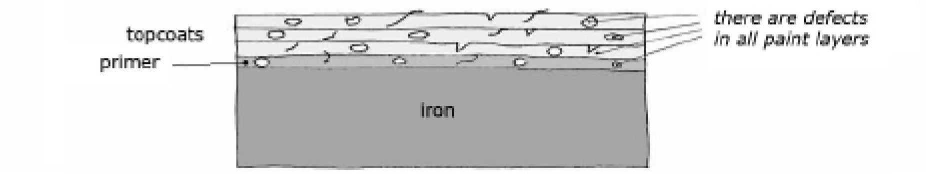
To address this danger, an undercoat (**primer**) is always applied as the first layer on the metal; the primer always contains a substance that is considered apt to hinder the progress of corrosion, e.g., by providing electrons to the metal that is losing them because of the activity of the galvanic cell.

Until the first half of the twentieth century, the standard primer for ferrous metals was based on **red lead** (Pb_3O_4 **minium**) and linseed oil; it is easily recognized in old paints because of the orange-red hue of lead oxide. Because of its toxic properties, red lead was progressively replaced with other pigments: first by some chromium salts (**chromates**), the color of the undercoats turning to yellow, then by **micaceous iron oxide**, red in color, whose protective action is believed to be improved by the shape of its crystals (flat flakes) that form an efficient cover over the metal surface. Also, linseed oil was progressively replaced with alkyds first, then with acrylics, polyurethanes, and epoxies.

In recent times, new corrosion inhibitors were introduced based on particular compounds of lead (e.g., **calcium plumbate**) or zinc (e.g., **zinc phosphate**). Also, paints pigmented by metal powders (**zinc** or **aluminum**) are proving to be quite efficient primers. As a consequence, the color of the undercoat may now be white or metallic gray; the red color (iron oxide) still prevails, however, over large metal elements on which the primer is applied in the shop before they are shipped to the site to be assembled.

When a very good corrosion resistance is required, two or even three layers of the top coating are applied. The reason is that the durability of a coating is frequently compromised by defects included in the paint layer during its application (air bubbles, dust, fibers, hair); defects are unavoidable in any paint layer, even if the painting shops are normally kept as clean as possible. As a defective point opens the way for atmospheric water to reach the metal surface, in a multilayer coating the probability that defects will be present in the same position in all layers obviously decreases very rapidly as the number of layers increases; experience proves that, at equal total thickness, a multilayer coating is far more durable than a single-layer one. The U.S. Navy used to require the application of one undercoat and three topcoats for all paints over metal surfaces.

Figure 5.41



multilayer coatings offer better protection than single-layer ones

e. Aging of paints

All organic materials undergo oxidation reactions when they are exposed to oxygen and light (see chapter 6.6); the rate of such reactions is variable according to the nature of the organic substance and may be retarded by the introduction of protective compounds in the formulation of paints, but they can never be completely stopped.

Oxidation results in the change of color, progressive loss of water repellency, and embrittlement and cracking of the coating, which progressively loses its protective value. All painted metal structures exposed to the external environment may be kept functional only if a maintenance cycle, involving cleaning and re-painting, is established and observed.

5.2 Notes on Non-ferrous Metals Relevant to Architectural Conservation

5.2.1 Lead

Lead was probably the first metal smelted by man in prehistoric times because of its low melting point (327°C). The metal has a high density (11.3) and low hardness; it is malleable, easily deformed, but its mechanical strength is low.

Lead shows a very good resistance to atmospheric corrosion even in polluted urban atmospheres, because acid attack produces lead carbonates and lead sulfate, which form an **insoluble patina** on its surface. Lead is attacked, however, by organic acids and nitric acid.

5.2.1.1 Lead sheet; roofing and flashings

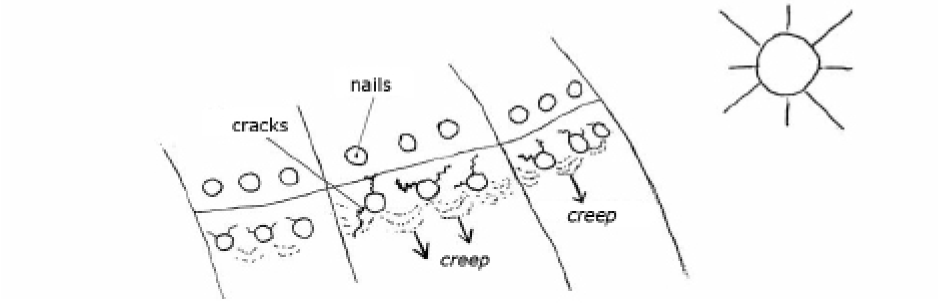
Lead sheet has been widely used in architecture to protect buildings against rainwater. Lead roofing is frequent in northern climates, while **lead flashings** are applied over cornices, windowsills, and all protruding parts of historic façades to protect them against rainwater. Lead flashings should form drips that prevent the flow of water over the surfaces below them (see section 4.4.1).

The durability of lead sheets depends upon their **thickness**; 2 mm grade or higher should be used in historic preservation. Service life may be increased by painting the metal, a practice that also allows the metal to hide its presence when the visual impact of abundant lead flashings over an important architecture is too obtrusive.

When lead roofing is used, care must be taken to ensure both thermal insulation and proper ventilation under the lead layer, because condensation may easily occur there and cause serious deterioration to the wood structure of the roof or to the ceilings below.

Creep may be a serious problem when lead is applied over steep surfaces, as in the case of cupolas, because with such a low melting point, a Θ (theta) value of 0.5 is reached at only 27°C (see section 5.1.4).

Figure 5.42

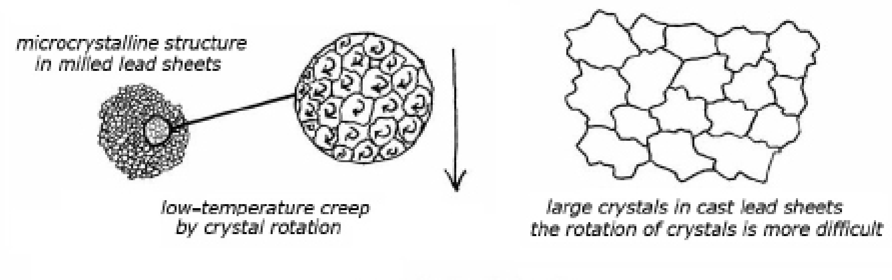


creep and cracking of lead sheet over a steep surface

Aging reduces the plasticity of the metal, so creep frequently results in cracking around the nails securing the sheets to their support. As lead is quite expensive, it is normally recovered from aged roofs and re-melted to produce **cast sheets**, which actually appear to have better resistance to creep than new sheets fresh from the rolling mills.

Materials science offers an explanation of the different behavior of cast and **milled sheets**. In lead the mechanism of the low-temperature creep is the rotation of the metal crystals, which is different from the high-temperature creep of other metals, which flow because atomic planes slide inside crystals, as in normal plastic deformation. When a lead sheet is compressed in the mill, the metal re-crystallizes after the deformation, even at room temperature, and this results in crystals of small size that rotate more easily than the large crystals formed by the slow cooling of the molten metal in the casting process.

Figure 5.43



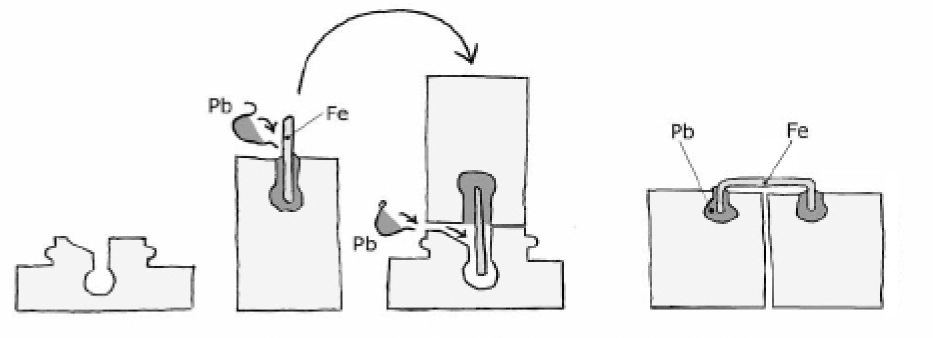
creep in lead sheets

Impurities in ancient lead may also contribute to stiffen the metal structure.

5.2.1.2 Bonding iron cramps to stone

Since classic antiquity, stone construction has relied on metallic connections between stone blocks to improve the cohesion of the built structures. The bonding of iron cramps to stone is invariably realized by inserting the cramp in a prepared cavity (whose inner part is slightly wider than its neck) and pouring molten lead into it.

Figure 5.44

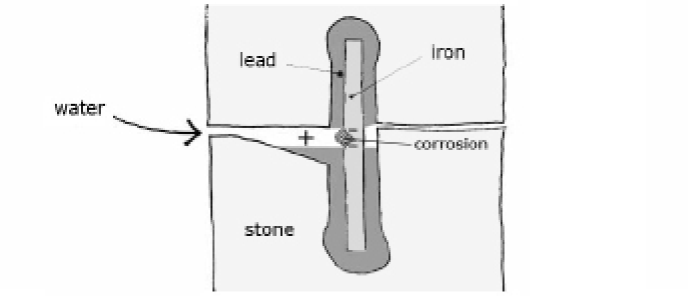


connecting stone blocks with iron cramps and lead

The plasticity of the lead connection between blocks, besides its durability, offered also the advantage of absorbing stresses caused by thermal movement or other chance occurrences. After the collapse of the Roman Empire, stone buildings became quarries for quality stone and the only possible sources of iron and lead; the massive recovery of these useful materials was actually one of the causes of their ruin.

Metal cramps bound by lead were intensively used in stone construction from the Middle Ages up to modern times. Lead protects iron against corrosion, but only if it covers it completely; if a cramp is sealed with an insufficient quantity of lead, the free iron surface may corrode in depth because lead is positive with respect to iron. Cases of incompletely protected iron cramps that were totally severed by corrosion have been observed.

Figure 5.45



corrosion of a cramp incompletely covered by the lead

5.2.2 Aluminum

5.2.2.1 History and general properties

Aluminum metal could not be smelted in large quantities until very recent times because coal cannot remove oxygen from aluminum oxide (alumina) or hydroxide (bauxite), which are found in nature. The modern industrial process (1886) is based on the electrolysis (electrical cleavage) of a molten aluminum salt.

The melting point (660°C) and the low hardness of the metal suggest the presence of a weaker bond between the atoms in the metal crystals; this is confirmed by the low density (2.70 compared to 7.86 of iron), which, however, came to be its winning property in several mechanical applications where light weight is a capital requirement.

The mechanical properties of aluminum are improved by alloying it with magnesium or copper; in the latter case a further gain is obtained through a special quenching process (precipitation quenching).

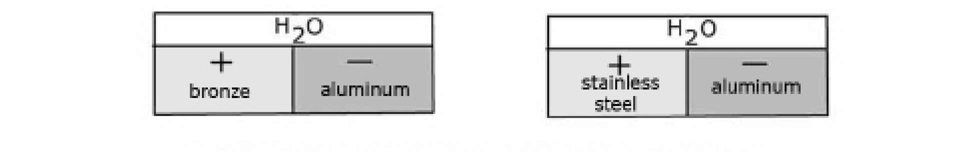
The rather large coefficient of thermal expansion (24×10^{-6}) must be carefully considered when aluminum is used in conjunction with other materials as it is more than double that of steel (11×10^{-6}).

5.2.2.2 Corrosion resistance

Corrosion resistance is another quality that determined the wide use of aluminum in modern technology, a fact that looks surprising because aluminum occupies a very low position in the electrical potential scale. Corrosion resistance, in this case, is due to the high reactivity of the metal with oxygen, which results in the formation of a **compact layer of aluminum oxide on its surface** as soon as the metal is exposed to air.

The oxide layer ensures the protection of aluminum in normal atmospheric conditions and even in a marine atmosphere, upon the condition that aluminum not be in electrical contact with any other metal. When such a contact exists, a galvanic cell is formed as soon as the surface gets wet and the aluminum is corroded in depth because almost all metals are nobler than it.

Figure 5.46



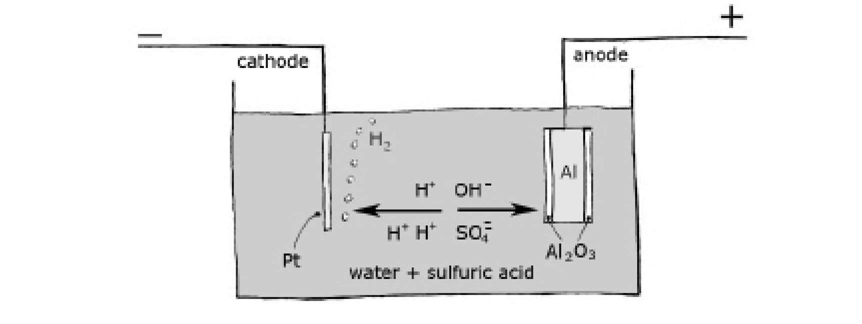
aluminum is corroded in contact with most metals

Aluminum sheet was occasionally used for roofing; the cupola of the Great Synagogue of Rome (1904) is an example.

5.2.2.3 Anodization

The corrosion resistance and the general appearance of the metal are improved by the anodization process, which creates a thicker and more impervious oxide film on its surface.

Figure 5.47



anodization of aluminum

The metal is immersed in **diluted sulfuric acid** and connected to the positive pole of a converter providing direct current.

The film of aluminum oxide is a good base for a paint or, alternatively, it may be dyed.

Note that:

- in electrolytic processes, like **anodizing** or **electroplating**, the electrode connected to the **positive** pole of the converter is called the **anode**;
- in **electrochemical corrosion** processes, **anode** is the **negative** pole in the **galvanic cell** that causes the corrosion, and is the part that is corroded. The reason for this apparent confusion is that *anode* is the name given to the electrode that attracts negative ions in the liquid, and *cathode* is the name given to the electrode that attracts positive ions.

5.2.2.4 Welding

The welding of aluminum requires the elimination of the oxide film that would impair the adhesion of the molten metal; actually the whole operation must be performed in an oxygen-free atmosphere (argon gas is usually blown over the surface to be welded) because at the welding temperature the oxide film would be formed in a matter of seconds.

5.2.3 Copper

Copper is easily distinguished from other metals because of its red color; it is a rather heavy metal (specific gravity is 8.92), melting a little above 1000°C (1083°C).

Copper has low hardness and is quite **malleable**; it is easily worked by plastic deformation to make sheets and wires, but it is **not suitable for structural purposes**. The thermal expansion coefficient (16×10^{-6}) is almost equal to that of stainless steel, but about 50% larger than that of normal steel (11×10^{-6}).

Its widespread use came quite early in human technology, around the midpoint of the fifth millennium BCE, and gave rise to the first phase of civilization based on an extensive use of metals (Chalcolithic age), which lasted until the third millennium BCE.

When copper is exposed outdoors, its corrosion is only superficial; a **green patina** of copper carbonates, or sulfates, is formed, which becomes darker, even black, in polluted urban atmospheres.

In architectural conservation, copper is widely used in roofing, gutters, downpipes and spouts. Copper cramps were used in the past to hold stone veneer facing onto exterior walls. A serious drawback of the use of copper in conservation is the fact that the runoff from its weathered surfaces over stones and plasters causes the appearance of green stains that are quite difficult to remove.

5.2.4 Bronze

5.2.4.1 History and general properties

When copper is alloyed with other metals the melting point is lowered and the mechanical properties are often improved. In the Chalcolithic period, impurities present in the copper ores frequently joined the metal, causing a modification of properties, occasionally favorable ones that were then reproduced intentionally; as arsenic, which was a rather common occurrence in the ores used at the time and improves the mechanical performance of copper, it is not surprising to find a frequent use of copper-arsenic alloys in the last part of that period.

In modern technical language, most copper alloys are called bronzes, so the modern name of the late Chalcolithic metals would be arsenic bronzes; but in the history of technology the term *bronze* is normally applied only to **copper-tin alloys**, so the Bronze Age begins only when tin started being used.

Tin is an impurity more rare than arsenic in copper ores, and tin ores are found only in some regions in the Mediterranean and the Middle East, but the advantages it provided (far fewer health dangers for the metalworkers and better mechanical properties) made the tin-bronzes the preferred metal from about 2500 BCE to the second half of the second millennium BCE, i.e., until the start of the Iron Age.

The addition of 10% to 20% tin to copper significantly lowers the melting point of the metal, which therefore is well suited to **casting** techniques of production. Above 20% tin, the metal becomes too brittle for most uses, but it could be polished to make bright but fragile mirrors.

In Roman technology, the melting point and the viscosity of the molten metal were further reduced by the addition of lead.

The thermal expansion coefficient of bronze is close to the coefficients of copper and stainless steel (16×10^{-6}).

5.2.4.2 Corrosion resistance

Another good point about bronze is its resistance to corrosion, which is proven by the survival of bronze statues cast in the classical age and exposed outdoors ever since; examples are the Marcus Aurelius monument in Rome and the four horses on St. Mark's Basilica in Venice. Other architectural uses have been monument doors and roofing tiles.

In fact, the major cause of the loss of most bronze monuments from antiquity was the recovery of the precious metal and not its corrosion.

Bronze resists corrosion even in marine atmospheres, although burial in salt-rich soils results in a deep corrosion process that is not easily controlled, even inside museums.

Most alloys resist corrosion less than the pure metal, but in the case of bronze the fact that the components of the alloy are very close in the scale of galvanic potentials should have a favorable effect. Also, the low solubility of tin and lead compounds formed in the initial corrosion process contributes to the stability of the bronze patina.

The bronze patina is similar in appearance to that of copper and shows the same defect, i.e., green stains formed by the runoff over stone and plaster. This limits the usefulness of bronze in making cramps to consolidate stone structures and sculptures.

5.2.4.3 Terminology

Modern alloys of copper with other metals are also called bronzes: e.g., nickel bronze, silicon bronze, and aluminum bronze. Occasionally even copper-zinc alloys are called bronzes, but here the traditional name, *brass*, will be used (see section 5.2.5).

Phosphor bronzes are normal tin bronzes, which have been de-oxidized by the addition of a small amount of phosphor; this results in better mechanical properties and improved resistance to corrosion.

5.2.5 Brass

5.2.5.1 History and general properties

Brasses are alloys of copper and zinc. Zinc and copper are not easily mixed in the liquid state because molten zinc boils (at 907°C) below the melting point of copper (1083°C); in order to make a copper-zinc alloy, zinc ore must be added to molten copper. This explains why brass technology started much later and was never as important as bronze technology in the Greco-Roman world; the earliest finds of brass objects are dated to the last centuries BCE.

As zinc lowers the melting point of copper much less than tin, brass has been mainly used in objects to be machine worked rather than cast, although casting is used for the mass production of small objects (e.g., door handles).

Zinc in brasses may vary from 5% to 40%, the color of the alloy changing as the zinc concentration increases, from red like copper (10%) to yellow as gold (20%), and finally to yellow ochre (40%).

Also, the mechanical properties change as the color changes; the low-zinc grades are malleable and easily worked by plastic deformation (stamping, forging, drawing), while high-zinc alloys are better suited for machining with cutting tools, in particular if some lead (1% to 3%) is added to the composition (leaded brass).

The thermal expansion coefficient of high-zinc alloys shows only a slight increase above that of copper (16×10^{-6}).

5.2.5.2 Resistance to corrosion

Resistance to corrosion of all brasses is good; the runoff of rainwater off the brass cramps used around the year 1900 to consolidate the travertine façades of the baroque Roman churches did not cause any green stain, contrary to what is normally observed below copper or bronze in outdoor exposure.

Normal brasses, however, are corroded in marine atmospheres, or in general in the presence of chlorides, by a process in which zinc is preferentially attacked (de-zincification), but the problem may be overcome by the use of special alloys like “admiralty brass” (28% Zn, 1% Sn, 0.4% As) or “naval brass” (39% Zn, 0.75% Sn).

5.2.5.3 Terminology

The modern terminology of brass is confusing because some brasses are marketed as “bronzes” and traditional names are also used. The best information about the composition of a brass is offered by the ISO classification, which reports the nominal composition of the alloy by listing the chemical symbols of the metals, each followed by a number that is its percentage in the alloy; copper (Cu), as the main component, comes first and is not followed by a number.

So “Cartridge Brass” is ISO CuZn30, “Muntz Metal” is ISO CuZn40, and “Free Cutting Brass,” the alloy most suitable for machining small parts, is ISO CuZn36Pb3.

“Orichalcum” was the alloy used by the Romans to make coins, similar to the modern ISO CuZn20, which is occasionally marketed under the ancient name.

Special brasses are used in the modern euro coins: "Nordic Gold," an aluminum brass with some tin (5% Zn, 5% Al, 1% Sn) in 10-, 20-, 50-cent coins, and "Nickel Brass" (20% Zn, 5% Ni) in the yellow parts of 1- and 2-euro coins. The addition of aluminum or nickel increases the resistance to abrasion and corrosion.

5.2.6 Titanium

5.2.6.1 History and general properties

Titanium-containing minerals are abundant in the earth's crust, but it is extremely difficult to win the metal out of them because of titanium's high melting point (1668°C) and the very strong bond it forms with oxygen.

The large-scale production of the metal started only in 1955; it was achieved thanks to the transformation of the titanium ores in titanium chloride, followed by the decomposition of this salt.

The first use of titanium in architectural conservation was for the cramps used in the consolidation of the marble structures of the Athens Acropolis (1976). The first use of titanium in conservation in Italy was in 1988 (Marcus Aurelius Column, in Rome).

The properties of titanium make it suitable for use in architectural conservation, but the high cost (about ten times as much as stainless steel) has been initially a negative factor. Now the cost is being progressively reduced as the technology of production improves, and experience shows that economies can compensate for the price due to titanium's peculiar properties.

Titanium is unique among the metals of common use because of its low coefficient of thermal expansion (8×10^{-6}), which among the metals is the closest to that of most of the stones used in buildings or works of art (e.g., 7.5×10^{-6} for Carrara marble). This minimizes the stresses arising from differential thermal expansion under daily and seasonal changes of temperature.

The elastic modulus of titanium (slightly above 100,000 MPa) is about half that of stainless steel (around 200,000 MPa), but titanium is much lighter (specific gravity is 4.51 vs. 8.03) and so it can successfully compete with other corrosion-resistant metals in important mechanical applications. Titanium alloys, with aluminum plus minor additions (tin, vanadium, chromium), also offer improved mechanical properties.

5.2.6.2 Corrosion resistance

Titanium holds a rather low position on the scale of galvanic potentials (it is not a noble metal), but when the metal is in contact with air, a very strong and impervious layer of titanium oxide spontaneously forms on the surface and protects it quite efficiently in normal atmospheric conditions. As in the case of aluminum, however, this passive state is compromised if titanium is in electrical contact with a noble metal.

The thickness and compactness of the oxide layer may be increased by anodizing the metal, as in the case of aluminum, or more simply by heating it.

5.2.6.3 Welding

As in the case of aluminum, welding requires an inert gas atmosphere (mostly argon) to avoid the presence of the oxide layer, which would impair the adhesion of the joined surfaces.

5.2.6.4 Titanium roofing

In civil engineering, titanium roofing and cladding is gaining widespread use, since the light weight and low thermal expansion allow considerable economy in the construction, while the corrosion resistance offers a long estimated service life and a low cost of maintenance.

In March 2008 it was estimated that about one million square meters of titanium roofing and cladding had been used in recent construction projects, the Guggenheim Museum in Bilbao being an outstanding example.

Part 6

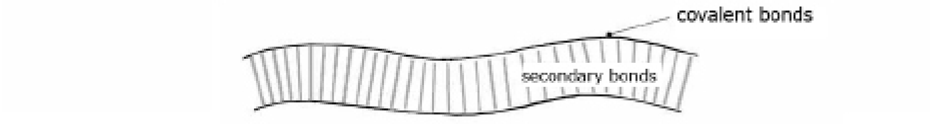
Natural and Synthetic Polymers

6.1 Polymers

Many materials used in architecture belong to organic chemistry; this means that the fundamental units that constitute them are molecules made of carbon and hydrogen atoms, occasionally linked to oxygen or nitrogen or still other kinds of atoms.

Solid organic materials are composed of large molecules that are bound to each other by secondary bonds, molecular attraction forces (see chapter 1.4) that are very weak if single atoms are considered but add up to significant values when the number of atoms involved is great.

Figure 6.1



attraction between long molecules due to molecular forces

Organic materials formed by large molecules show a cohesion that is largely adequate for many practical uses, even if such mechanical properties as elastic modulus and hardness, which depend directly upon the strength of the bonds that connect the fundamental units, are inferior to those of the materials in which atoms are linked by primary bonds (e.g., stones or metals).

Organic materials, however, may possess peculiar properties such as flexibility, adhesiveness, or easy workability, which make them useful in several branches of technology.

In chemistry, most large molecules are termed **polymers** (in ancient Greek: “many units”) because they are formed by the joining of a great number of simple building blocks, called **monomers** (in ancient Greek: “a single unit”). The chemical reaction that carries out the connection of the monomer units is called **polymerization**.

Figure 6.2

polymerization reaction

When the monomer units are linked to form a **chain**, the large molecule that is formed is called a **linear polymer**, a frequent form among natural and synthetic materials. The linear polymers frequently show **branching** points and **side chains** (i.e., parts of the molecule sticking out of the main chain, like branches off the trunk of a tree); these may have varying length and may contain specific atoms or groups of atoms that modify the properties of the basic chain structure.

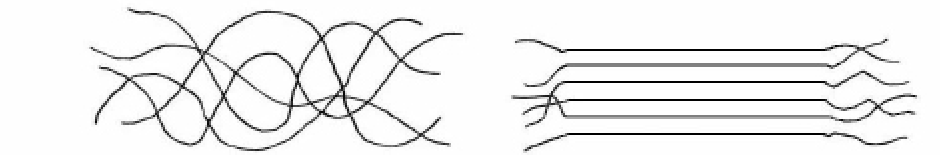
Figure 6.3

branched linear polymer

The molecules of the linear polymers may have various lengths and may be attracted to each other by different types of secondary bonds (Van der Waals forces, see section 1.4.1; dipole or hydrogen bonds, see section 1.4.4); as a consequence, the resulting physical and mechanical properties of the polymeric materials may be quite variable even if the chemical composition is the same.

The strength of the attraction between polymer molecules, and so their physical and mechanical properties, is also strongly influenced by their spatial arrangement. As was mentioned in section 1.4.3, the large molecules may arrange themselves in a disordered way (**amorphous** structure) but may also form **crystallites**, bundles of parallel chains strongly attracted to each other because they are very close (the strength of molecular bonds increases when the distance between the molecules is smaller).

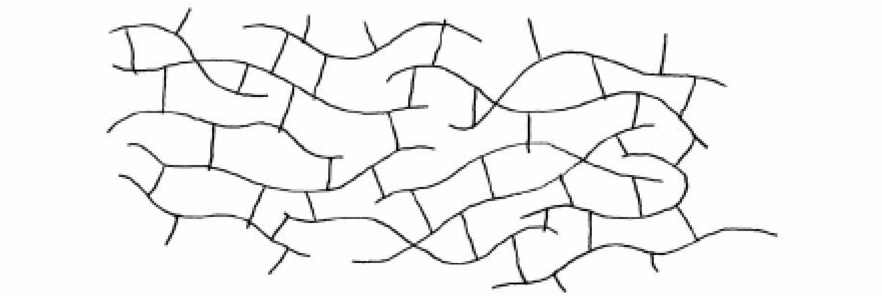
Figure 6.4



amorphous material crystallite

Not all polymers have a linear structure, however, because a **three-dimensional structure** may also be formed when primary bonds, called **cross-links**, are established between the linear polymeric molecules by some natural or synthetic process. In a cross-linked polymer, the individual molecules are not recognizable anymore, the whole mass of the material being actually a single molecule of macroscopic dimension.

Figure 6.5



cross-linked polymer

Cross-linking of polymers greatly improves their mechanical properties, but other useful properties, like flexibility or solubility, may be lost.

The structure of the solid materials created by the cross-linking reactions is always disordered (**amorphous**), not crystalline.

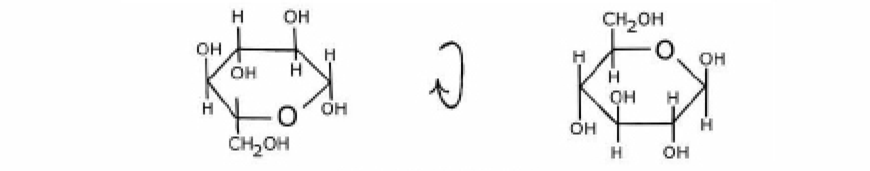
6.2 Natural Polymers

6.2.1 Cellulose

Cellulose is a **polymer of glucose**, a sugar molecule that is synthesized by plants from carbon dioxide, water, and energy provided by light (photosynthesis), thanks to the catalytic action of the chlorophyll contained in the green leaves.

In the glucose molecule, **five hydroxyl** (**O-H**-) groups are attached to a **six-membered ring** made of five carbon and one oxygen atom.

Figure 6.6

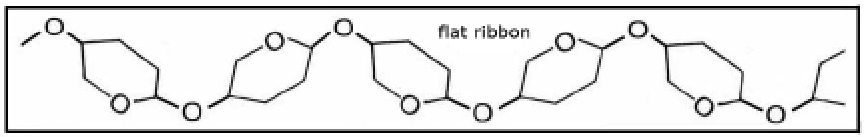


glucose molecules

Plants proceed to polymerize glucose by removing a molecule of water from couples of molecules, which thus remain linked through an oxygen atom (an “oxygen bridge”); in the case of cellulose, one of the glucose molecules is turned upside down before the link is made, and then the polymer is built by adding other molecules, each one upside down with respect to its neighbor. In chemical language, this connection between two glucose molecules is a **β-glucosidic** one.

Cellulose molecules are chains of over a thousand molecules of glucose linked by the β-glucosidic bond; the beta connection allows the shape of the molecule to be a sort of **ribbon** in which the single rings are held in position by hydrogen bonds formed by the hydroxyl groups of one molecule with those of its neighbors.

Figure 6.7

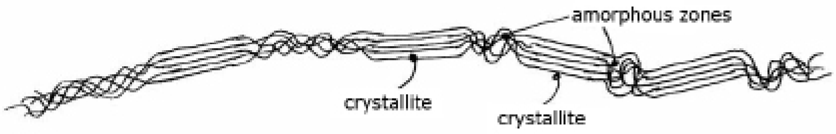


cellulose molecule: β-glucoside connection between glucose molecules

Several ribbons may connect to form an organized structure, a stack of planes of atoms that is a **crystallite**.

A bundle of cellulose molecules forms a fiber in which crystallites alternate with zones of random arrangement of the polymeric chains; while the crystalline sections provide strength, the amorphous parts ensure the flexibility of the fiber.

Figure 6.8



cellulose fiber

Cellulose is a hydrophilic material (see section 1.7.1) because the numerous hydroxyl groups in its molecules attract water; cellulose fibers in paper or cotton cloth increase in thickness when exposed to humid air, but they do not dissolve in water because the attraction force between the long molecules, resulting from about 3000 hydroxyl groups per molecule, is too strong to be overcome by the increase in disorder that would be caused by a solution of the polymer (see section 1.6.1 on the laws of solubility).

Cellulose derivatives, which are soluble in water or organic solvents, are produced by chemical modifications of cellulose (see section 6.2.3).

6.2.2 Starch

Starch is a polymer of glucose, like cellulose, but its polymeric chain is formed by **α-glucosidic** bonds, which do not involve turning over the molecule of glucose at each step when the polymer is formed; also some branching occurs. In this disposition some degree of crystallinity is achieved by a double-helix arrangement of parts of the molecules, but hydrogen bonding of hydroxyl groups within the same polymeric chain is not possible and flat ribbons are not formed.

Figure 6.9

starch

As a consequence, the material is not suitable to make fibers; plants, rather, use it as energy storage in roots (potatoes) or seeds (rice).

Natural starch becomes soluble in water and is used as an adhesive (e.g., in paper conservation), when the length of the molecules is reduced by reactions with acids or by a natural aging process caused by microorganisms, as practiced in Japan (*furunori*).

6.2.3 Cellulose derivatives

Several chemical processes have been devised since the nineteenth century to make cellulose soluble; this can be achieved by reducing the length of the polymeric chain while some or all the hydroxyl groups are transformed in such a way that the number of hydrogen bonds that are formed between the molecules is sharply reduced.

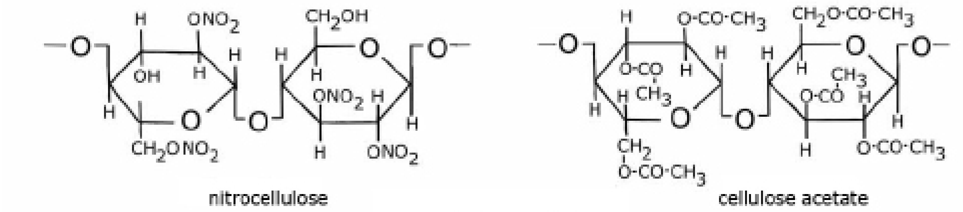
One way to achieve this result is the **reaction with acids**, which transforms the hydroxyl groups (alcohol groups) into **esters** that are soluble in organic solvents.

Reaction with nitric acid shortens the polymer molecules and forms **nitrocellulose** (first patent 1856), which was used as an explosive and, still today, as a binder for paints.

The addition of camphor (a natural resin) to nitrocellulose results in a plastic material that is easily molded, called **celluloid** (first patent 1872), which enjoyed vast success and today is mentioned as the first modern plastic material in the history of technology.

An important use of celluloid was in the production of **photographic and cinema film**; in the long run, however, the fact that celluloid is highly flammable and unstable on aging led to its substitution in the twentieth century with another cellulose ester, **cellulose acetate**, produced by the reaction of acetic acid and cellulose.

Figure 6.10

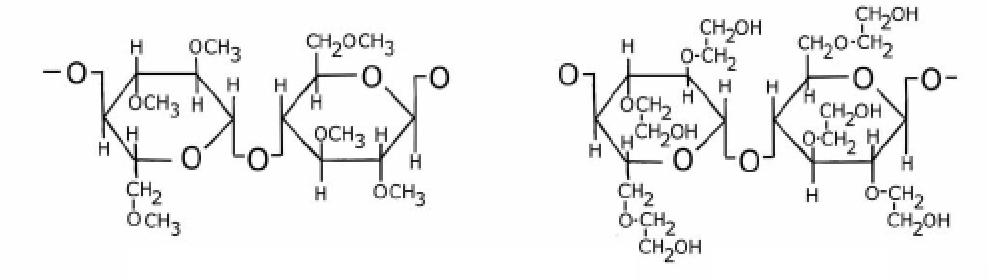


nitrocellulose cellulose acetate

cellulose esters

Water-soluble cellulose derivatives are obtained by reactions with alcohols, which produce **cellulose ethers**.

Figure 6.11



methyl cellulose hydroxy-propyl cellulose

cellulose ethers

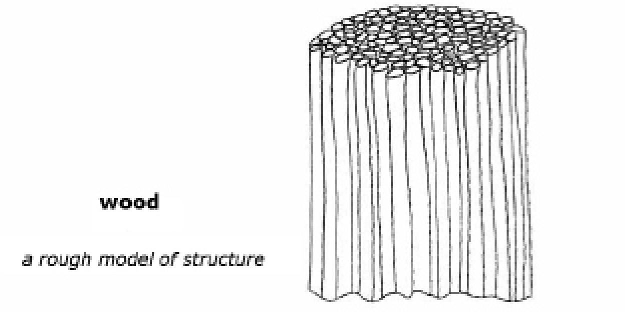
Methyl cellulose is used as an adhesive for paper, while **hydroxy-ethyl cellulose** and **hydroxy-propyl cellulose** are added to cement or hydraulic lime in the composition of grouting mixtures as anti-bleeding agents (see section 4.3.2).

6.3 Wood: A Short Note on Properties

6.3.1 Mechanical properties

The elongated cells that form the trunk of a tree lose in the course of seasoning all the organic material that fills them, and only the cell walls are left; therefore, in an oversimplified model, wood may be represented as a bundle of empty microscopic tubes composed mainly of interwoven cellulose fibers.

Figure 6.12

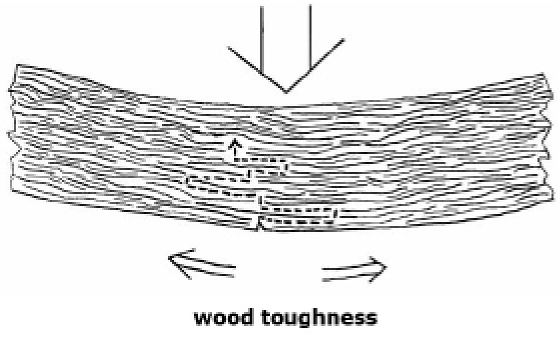


Cellulose is the main constituent of seasoned wood (60%), but the cell walls include, besides the fibers, some non-structural material (natural resins, lignin, hemi-cellulose), some of which contributes to the cohesion of the fibers.

Wood is a highly **anisotropic material** that shows different physical and mechanical properties when tested along the direction of the fibers or across them.

The mechanical behavior of wood when a stress is applied perpendicularly to the direction of the fibers is quite similar to that of the modern composite materials (see section 6.5.4). Under an excess load, a wood beam would start breaking at a weak point on the surface that is subject to a tensile stress, then the fracture would advance following a line of minimum resistance along the fibers and progressing inside the material only at the fiber ends. The result is a slow development of the breaking process, and even when a crack completes the crossing of a beam the broken parts cannot rotate and thus collapse because they are entangled with each other. More energy is then required to set the broken ends free.

Figure 6.13



Wood is therefore a tough and reliable material if it works against stresses that tend to break it across fibers. It is much easier to split it along the fibers.

6.3.2 Thermal expansion, hygric expansion, biodeterioration

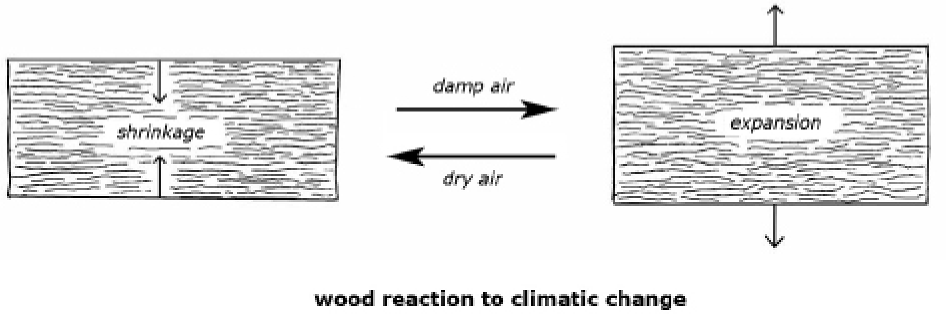
The thermal expansion of wood varies from species to species, but a much larger difference is observed within a single piece when it is tested in the direction parallel to the fibers and in that perpendicular to them: the thermal expansion across the fibers is on average ten times larger than the one measured along them.

The coefficient of thermal expansion along the fibers is actually very low, as an average value of 5×10^{-6} may be assumed for wood in general; this is not far from the coefficient of most traditional building materials, a quite favorable fact because wood beams, even when very long, are not liable to cause stresses on the masonry because of differential thermal expansion under the thermal cycles induced by the environment.

An average coefficient of 50×10^{-6} may be considered for thermal expansion across fibers, but this is not bound to cause much trouble because of the small dimensions normally involved in this direction.

Wood also expands when it absorbs water and, again, the expansion along the fibers is negligible while the one across the fibers is important and much larger than the thermal expansion (e.g., a 100-mm-thick piece of wood that would expand about 0.1 mm for a temperature increase of 20°C expands 3 to 4 mm on passing from a dry to a wet condition).

Figure 6.14



Such a large movement may well cause damage to the adjoining materials if no expansion joint is available; as an example, a practice of extraction in stone quarries, used in ancient Egypt and still in the late twentieth century in a quarry near Rome, is based on the wetting of dry wood wedges hammered into a sequence of superficial notches carved along a well-chosen line in the stone bed. The stress caused by the expansion of the wood is large enough to split the Egyptian granite.

Wood can absorb water directly from damp air and lose the absorbed water if exposed to dry air. The **dimensional change** caused by the variations of relative humidity of ambient air may cause stresses that are large enough to break the wood or cause a permanent deformation.

From a mechanical point of view, the most dangerous climate for wood conservation is a very dry one, e.g., a heated interior in a cold exterior environment.

A very damp condition may instead cause biological deterioration by **fungal attack**, e.g., “dry rot” (*Merulius lacrymans*). In buildings, the microbiological attack of wood is frequent in parts of beams inserted in masonry that has become damp because of leaking roofs or faulty hydraulic systems.

Also, the attack of wood by **insects** (termites or beetles) is favored by a damp condition.

6.4 Linear Synthetic Polymers—Thermoplastics

Synthetic polymers are better discussed keeping the linear polymers separate from the cross-linked ones because the two groups have quite different physical and mechanical properties.

Linear synthetic polymers are frequently called **thermoplastics** (or thermoplastic resins) because when heated they **soften first**, **then melt**, forming a viscous liquid. The relatively low temperatures for softening and melting of these materials, and the low pressure required for plastic deformation, allow the use of casting or shaping techniques that are much simpler and less expensive than those used for working metals.

Other properties that favor a widespread use of thermoplastics are impact resistance and light weight.

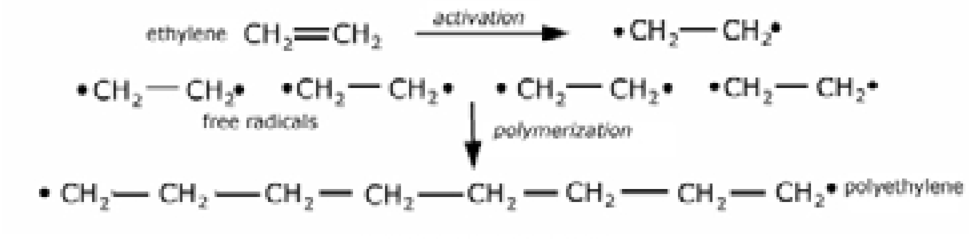
6.4.1 Polymerization

6.4.1.1 Addition polymerization

The structure of synthetic polymers is much simpler than that of natural polymers. Most linear polymers are synthesized starting from small molecules (**monomers**) that possess a carbon-carbon double bond (see section 1.4.5) **activated** by means of heat, radiation, or a catalyst, or a combination thereof. The polymerization then proceeds by **addition** of the activated molecules (**free radicals**).

The simplest polymerization reaction is the synthesis of polyethylene from ethylene.

Figure 6.15



addition polymerization

The chemical formula of a polymer may be written in a simple form, placing a monomer unit within brackets and adding a subscript that indicates the average number of monomer molecules that are included in one molecule of the polymer.

Figure 6.16

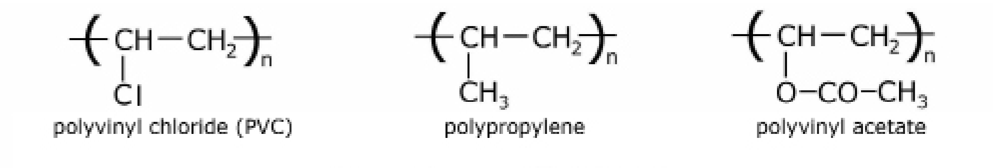
$$\left(CH_2 - CH_2 \right)_n$$

n = average number of monomer units in the polymer molecule

The number of monomer molecules is always very large as this is required to achieve a sufficient force of attraction between polymer molecules.

Other important polymers are made starting from monomers derived from the ethylene molecule by substituting one or two hydrogen atoms with different atoms, e.g., **chlorine** in polyvinyl chloride (PVC), or with a **side chain** of carbon and hydrogen atoms that frequently also contains oxygen.

Figure 6.17



linear polymers with side chains

The inclusion of chlorine or oxygen atoms in the polymer molecule creates **electric dipoles** (see section 1.4.4), which modify the physical and mechanical properties of the plastic material (adhesiveness, solubility, strength).

Polymerization of a mixture of two different monomers results in a polymer molecule in which both monomers are randomly distributed, a **copolymer** whose properties are intermediate between those of the polymers formed by the pure monomers.

Figure 6.18

copolymer

Paraloid B72 (in the United States, Acryloid B72), an acrylic polymer that has been widely used in conservation, is an example of a copolymer achieving the desired properties thanks to an appropriate combination of two monomers.

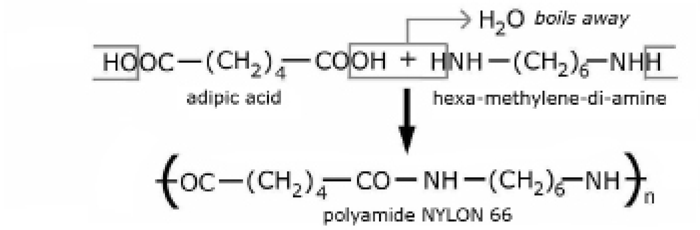
6.4.1.2 Polymerization by condensation

In chemical language, **condensation** is the name given to a reaction that joins together two different molecules by eliminating some atoms from the reactive groups they possess (**functional groups**) and forming a link between them. In many reactions of condensation, molecules of water are formed by the discarded atoms and boil away as the reaction usually develops at a temperature above the boiling point of water.

If both molecules involved in a condensation process have two functional groups (bi-functional molecules), a **chain reaction** follows and a linear polymer is formed.

An example is the synthesis of nylon; in this case the functional groups are the **acid** group (–COOH) and the **amine** group (–NH_2), which combine to **form the amide** link (–CO-NH–). A bi-functional acid with a di-functional amine form a linear polymer, a **polyamide**. Nylon 66 is the commercial name of one particular polyamide (formed by the reaction of a six carbon atoms acid with a six carbon atoms amine).

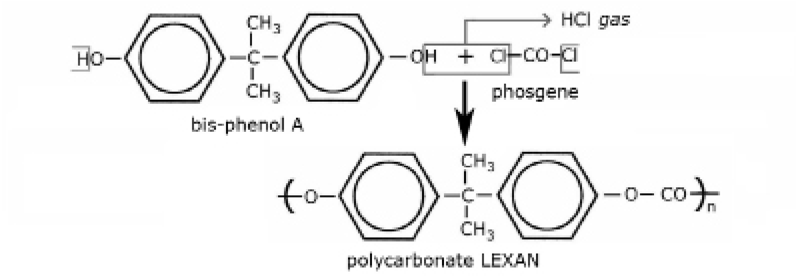
Figure 6.19



polymerization by polycondensation

The synthesis of polycarbonate, a synthetic polymer of interest in architecture, involves the removal of hydrochloric acid in the condensation reaction.

Figure 6.20



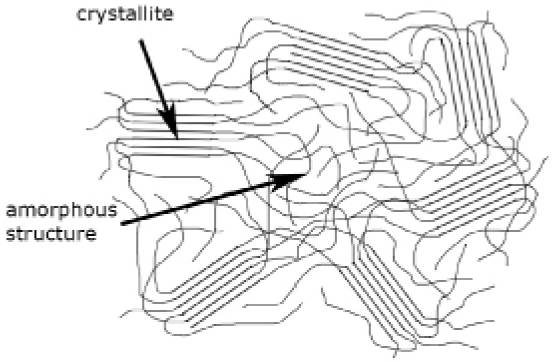
synthesis of polycarbonate by polycondensation

6.4.2 Structure and properties of thermoplastics

In most synthetic thermoplastics, the spatial arrangement of the long molecules is only in part random (**amorphous** zone) because segments of the molecules form **crystallites**, bundles of parallel chains of atoms.

Round clusters of variously oriented crystallites, called **spherulites**, are observed in some cases.

Figure 6.21



crystalline and amorphous phases in thermoplastics

In the crystallites, the attraction between molecules is stronger than in the amorphous phase and the molecules are not free to bend; as a consequence, thermoplastics that possess a large crystalline fraction soften and melt at higher temperatures and are stronger than the prevalently amorphous ones. The amorphous phase, however, can absorb stress thanks to the flexibility of the polymeric molecules and so its presence is necessary to achieve the impact resistance that is a typical property of many thermoplastic polymers.

The flexibility of the molecules in the amorphous phase is not a permanent characteristic of the thermoplastic polymers, however; it disappears at a temperature called the **glass transition temperature** (**T_G**), below which the molecular chain "freezes" and becomes stiff because the atoms that form the chain have lost the ability to rotate around the links.

The glass transition temperature and its effects depend upon the structure of the polymer. Plastic materials with an important crystalline phase show little difference across the transition temperature because the molecules that are rigidly tied anyway inside the crystallites are not affected by the blocking or unblocking of the rotation of atoms in the molecules.

A thermoplastic material with a prevailing amorphous structure may instead exist in three states: glassy (below T_G), rubbery (above T_G but below the melting point), and viscous liquid (above the melting point).

Among the great number of thermoplastics available on the market, three main groups may be recognized.

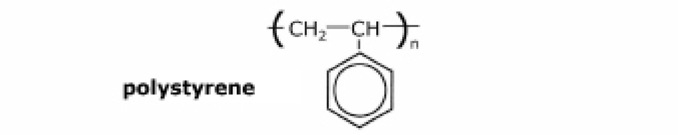
1. **Glassy** materials, which have an important amorphous phase and may be used in a stiff condition as substitutes for glass, because their T_G is above the range of ambient temperatures.
2. **Rubbery**, **flexible**, **impact-resistant** materials with a partly crystalline structure that have a T_G much below the range of ambient temperatures or have an important crystalline component, though not large enough to cause brittleness. These are used to make films, fibers, or impact-resistant objects.
3. **Semi-rigid** materials whose crystallinity is low and T_G falls within the range of room temperatures; they are mainly used as general purpose adhesives.

6.4.3 Glassy thermoplastics

The high glass transition temperature (T_G) of these polymers is explained by the structure of their molecules.

In the polystyrene molecule, the difficult rotation around the chain links is explained by the weight and stiffness of the side chains which are benzene rings (see section 1.4.5) that hang out of the main chain every second carbon atom. The glass transition temperature of the commercial grades ranges between 90° and 100°C.

Figure 6.22



In the polymethyl-methacrylate molecule, stiffness is related to the presence of two side chains that branch off from every second atom. Glass transition temperature is 104°C.

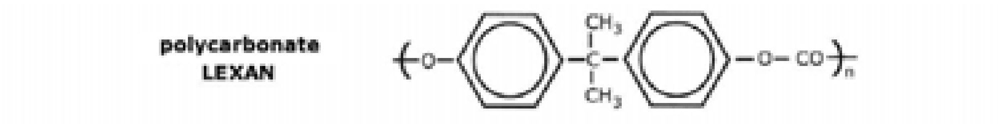
Figure 6.23

$$\left(-\overset{CH_3}{\underset{CO-OCH_3}{C}}-CH_2-\right)_n$$

The stiffness of polycarbonate is explained both by the presence of couples of rigid benzene rings in the main chain and by the two side chains attached to the carbon atom between them.

Glass transition temperature is about 145°C.

Figure 6.24

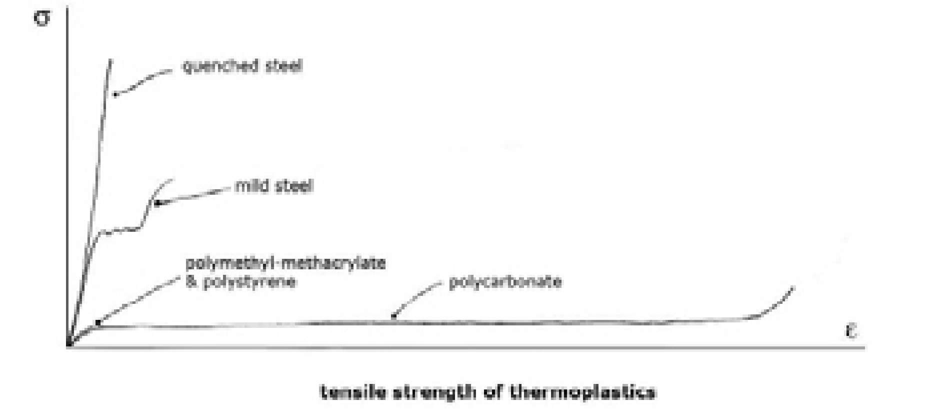


6.4.3.1 Mechanical properties of glassy thermoplastics

The mechanical properties of thermoplastics are determined in the first place by the nature of the bonds between the molecules, which are weak secondary bonds. Thus the **elastic modulus**, which depends directly upon the strength of the bonds in the solid, is much lower than those of materials that are formed by primary bonds (metals, stone, etc.). As an example, the elastic modulus of steel is about 200,000 MPa, while that of polymethyl-methacrylate and polycarbonate is 2,400 MPa and 3,100 MPa, respectively. The tensile strength of metals used for structural purposes ranges between 5 and 10 times higher than that of these thermoplastics.

The shapes of the stress-strain curves obtained by tensile tests on metals and glassy thermoplastics are roughly sketched in figure 6.25.

Figure 6.25



Polystyrene and polymethyl-methacrylate are rigid, brittle materials when tested at room temperature; elongation at break of polystyrene (3%) and polymethyl-methacrylate (5%) is even less than that of quenched steel (6%) and much smaller than that of wrought iron (25%).

The behavior of polycarbonate under tensile stress is different and quite surprising for a thermoplastic tested below its glass transition temperature. Elongation at break may surpass 100%, while the general mechanical properties are those of an impact-resistant material: for instance, a 3-mm-thick sheet may be bent 180°

without breaking, at room temperature. Thicker sheets show less flexibility and impact resistance but still are far superior to that of the other glassy thermoplastics.

The anomalous performance of polycarbonate is explained by the length of the monomer unit (12 atoms instead of 2, as in most other monomers), which allows some partial movements of small parts of the polymer chain at temperatures below T_G.

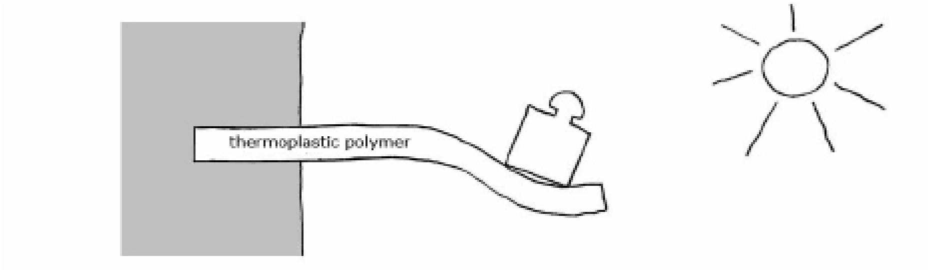
6.4.3.2 Influence of heat on mechanical properties

The strength of the glassy thermoplastics decreases quite rapidly when the ambient temperature approaches the glass transition temperature.

Some information about this phenomenon is offered by the **temperature of deflection under load** (a modest load, 1.8 MPa according to ASTM D648), which is normally provided by the manufacturers of commercial polymers; it may also be used for an approximate evaluation of the glass transition temperature because the latter is normally not much lower.

Thermoplastics, however, do suffer creep phenomena under strong loads also at temperatures below the T_G; as a consequence, even the stiffest thermoplastics cannot be considered structural materials, i.e., materials that can bear important stresses for long periods.

Figure 6.26



creep of thermoplastics

6.4.3.3 Glassy thermoplastics as substitutes for glass

Polymethyl-methacrylate (e.g., Plexiglas or Perspex) and polycarbonate (e.g., Lexan) are frequently used in architecture in place of glass as transparent protective materials.

Polymethyl-methacrylate has remarkable optical properties, high transparency, and reflectivity (4% of light lost crossing each face of a sheet); its scratch resistance, however, is low, though superior to that of the other thermoplastics. It is a brittle material, but its impact resistance is superior to that of untreated glass and, when it breaks, the fragments are far less dangerous. When ultraviolet (UV) radiation absorbers are included in the polymer, polymethyl-methacrylate ages well without discoloration.

Polycarbonate (e.g., Lexan) is an impact-resistant material; its surprising mechanical properties allow it to bend easily at sharp angles and narrow curvatures, although some superficial crazing may be caused by high stress or by aging. Addition of UV radiation absorbers is desirable to improve its aging resistance because it may discolor slightly under solar light.

The main drawback of both glassy thermoplastics presently used in architecture is their high thermal expansion coefficient (60 to 70 × 10^{-6}), almost ten times larger than that of normal glass (8×10^{-6}); a very careful design of their connection to masonry or to metal structures is thus required to avoid damage caused by thermal stress.

It should also be noted that, as in the case of glass, transparent glazing made of thermoplastics causes a greenhouse effect; high temperatures may be measured behind plastic screens when the sun shines on them, even if the space behind is not completely sealed.

6.4.4 Flexible thermoplastics

Linear synthetic polymers with no (or very small) side chains, such as polyethylene and polypropylene, have glass transition temperatures well below the range of ambient temperature, so they are normally in their "rubbery," flexible state and are used to produce plastic films and impact-resistant objects.

Figure 6.27

$$-\!\left(CH_2-CH_2\right)_n-$$

$$-\!\left(\underset{CH_3}{\underset{|}{CH}}-CH_2\right)_n-$$

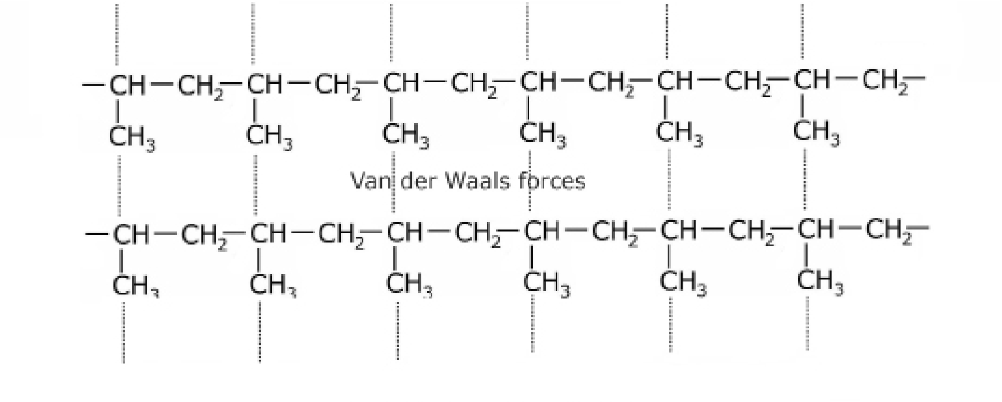
flexible thermoplastics

The **length of the molecules** has a strong influence on the physical and mechanical properties of these polymers: a longer chain determines an increase of the forces of attraction between molecules and so an increase of mechanical strength and melting point, but also a decrease of solubility (very long polymer molecules are frequently insoluble).

In **polyethylene** the number of monomer units linked to form the polymer is not much more than 1000 for **low-density polyethylene** (**LDPE**), used mainly to make plastic film, while it is larger than 10,000 for **high-density polyethylene** (**HDPE**), which is used to mold impact-resistant objects.

In the case of **polypropylene**, improved mechanical properties are obtained by producing polymers in which the side chains are all on the same side of the main chain (**isotactic polypropylene**) thanks to a special catalyst used in the polymerization process. Isotactic molecules can get closer to each other to form bundles (crystallites) and clusters (spherulites), allowing an increase in the degree of crystallization.

Figure 6.28

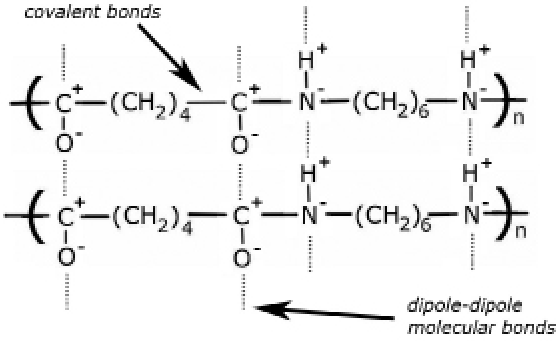


isotactic polypropylene

Other flexible polymers are the **polyamides** (e.g., nylon 66), which have higher glass transition temperatures but also a higher proportion of the crystalline phase.

The crystallinity of the polyamides is due to the **attraction between the polar amide groups**, which favors the formation of the crystallites; as a consequence, the "freezing" of the limited amorphous zones at temperatures below the T_G does not significantly influence their mechanical properties.

Figure 6.29

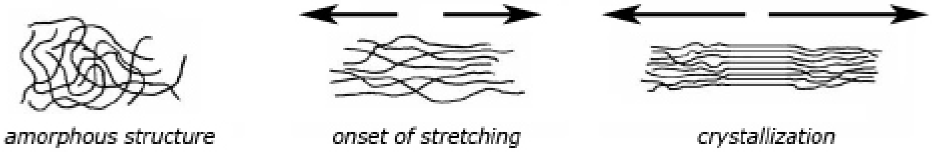


dipole-dipole bonds between polyamide molecules

In the polyamides of the nylon family, sufficient flexibility is ensured by the length of the chain of **$–CH_2–$** groups present in the molecules of both the amine and the acid component of the amide.

The crystallinity of polyamide fibers is further improved by stretching them as soon as they are formed; the result is a sharp increase of mechanical strength.

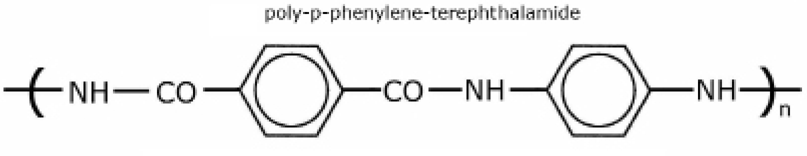
Figure 6.30



crystallization induced by stretching

A very special polyamide is **aramid** (Kevlar), a linear polymer that came on the market in 1973. The molecule of aramid is made up exclusively of benzene rings and polar **C^+-O^-** and **N^--H^+** groups, a highly polar, rod-like structure that favors a parallel alignment of the molecules even in the liquid state, when the polymer melts (formation of "liquid crystals").

Figure 6.31



aramid fiber (KEVLAR)

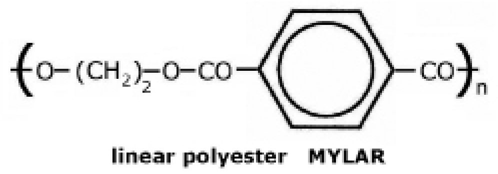
The exceptionally high values of tensile strength and modulus of aramid fibers are due to the fact that when they are formed from the melt and are immediately stretched, an extremely high degree of crystallinity is obtained in the solid material.

Another surprising property of aramid fibers is that they show a slightly negative thermal expansion coefficient (i.e., they contract slightly when heated).

An interesting group of flexible thermoplastics is that of the **linear polyesters** whose flexibility and strength are explained by mechanisms similar to those discussed in the case of polyamides.

Linear polyesters are synthesized by condensation of di-functional acids with di-functional alcohols; an example is **polyethylene-terephthalate**, which has been used to make strong fibers (e.g., Dacron, Terylene) and films (e.g., Mylar).

Figure 6.32



In this case, the **C^+-O^-** groups provide dipoles for the attraction and the high tendency to form crystallites, while some flexibility is allowed by the oxygen atoms that interrupt the chain of carbon atoms. A drop of temperature below the T_G does not cause brittleness.

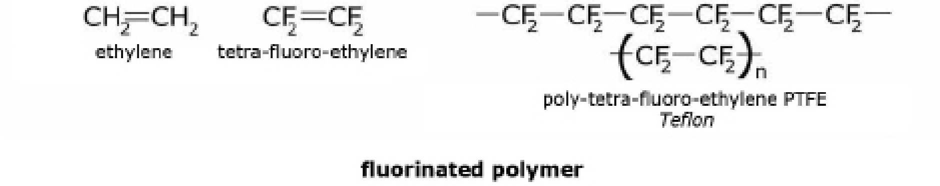
As in the case of polyamides, crystallinity is increased by stretching polyester fibers as soon as they are formed; in polyester films, a bi-directional stretching is applied to achieve maximum strength.

The crystallinity of the fibers allows them to reach very high tensile strength values; the ultimate tensile strength of nylon and polyester fibers is in the same range as that of low carbon steel (mild steel) wire while that of aramid fibers is largely superior.

6.4.5 Fluopolymers

Fluopolymers are synthesized starting from monomers in which the hydrogen atoms of the organic molecule are substituted in part or completely by fluorine atoms. An example of total substitution is poly-tetrafluoro-ethylene (**PTFE**), first synthesized in 1938 and better known under the trade name **Teflon**, a linear polymer that exhibits very peculiar properties.

Figure 6.33



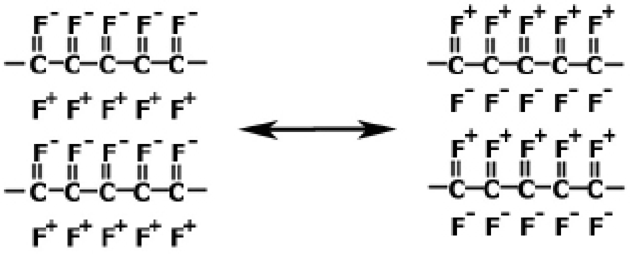
As fluorine is a very electronegative atom, like oxygen (see section 1.1.2), one might expect a very polar substance, but in reality the dipoles appear to cancel off because of the symmetrical arrangement of the fluorine atoms around the carbon atoms. The dipoles, in fact, cannot be measured, and as a consequence, dipole-

dipole bonds should not exist, but the properties of the polymer show, nevertheless, a strong attraction between molecules.

According to Linus Pauling (around 1920), the strong attraction is caused by a phenomenon called **resonance**, a term that in chemistry has a peculiar meaning; a very rough model for the PTFE resonance is that of full negative and positive charges appearing on the sides of the polymeric chain and switching positions so fast that it is impossible to see them.

The symbol for resonance is an arrow pointing both ways, as shown in figure 6.34.

Figure 6.34



resonance in the Teflon molecules

The electrical charges that nobody can see generate all the same a very strong attraction between molecules. In more recent views, it is the spiral arrangement of fluorine atoms around the carbon that is responsible for the interlocking of polymer molecules to form crystallites and so for the extraordinary **heat resistance** of the polymer. PTFE melts at 327°C and can resist continuous heating at temperatures (above 300°C) that are far above the normal field of operation of the synthetic polymers. Also PTFE is insoluble in all types of solvent.

But, as no permanent dipole is there, PTFE is **hydrophobic** and totally **non-adhesive**; it is frequently used to create self-lubricating surfaces.

Polymers made of incompletely fluorine-substituted monomers exhibit less extreme properties; they show some polarity and may be dissolved in appropriate solvents.

All fluopolymers possess a property that makes them potentially interesting in conservation technology: **resistance to aging by oxidation**. Because of its extreme electronegativity, fluorine can compete with oxygen in attracting electrons and so can hinder the oxidation of organic molecules by removing negative charges from the preferred points of attack (see chapter 6.6).

Fluorine-modified thermoplastics offer therefore some hope for the creation of long service life protective coatings for architectural surfaces of historic or artistic importance.

A first group of materials marketed in Italy under the trade name Akeogard showed good resistance in artificial aging tests but also a strong tendency to attract dust, which makes them unsuitable for the protection of white materials (e.g., Carrara or Greek marble).

Dust attraction probably results from the asymmetrical distribution of fluorine atoms when not all the hydrogen atoms have been substituted by fluorine; asymmetry does not permit resonance and generates strong dipoles, efficient attractors of dust.

Teflon does not attract dust, but it yields only opaque and non-adhesive films produced by a powder technology similar to the one used for some ceramic materials.

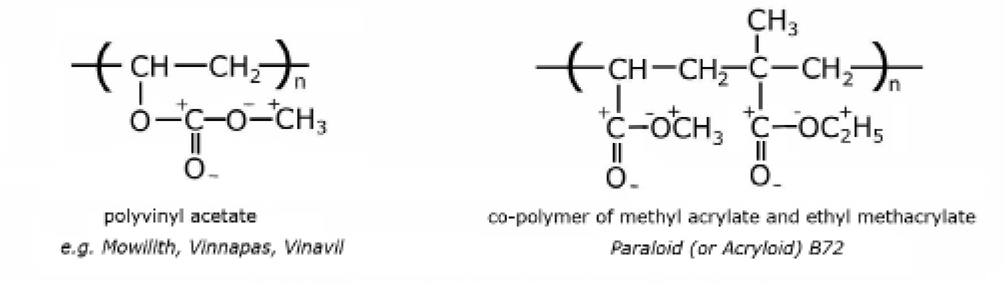
6.4.6 Semi-rigid thermoplastics

Polar groups on the side chains of polymers increase the force of attraction between molecules and so the strength and hardness of the plastic material. Also, the glass transition temperature increases and falls frequently within the range of ambient temperatures; these thermoplastics, as a consequence, are not brittle within the range of temperatures prevailing in the terrestrial environment.

Dipoles on the side chains allow them to establish electrical attraction towards surfaces that have a polar character; these are the hydrophilic surfaces (see section 1.7.1), in practice the surfaces of all materials used in architecture (with the exception of low polarity synthetic polymers, e.g., polyethylene).

Polymers and co-polymers of vinyl acetate and acrylic esters belong in this class and are used as adhesives and film-forming materials in paints.

Figure 6.35



polyvinyl acetate
e.g. Mowilith, Vinnapas, Vinavil

co-polymer of methyl acrylate and ethyl methacrylate
Paraloid (or Acryloid) B72

semi-rigid thermoplastic polymers used as adhesives

These polymers are frequently marketed as emulsions in water (see section 1.6.3) rather than as solutions in organic solvents, because present regulations tend to limit the industrial use of volatile organic compounds (VOC).

Acrylic co-polymers are widely used in paints for exterior surfaces of buildings.

Polyvinyl acetate and acrylic ester polymers and co-polymers are efficient adhesives suitable for a wide range of materials, but they are not structural adhesives (see section 6.5.5.3) because of the tendency of all thermoplastics to flow (creep) under heavy loads and high ambient temperatures.

6.5 Cross-linked Synthetic Polymers—Thermosetting Resins

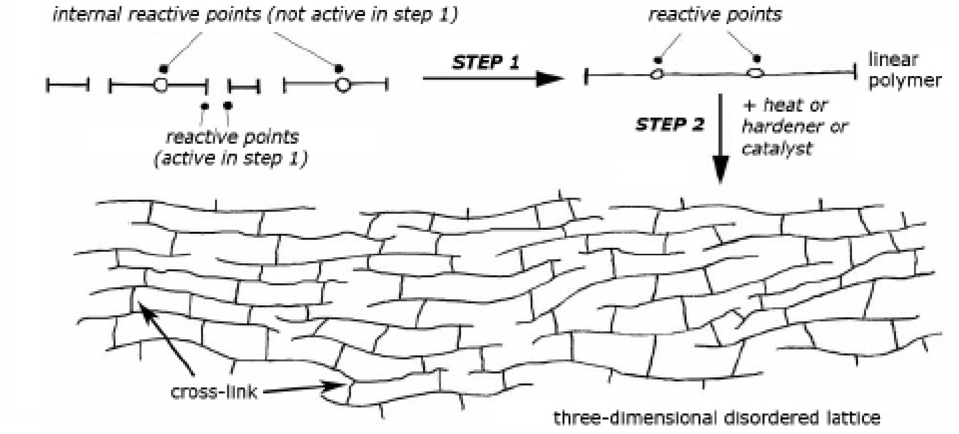
6.5.1 Polymerization and cross-linking

Cross-linked polymers are synthesized in two (occasionally three) steps. Initially a linear polymer of limited length is formed, most frequently by a condensation reaction; this is a viscous liquid or a soft solid that is sold on the market by the manufacturer. The cross-linking of the polymer to produce a hard, insoluble, and infusible mass is then carried out by the industries or individuals who use it for various purposes.

The name *thermosetting resins* was given to these polymers because the first ones that were commercially available (e.g., Bakelite, 1907) were cross-linked by the action of heat. Polymers that could be cross-linked at room temperature by the addition of catalysts or chemical reagents (hardeners) appeared on the market mostly after the Second World War and are now widely used, but the term *thermosetting resin* remained in use for the whole class of cross-linked polymers.

The complex chemical reactions involved in the synthesis and use of thermosetting resins are not discussed in these lectures, an exception being made for epoxy resins. A general scheme of these processes is shown in figure 6.36.

Figure 6.36



general scheme of the polymerization of thermosetting resins

Phenolic resins are synthesized, creating the linear polymer by a condensation reaction of a phenol with formaldehyde and are cross-linked by heating them at about 180°C; they are the first fully synthetic polymer produced by industry. In architecture, phenolic resins are used mainly as the adhesive component of laminated fibrous materials (e.g., laminated timber, particleboard).

Cross-linked **polyester resins** harden at room temperature by the addition of a small amount of a catalyst; the linear polymer prepared in step 1 contains many double bonds and is marketed dissolved into a solvent (styrene) that also has a double bond in its molecule. When the double bonds are activated by the **catalyst**, the solvent molecules bind to the polymer molecules by an addition reaction (see section 6.4.1.1) and the material hardens. The combination of polyesters with glass fibers, hardened at room temperature, allows the mass production of large objects at low cost (e.g., plastic boats).

In architectural conservation, the most interesting thermosetting polymers are the epoxy resins, which are discussed in section 6.5.3.

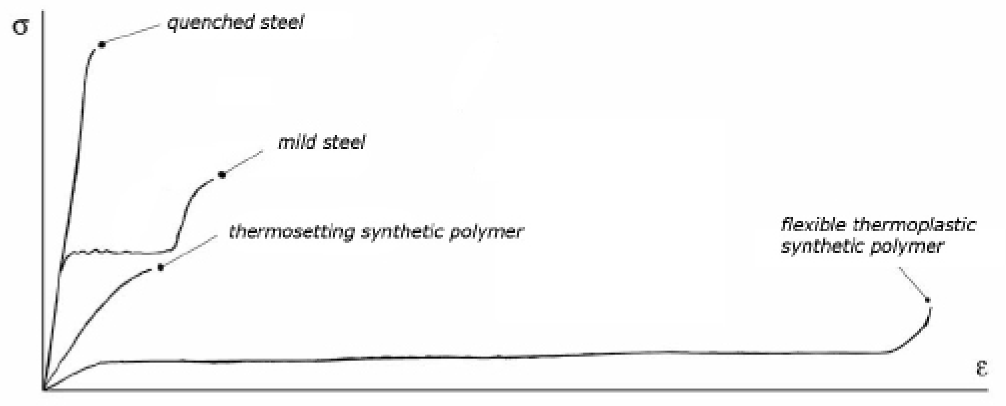
6.5.2 General properties of thermosetting resins

The existence of cross-links, primary chemical bonds, between the molecules does not allow them to separate by purely physical means; thermosetting resins therefore are **insoluble**. When heated, they do not soften or melt, but when the temperature is high enough to break a primary bond, the whole structure is decomposed and the original material is not recovered upon cooling; thermosetting resins therefore are considered to be **infusible**.

Cross-links increase the cohesion of the molecules; as a consequence, the elastic modulus of thermosetting resins is much greater than that of the thermoplastics. Cross-links also hinder the movement of the molecules and impede their flow under stress; as the number of cross-links increases, the material becomes **hard**, flexibility is reduced, plastic deformation is impossible, risk of creep is drastically reduced, but the material is **brittle**.

In figure 6.37, the shape of the stress-strain graph for a thermosetting polymer is roughly compared with those of a thermoplastic polymer, a mild steel, and a quenched steel.

Figure 6.37



comparing tensile strength of steel and polymers

6.5.3 Epoxy resins

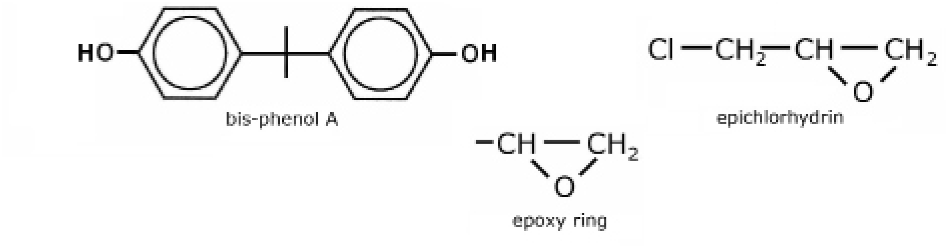
Epoxy resins came onto the market around 1950; they are marketed as two separate components, the **resin** (a short linear polymer) and the **hardener** (normally an amine), which the user must mix in the right proportion at the moment of use. Hardening normally takes place at room temperature, but occasionally a high temperature is applied to special resins and hardeners when a very high and reliable adhesive strength is required.

The name of these resins is the chemical name of a group of three atoms (two carbon and one oxygen) forming a ring: the **epoxy ring**. A three atom ring is not common in organic chemistry because the bonds must be strained out of their normal angle to form the triangular loop; as a consequence, the epoxy ring is unstable and tends to split open when in contact with suitable molecules, in particular those that contain an "active" hydrogen atom (an "active" hydrogen atom is one that is linked to an electronegative atom like nitrogen or oxygen).

The epoxy ring plays a key role in the preparation of the polymer, in its hardening process, and in its strong adhesion to all hydrophilic materials.

Step 1 in the synthesis of the standard type of epoxy resins is the reaction of a molecule containing the epoxy ring (epichlorhydrin) with bis-phenol A (a molecule we already met in the synthesis of polycarbonate, section 6.4.1.2).

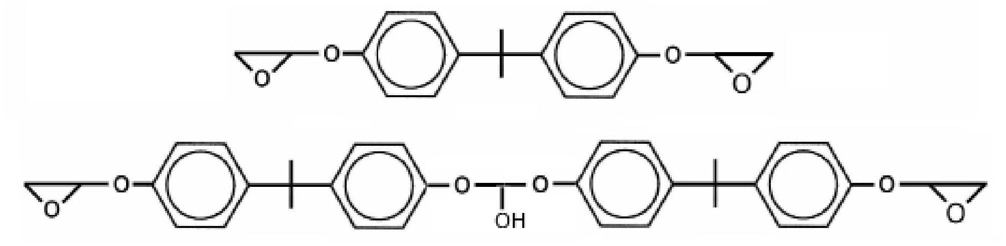
Figure 6.38



starting point for the synthesis of epoxy resins

Step 1, polymerization, leads, through a condensation reaction, to the formation of a rather short linear polymer; the number of repetitive units in the chain may be as small as one, two, or three to a maximum of ten. This is the component that is normally called the resin. As the length of the chain increases, so does the viscosity and so, according to the needs, resins of different viscosity are produced. Epoxy rings are preserved at both ends of the chains.

Figure 6.39



synthesis of epoxy resins, step 1, chains of variable length

Epoxy resins are widely used in architectural conservation as adhesives and consolidants, but they are seldom used without additions. Since the linear polymer produced in step 1 is a more or less viscous liquid, it is possible to mix it with a **filler**, a solid material in the form of a powder or short fibers that do not take part in the hardening reaction. Inert fillers lower the cost and modify the physical and mechanical properties of the final product in a favorable way, e.g., increasing strength, reducing brittleness and thermal expansion. They also reduce the amount of heat that is produced in the reaction, which may create serious problems when large amounts of resin are cast.

Step 2, cross-linking and hardening, is based on the reaction of the epoxy rings with a **hardener**, a molecule that contains several "active" hydrogen atoms (at least three, but in most cases four, five, or six).

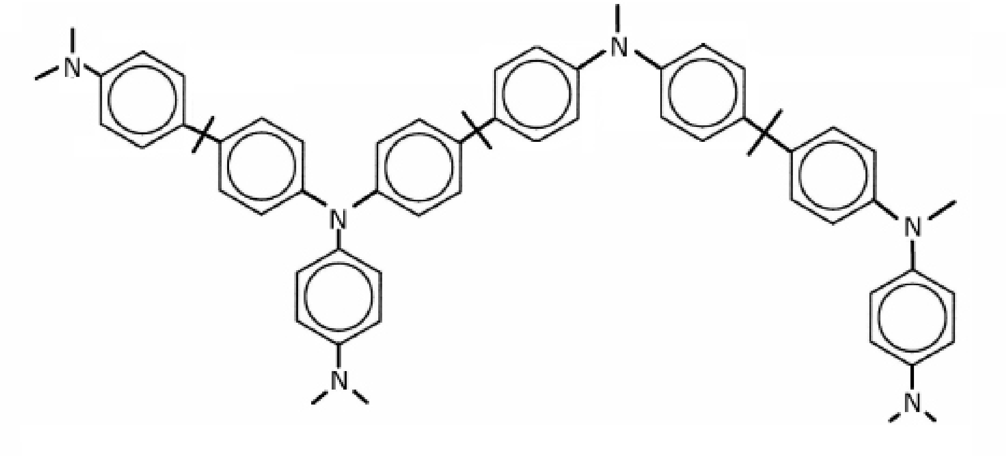
The hardeners used in architectural conservation are **amines**, which allow the hardening reaction to be carried out at room temperature.

Figure 6.40

a hardener for epoxy resins

In figure 6.40, phenylene-di-amine is presented as an example; in a bi-functional amine, two $-NH_2$ groups offer four “active” hydrogen atoms and so may bind with four resin molecules, while each resin molecule binds with two amine molecules. In this way, a disordered solid mass is formed whose cohesion is determined by both primary, covalent, bonds and secondary, molecular ones, where the molecular chains happen to be close.

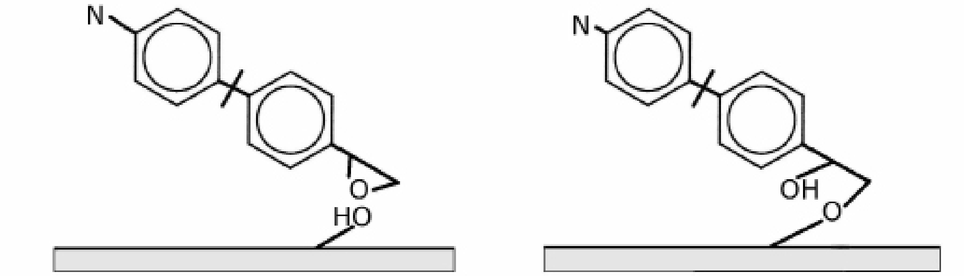
Figure 6.41



cross-linking of an epoxy resin

In the course of the cross-linking reaction, epoxy groups react also with “active” hydrogen atoms present on the surface of the filler, establishing a strong connection through a primary bond. This type of connection explains the great adhesion epoxy resins exhibit on all hydrophilic materials (see also section 6.5.5.3).

Figure 6.42



adhesion of an epoxy resin to a hydrophilic surface

Also, one of the hydrogen atoms in the water molecule is an “active” hydrogen, but one water molecule only opens one epoxy ring without forming cross-links; its effect on the hardening of the resin is thus negative. The hardening of epoxy resins may fail in a damp atmosphere or when moist fillers are added.

As an alternative to adding a filler to the resin, a fluid resin mixed with the hardener may be used to impregnate a fibrous material (tissue or non-woven cloth), the cross-linking reaction developing later inside the host material; the result is a composite material whose mechanical properties are far better than those of the non-filled hardened resin (see section 6.5.4).

Hardened epoxy resin undergoes oxidation reactions under the action of light and air, which result in discoloration and loss of hydrophobic properties (see chapter 6.6); if it is not directly exposed, however, its aging properties are quite reliable as, for instance, in the case of epoxy adhesives (see section 6.5.5.3), which are applied between opaque materials or epoxy resins injected into deteriorated concrete.

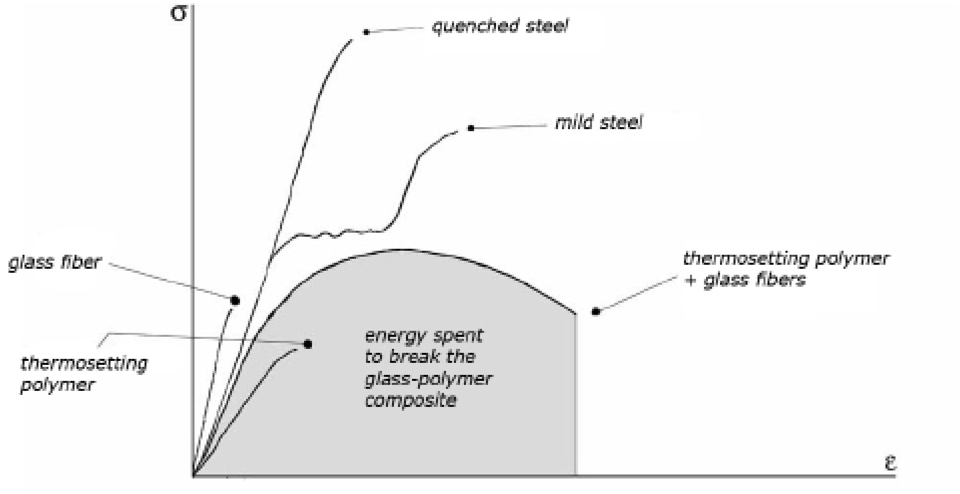
6.5.4 Composite materials

Composite materials are composed of a **synthetic polymer matrix** in which many **high-strength fibers** are imbedded. The inclusion of fibers increases the toughness of the polymer in particular when the fibers are aligned across the probable direction of progress of a crack advancing under tensile stress. Cracks must follow paths of minimal strength along the fibers, the adhesion between polymer and fiber being the weakest point in the composite; so they progress slowly on an irregular path, the existence of weak joints paradoxically becoming the factor that determines a remarkable toughness of the composite material. Also, when a crack has completely crossed the whole thickness of the composite the breaking process is not finished because, in order to allow the free rotation of the severed sections, further energy is required to extricate them.

On the whole, the mechanical behavior of composites under stress may be likened to that of wood (see section 6.3.1).

A rough sketch, comparing an ideal stress-strain diagram of a mild steel with that of a thermosetting resin and that of a composite, made of the same resin and glass fibers, is shown in figure 6.43.

Figure 6.43



toughness of composite materials

Since the energy spent to break a material, its **toughness**, is measured by the area underlying the stress-strain diagram, it is evident that the toughness of the glass-resin composite is comparable with that of a metal and far superior to that of the resin alone.

Also, the **elastic module** of composites, i.e., the initial slope of the stress-strain diagram, is not far from that of the metals because the modulus is the weighted average between the modulus of the fibers (which is higher than that of steel) and that of the resin (which is lower).

If the mechanical properties of synthetic resin composites are compared with those of steel at equal weight (rather than at equal cross section), those of the composites are far superior because their specific gravity is much lower (less than half that of iron).

Composites also show good creep resistance because the covalent cross-links do not allow the polymer chains to slip along each other.

Epoxy resins and **polyesters** are most frequently used to form the matrix, glass fibers being the normal fibrous component up to recent times. The best mechanical properties are obtained when the material contains the maximum possible percentage of fibers, provided the amount of the resin is sufficient to establish a complete adhesion between them, leaving no voids.

Glass fiber–polyester resin composites show thermal expansion coefficients of 20 to 30 × 10^{-6} when fibers account for 50% to 65% of the composition. Glass-polyester bars are used in architectural conservation to support heavy fragments of stone when they are repositioned on a building surface with a structural adhesive (see sections 4.3.1 and 6.5.5.3).

In recent times, other fibers have made it possible to achieve strength and toughness superior to those offered by glass-fiber composites.

Carbon fibers are produced by carbonizing thermoplastic fibers in an oxygen-free atmosphere; if the process is pushed to higher temperatures, the crystalline structure of **graphite** is formed in the **fibers** and their strength is further increased. As these fibers show a minimal (or even negative) thermal expansion, it is possible to produce a composite that does not expand or contract at all in the range of ambient temperatures.

Properties similar to those of carbon fibers are exhibited by the **aramid fibers** of even more recent production (see section 6.4.4). Like some carbon fibers, aramid fibers also show a slightly negative thermal expansion coefficient.

Carbon or aramid fibers, as ribbons or woven cloth impregnated with epoxy resins, are now currently employed in the consolidation of reinforced concrete structures damaged by the corrosion of steel reinforcement bars.

6.5.5 Adhesion and adhesives

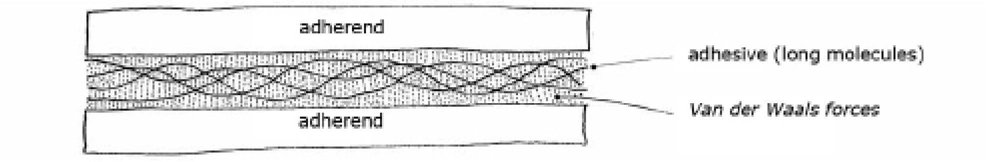
Adhesives are used to join two separate pieces of solid matter (in technical language, the **adherends**) either to repair a broken material or to assemble a new structure.

A general discussion of adhesion is organized here by grouping the adhesives according to the type of bond they can form with the surfaces of hydrophilic or hydrophobic materials, because the strength that can be provided by an **adhesive joint** depends essentially upon the bonds established between adhesive and adherend.

6.5.5.1 Adhesion by molecular bonds of the Van der Waals type

This class of adhesives is composed of **long, low-polarity molecules** dissolved in a low-polarity solvent; the bonds they form with any surface (either hydrophilic or hydrophobic) are due to **dispersion forces** (see section 1.4.1) and are individually weak, but the length of the molecules and the fact that they are tightly interwoven results in a sizable force of attraction.

Figure 6.44



contact adhesive

A typical example is offered by adhesives based on **rubber** (either natural or synthetic) dissolved in organic solvents. These are spread on both surfaces to be joined and develop a **tack** (i.e., a stickiness of the surface) after most of the solvent has evaporated; the adherends must be joined after the tack has developed, otherwise a defective joint may be obtained because of the solvent that remains trapped inside the adhesive.

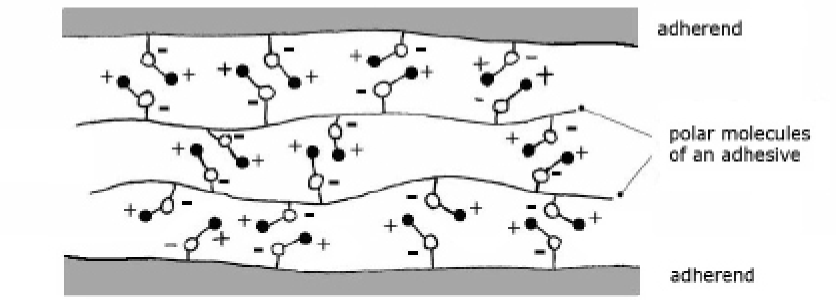
Adhesives in this class are frequently called **contact adhesives**; they are impact resistant and operate quite well under compressive stress (e.g., in shoe soles), but they have low creep resistance and cannot be used as structural adhesives, which are designed to carry heavy loads over long times.

Rubbery materials age and become brittle because of oxidation (see chapter 6.6) when they are exposed to air and light.

6.5.5.2 Adhesion by dipole-dipole attraction

Adhesives in this class are **polymers**, which possess **many polar groups** of atoms in their side chains (see sections 1.4.4 and 6.4.6). Adhesion in this case depends upon **electrical attraction** between dipoles, therefore the presence of polar groups on the surface of the adherends is required.

Figure 6.45



adhesion by dipole-dipole attraction

Typical members of this class are poly-vinyl and poly-acrylic synthetic resins (see section 6.4.5), cellulose derivatives like cellulose acetate and nitrocellulose (see section 6.2.3), and natural polymers like the adhesives derived from starch (see section 6.2.2).

They are used either in solution in appropriate solvents or as emulsions in water; because of the risks involved in the use of solvents (see section 1.6.3), current regulations encourage the use of water emulsions for the adhesives that are not soluble in water (all of the above mentioned, with the exception of starch).

If the surfaces on which the adhesive should be applied are moist (a condition that is occasionally met in architectural conservation and quite frequently in archaeology) and the polymer is not soluble in water, it must be dissolved in a solvent that is immiscible with water, contrary to what one might expect; in fact, if the solvent absorbs water the polymer coagulates out of the liquid as an opaque film with no adhesive action (this, by the way, is a good system to remove a polymer from a surface). A low-polarity solvent can instead displace the water from the surface, as it has a lower surface tension, and deposit the adhesive there when it evaporates.

The presence of a multitude of polar groups determines an increase of the adhesion strength with respect to the contact adhesives, but adhesion is not possible if there are not enough polar groups on the surfaces to be joined; i.e., these adhesives do not work on non-polar hydrophobic surfaces.

Adhesives in this class cannot be considered structural adhesives, even if the strength of the joints they produce is considerable, because their adhesion is based on molecular bonds that are individually at least ten times weaker than primary chemical bonds and creep is possible under a high and continuous stress.

6.5.5.3 Adhesion by chemical bonds

In the discussion of the properties of **epoxy resins** (section 6.5.3), it was mentioned that the epoxy group can form a chemical bond with the hydroxyl groups of hydrophilic surfaces in the course of the cross-linking reaction.

Epoxy resins are used to formulate structural adhesives because the joints show good tensile strength (in the range of 5 to 10 MPa) and creep resistance, provided the temperature is not much above the normal ambient range.

The composition of epoxy adhesives may include **fillers**, to reduce thermal expansion, and **plasticizers**, such as non-vulcanized synthetic rubber or polyamides, to avoid brittleness.

The use of epoxy resin in a worksite is not easy, however, and requires care and competence:

- the adhesive is always sold as **two components**, the resin and the hardener, which must be mixed well and in the **right proportions**, otherwise it will not harden correctly;
- after mixing, the cross-linking reaction starts and all the work must be completed in a **limited time**;
- as was mentioned in section 6.5.3, the presence of **water vapor or water** in the form of moist resin, wet fillers, or damp air may cause softening or no hardening at all (the work area must be kept warm and dry in winter or in damp climates);
- the **shelf life** of the adhesive is limited and it is wiser to discard it after a given time rather than risk costly failures;
- the hardened adhesive is insoluble so the bond is **almost irreversible**, as only special chemical mixtures or overheating can disaggregate it.

Epoxy adhesives age quite well if they are hidden from the action of air and light, but they suffer discoloration and embrittlement when exposed on the surface of materials.

6.6 Aging—Oxidation of organic molecules

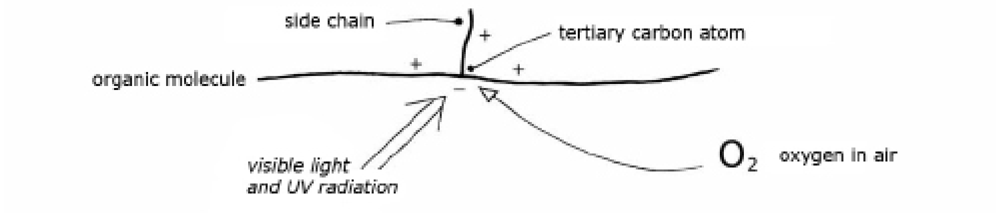
Organic materials exposed to air and light undergo a progressive decay of their mechanical properties (loss of flexibility, embrittlement) and a modification of some physical properties such as color (modified to yellow or brown) and hydrophobic character (progressively disappearing).

These changes are brought about by the action of oxygen (about 20% in the earth's atmosphere) stimulated by the energy input offered by electromagnetic radiation (visible light and UV radiation).

The **electronegative oxygen atom** (see section 1.1.2) is able to intrude in an organic molecule wherever a slight excess of negative charge occurs.

A typical example is a **branching point** in any chain formed by carbon and hydrogen atoms; the carbon atom to which the side chain is connected is bound to three carbon atoms and one hydrogen, while the neighboring carbon atoms are bound to two hydrogen atoms and two carbons (for this reason it is called a **tertiary carbon**). Because of a slight difference in electronegativity between hydrogen and carbon (which was not mentioned in section 1.1.2), all tertiary carbon atoms get a very small negative charge that marks them as a target for attack by oxygen.

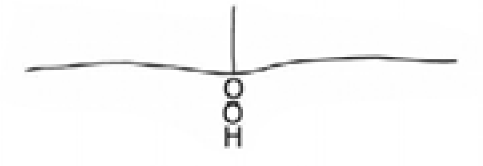
Figure 6.46



first step of the aging process of organic materials

In the first step of the oxidation reaction, an oxygen molecule sneaks in between the tertiary carbon and its hydrogen atom, forming a **hydroperoxide** group.

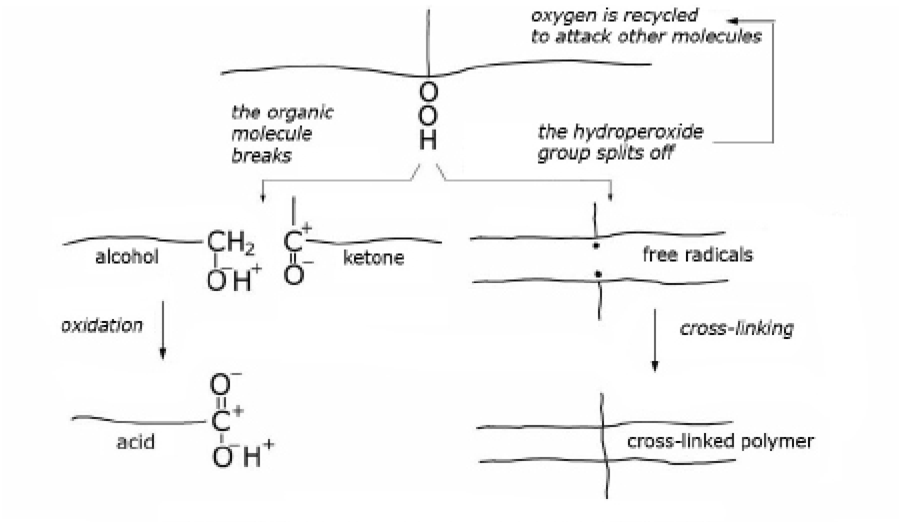
Figure 6.47



hydroperoxide

This is only the starting point of a complex process because the hydroperoxide is unstable and may cause **either a break** in the chain of carbon atoms **or a cross-link** with another molecule. Smaller oxidized molecules are formed from the breaking process, while cross-linking generates a network of carbon chains.

Figure 6.48



hydroperoxide transformations - oxidation reactions

The smaller oxidized molecules determine the color change and the loss of the hydrophobic character of the polymers. In the case of linear polymers, their solubility is also modified as more polar solvents are required to dissolve the aged material than those that were initially used to dissolve it in the pristine condition; furthermore, if much cross-linking occurs, the polymer may become insoluble. Cross-linking also reduces the flexibility of the carbon chain, the final phases of the process leading to a brittle material.

Organic materials may escape or retard oxidation for very long periods if they are protected against light, air, and water (which is the cause of biological decay processes); there are examples of survival of proteins, a perishable material in normal atmospheric conditions, inside fossil bones for thousands of years. Composite materials formed by the coupling of organic and inorganic materials and organic molecules inserted in the pores or cracks of a pre-existing inorganic material may thus survive for long periods and offer extended service lives.

Part 7

Silicates, Silanes, and Silicones

7.1 Silicates and Fluosilicates

7.1.1 Silicic acid (amorphous silica)

The outer electron shell of the silicon atom (chemical symbol **Si**) has four electrons, just as the carbon atom has, but it is an M shell, i.e., it lies farther away from the nucleus than the L shell of carbon. As the chemical properties are determined mainly by the outer electron shell of the atom, one may suppose that silicon should behave more or less like carbon, but, due to the larger dimension, this is true only in part.

Silicon is an essential component of the minerals (silicates and silico-aluminates) that are the most abundant in the earth's crust; silicon forms only one oxide when it combines with oxygen: silicon dioxide (**SiO_2**), which is better known by its ancient name, **silica**.

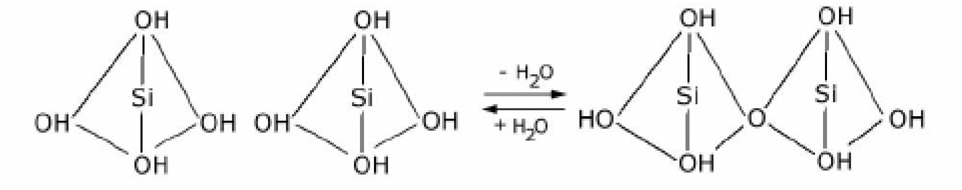
The **silicon-oxygen bond** was discussed in section 1.2.3, and it was shown that silicon forms four covalent bonds with oxygen (each with some polar character) that are directed towards the apexes of a **tetrahedron**. The silicon-oxygen tetrahedron is the fundamental unit that is found in all the forms of silica and in all silicate minerals. As an example, chains of tetrahedrons coiled to form spirals constitute the structure of the **quartz** crystal, the most common natural form of silicon oxide; silica tetrahedrons can also form chains (e.g., pyroxenes), bands (e.g., amphiboles), sheets (e.g., talc), or three-dimensional structures (e.g., zeolites).

Two less common crystalline forms of silica are known, tridimite and cristobalite, but also several types of **amorphous silica** (opal, chalcedony, silica gel), which may be considered derived from crystalline silica by a process of hydration in which the bonds between silicon-oxygen tetrahedrons are split by the addition of water.

A complete hydration of silica results in **isolated tetrahedrons**; the chemical formula for this material can be written $Si(OH)_4$, but chemists frequently write it H_4SiO_4, arranging the elements as in the formulas of the acids because fully **hydrated silica** has a slightly acidic character. This is shown also by another name given to hydrated silica: **silicic acid**.

Under still another name, **silica gel**, hydrated silica is used to control relative humidity of air in enclosed spaces. In a dry atmosphere, silica gel releases water molecules into the air and is partially dehydrated, re-forming some links between tetrahedrons, while in a damp environment it absorbs molecules from the air water, which splits those links again.

Figure 7.1



silicic acid's equilibrium with water vapor in the air

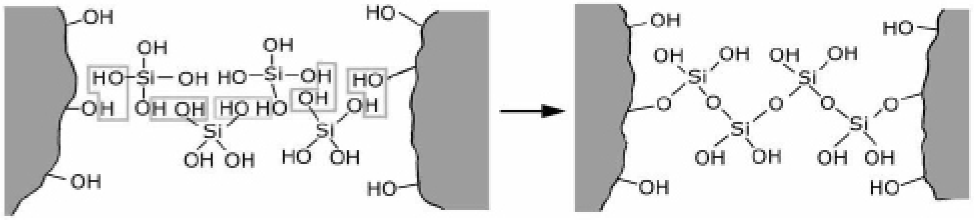
The word **gel** indicates an amorphous structure that can actually become a gelatinous mass if an excess of liquid is added; hydrated silica gels with the addition of suitable active compounds (e.g., chelating or surface active agents, see sections 1.5.6 and 1.6.3) are used as **cleaning agents** in the conservation of works of art.

Salts or esters of silicic acid have been used in architectural conservation as **stone consolidants**.

When a chemical reaction forms **silicic acid** in a free space, a powdery solid is obtained, obviously not usable as a consolidant. But silicic acid can consolidate hydrophilic materials if the solution of a salt or a liquid ester is used to impregnate the material, and then **the acid is formed inside the pores by a hydrolysis reaction.**

Inside the material, silicic acid can create bonds with the hydroxyl groups in the hydrophilic surface by splitting off water molecules and creating "oxygen bridges."

Figure 7.2



silicic acid as a consolidant

Some of the hydroxyl groups available around the silicon atom will form bridges with –OH groups on the surface of the solid, while others will create connections with other molecules of silicic acid.

As the process continues, a number of bonds are formed between parts of the solid, which had been separated by a decay process. The sequence of silicon-oxygen bonds, according to the experience gathered so far, can bridge gaps up to a few hundredths of a millimeter but not wider than 0.1 mm.

After consolidation, the porous system is obstructed by the silica gel, but this is only a temporary condition as the gel progressively contracts (**syneresis**) and the porosity is almost completely reestablished while a consolidating effect is maintained by strings of silicon-oxygen bonds.

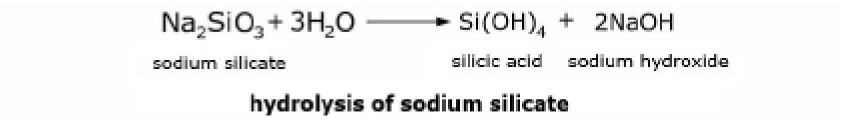
Salts, esters, and other derivatives of silicic acid that have been used in the past two centuries to consolidate stone and mortars are discussed in the following sections.

7.1.2 Sodium and potassium silicates

Alkaline silicates were synthesized in Germany around 1820 and very soon (Von Fuchs, 1830) their use was proposed for the consolidation of weathered sandstone.

Sodium and potassium silicate dissolve in water and very soon decompose by a hydrolysis reaction, forming silicic acid and sodium hydroxide (caustic soda).

Figure 7.3



The consolidation process enjoyed considerable success, in particular when it was improved (Kuhlmann, around 1850) allowing rapid application even on very large surfaces. Other, similar processes, based on slightly modified chemistry, were developed elsewhere in Europe (England, France). Soon, however, some negative side effects were reported and heavy criticism brought about a progressive abandonment of the process. Actually, alkaline silicates are effective consolidants, but their successful application to a built structure is not easy, and **the risk of failure is high** unless the treatment is applied by very experienced workers.

In the first place, the hydrolysis reaction is very fast, and frequently a large amount of silica gel is deposited in the proximity of the surface, obstructing further access of the liquid, which should reach the core of the damaged material; this may result in the production of a **hard crust over a low-cohesion material** with a high probability that the whole surface will be lost in a relatively short time.

But since the gel undergoes a contraction in a reasonable time by releasing water to the atmosphere, an experienced worker would know that he could repeat the impregnation after, say, a month, with a good chance of mitigating the defect; this, however, is hardly the case when a process is too successful and follows the laws of mass production.

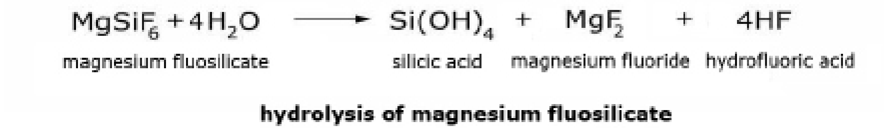
Another difficulty is caused by the **secondary product of the reaction**, caustic soda, which is transformed into **sodium carbonate** by the action of carbon dioxide; it is highly probable that a dangerous soluble salt is left on the surface after the treatment unless all the caustic soda produced by the process is removed from the surface. Complete removal of the secondary products of a reaction from a porous surface is not easy, even accurate washing may not be sufficient and absorption by means of poultices is required. It is not surprising, therefore, to learn that **salt efflorescences** appeared frequently after treatment.

7.1.3 Fluosilicates

After silicates fell out of fashion, fluosilicates became the most successful "stone preservative."

The Kessler patents (1883) covered the use of zinc and magnesium fluosilicate: also in this case the salts are hydrolyzed as soon as they come in contact with water, forming silicic acid.

Figure 7.4



Fluosilicates form no dangerous secondary product because the fluorides of zinc and magnesium are almost insoluble in cold water; they also have a favorable influence on the future conservation of the treated surface because they can prevent microbiological attack by fungi and algae. Also, the other secondary product, hydrofluoric acid, may turn out to be useful as it is quite efficient in removing algal growths and silica-rich incrustation over sandstones.

Fluosilicates present obvious advantages over the plain silicates, but the hydrolysis is still a fast reaction and the danger subsists that consolidated crusts be created over incoherent material.

Fluosilicate impregnation was used mainly to consolidate sandstones in Germany and France, but between 1949 and 1970 Professor Piero Sanpaolesi, of Florence University, applied it to Carrara marble in some famous façades (Ca' D'Oro in Venice, the Aragonese Arch of Castel Nuovo in Naples) and in sculptures (the external pulpit by Donatello in the Cathedral of Prato); actually, the chemistry of the process suggests that it might not be effective on calcareous stone, but experience shows that consolidation is possible, even if less efficient than in the case of sandstones.

Sanpaolesi tried to improve the penetration of the consolidant by applying it over compresses made of vegetal fibers and also attempted to create a void inside the stone to suck the liquid into its core; on the whole he obtained better results with marble than with sandstone (Church of San Michele in Pavia), but the marble treatments were heavily criticized, probably for aesthetic reasons.

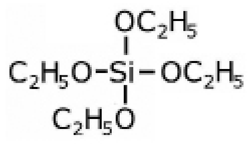
While in France the application of the fluosilicate process to historic buildings was formally forbidden early in the twentieth century, in Italy it was abandoned only around 1970, and it was abandoned even later in India, where the biocidal action must have proved useful.

The negative judgment that in the first part of the twentieth century fell upon all chemical consolidation processes, notwithstanding the fact that in general they yield good results in laboratory conditions, was due in part to the fact that at the time they were required to guarantee the conservation of the treated object without the support of all the other operations (cleaning, filling, grouting, protection) that now are deemed necessary for a satisfactory result, in terms both of aesthetics and of a long service life. In addition, it was required that the protective action should last an undetermined number of years, no maintenance being provided. The treatment of the Donatello marbles was declared a failure because some signs of decay were detected after about twenty-five years of open-air exposure in a polluted atmosphere; today, on the same grounds, it would be considered a success.

7.1.4 Ethyl silicate

Ethyl silicate is the **ethyl ester of silicic acid**. While the combination of an acid and a base forms a salt and a molecule of water (see section 1.5.4), the condensation of an acid with an alcohol results in an ester and a molecule of water. As silicic acid has four reactive positions in its molecule, it can combine with four molecules of ethyl alcohol, forming ethyl silicate and four molecules of water.

Figure 7.5



$Si(OC_2H_5)_4$

ethyl ester of silicic acid

ethyl silicate

The four **$–OC_2H_5$** groups that surround the silicon atom are called **ethoxy groups**; they can be hydrolyzed by water with the help of a catalyst, forming again silicic acid and ethyl alcohol.

Ethyl silicate is quite suitable for the consolidation by impregnation of a porous hydrophilic solid because it is a low-viscosity liquid that can easily penetrate in depth in pores and fissures to form silicic acid if some water is available there. An important point is that the hydrolysis of an ester is a slow reaction and so there is little danger that a consolidated crust will be formed on the surface, inhibiting further penetration of the treatment. Also, the secondary product of the reaction, ethyl alcohol, evaporates and so disappears without causing problems.

Figure 7.6

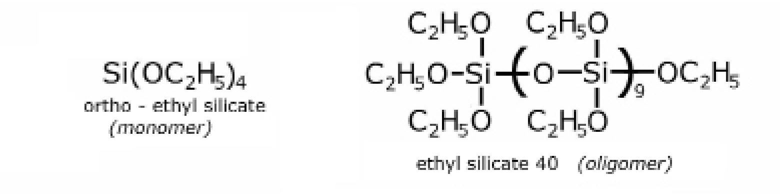
$$\underset{\text{ethyl ester of silicic acid}}{Si\,(OC_2H_5)_4} + 4\,H_2O \longrightarrow \underset{\text{silicic acid}}{Si(OH)_4} + \underset{\text{ethyl alcohol}}{4\,C_2H_5OH}$$

hydrolysis of ethyl silicate

Another problem arises, however, because ethyl silicate is rather volatile and, if the hydrolysis is too slow, may evaporate before reacting and no consolidation is achieved.

One way to solve that problem is to add a catalyst to the ester to accelerate hydrolysis; another is to form an oligomer of ethyl silicate by connecting a small number of molecules (about ten) through a partial condensation process; the oligomer does not evaporate and may be used without a catalyst. The technical name of the **monomer** ethyl silicate is **ortho-ethyl silicate** while that of the **oligomer** is **ethyl silicate 40**; both substances are marketed under various trade names (e.g., Silres or Dynasylan), but the number 40 (which is the percentage of solid matter produced by the complete hydrolysis of the liquid oligomer) always appears when the oligomer is involved. A lower number (e.g., ethyl silicate 28) implies that there are less monomer units in the oligomer molecule.

Figure 7.7



$Si(OC_2H_5)_4$

ortho - ethyl silicate *(monomer)*

$C_2H_5O-Si(OC_2H_5)_2-(O-Si(OC_2H_5)_2)_9-OC_2H_5$

ethyl silicate 40 *(oligomer)*

commercial types of ethyl silicate

Ethyl silicate had been synthesized already in the nineteenth century, but only in 1928 did A. P. Laurie publish a paper on its use as a stone consolidant. It still took about thirty years more and the experiments of Czech and German chemists to introduce it stably in stone conservation practice. The type initially most used was the monomer, ortho-ethyl silicate, but now there is a growing tendency to switch to the oligomer.

It must be remembered, however, that, as in the case of alkaline silicates and fluosilicates, it is unlikely that adhesion will be restored across gaps wider than 0.1 mm.

7.2 Silanes

As silicon can form covalent bonds with hydrogen, just like carbon, some chemists hoped to create a family of molecules based on silicon-silicon and silicon-hydrogen bonds that could be as vast and important as the carbon-carbon and carbon-hydrogen chemistry, i.e., the whole organic chemistry. But the dream could not be realized: the maximum number of silicon atoms that could be lined up was six, and all these compounds were unstable because the silicon-hydrogen bonds react immediately with oxygen and burn when in contact with air.

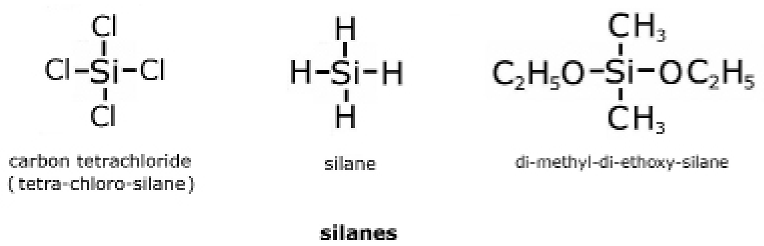
An interesting chemistry based on silicon-carbon bonds yielded instead a series of compounds provided with peculiar and useful properties.

The investigation of this branch of chemistry already had started in the nineteenth century, but the first compounds of practical interest appeared on the market halfway into the twentieth century.

The name **silane** was given to the simplest silicon-hydrogen compound (SiH_4) because of its similarity to the hydrocarbon methane (CH_4); it may be easily synthesized starting from silicon tetrachloride ($SiCl_4$), but it is too unstable to be of practical interest. Starting again from silicon tetrachloride, or even directly from silicon metal in fine powder, it is possible to tie carbon atoms of organic molecules directly to the silicon atom. These molecules are stable and are called **silanes**; they show properties that are typical of many organic materials (e.g., hydrophobic character) besides other ones (e.g., higher resistance to heat), which may be attributed to a partly inorganic character produced by the presence of the silicon atoms.

The reaction of carbon tetrachloride with alcohols also produces molecules that are stable; actually, ethyl silicate is produced in this way. Ethyl silicate might be considered a member of the family of silanes (a tetra-ethoxy-silane), but this would be misleading because ethyl silicate loses all its organic parts (the ethyl groups) when it reacts with water and shows no hydrophobic properties afterwards.

Figure 7.8



$$Cl-\underset{Cl}{\overset{Cl}{Si}}-Cl \qquad H-\underset{H}{\overset{H}{Si}}-H \qquad C_2H_5O-\underset{CH_3}{\overset{CH_3}{Si}}-OC_2H_5$$

In the **silanes**, one or more **organic radicals** (hydrocarbon molecules, less one hydrogen atom) are **attached directly to the silicon atom**, without the interposition of an oxygen atom. The silicon-carbon bond is not affected by any hydrolysis reaction, so **ethoxy silanes** (with one to three ethoxy groups, and three to one organic radicals) remain hydrophobic after hydrolysis.

The names of the organic radicals most frequently used in silane chemistry are listed in the table below.

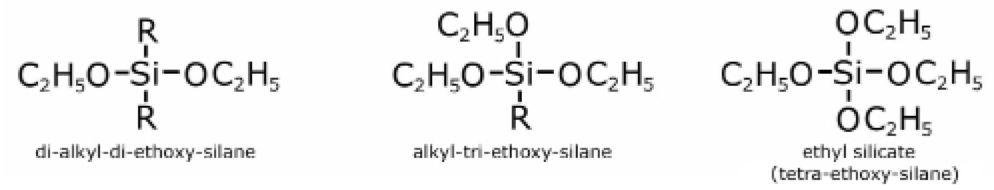
Organic Radicals			
Name	**Formula**	**Name**	**Formula**
methyl	CH_3	butyl	C_4H_9
ethyl	C_2H_5	amyl	C_5H_{11}
propyl	C_3H_7	phenyl*	C_6H_5*

* The phenyl radical is a complete benzene ring, less one hydrogen atom.

When a whole class of compounds is discussed, the radicals listed in the table are frequently represented by the letter **R** in chemical formulas and by the general term **alkyl**, which is applied to the radicals that do not contain a double bond (phenyl is thus excluded, as it belongs to the **aryl** family, of radicals derived from aromatic hydrocarbons).

The silanes used in architectural conservation possess one or two organic radicals attached to the silicon atom, while the remaining positions are occupied by ethoxy (C_2H_5O–) or, in some cases, by methoxide (CH_3O–) groups.

Figure 7.9



$$C_2H_5O-\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}-OC_2H_5$$

di-alkyl-di-ethoxy-silane

$$C_2H_5O-\overset{\displaystyle C_2H_5O}{\underset{\displaystyle R}{Si}}-OC_2H_5$$

alkyl-tri-ethoxy-silane

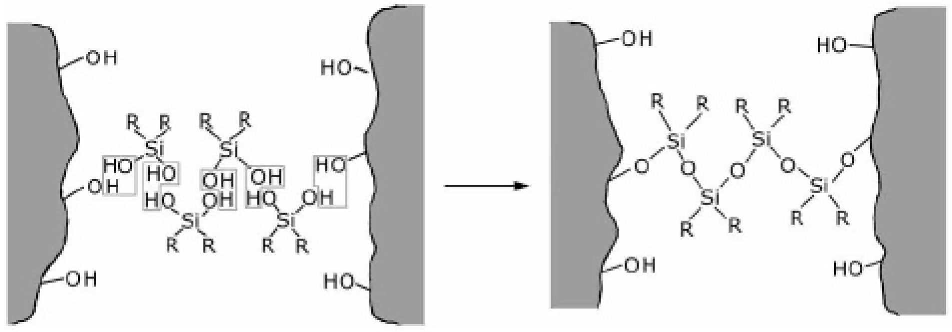
$$C_2H_5O-\overset{\displaystyle OC_2H_5}{\underset{\displaystyle OC_2H_5}{Si}}-OC_2H_5$$

ethyl silicate
(tetra-ethoxy-silane)

silanes used in architectural conservation

The interest for conservation lies in the fact that while the silanes act as consolidants of hydrophilic materials such as ethyl silicate, they also introduce some hydrophobic character into the treated material.

Figure 7.10



silanes can produce consolidation and water repellency

The silanes holding only one radical attached to the silicon atom produce a minor hydrophobic effect and a prevailing consolidating one, while the reverse is true for the silanes with two radicals. A mixture of these is frequently used in commercial products. The hydrophobic action also depends on the dimension of the organic radicals, the more voluminous ones inducing a stronger hydrophobic effect (they are more susceptible to aging by oxidation, however).

As in the case of ethyl silicate, it is unlikely that adhesion will be restored across gaps wider than 0.1 mm.

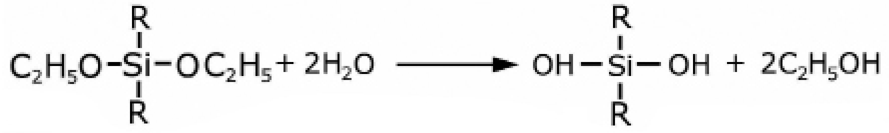
7.3 Silicones

7.3.1 Linear silicones

Silanes containing two radicals and two reactive groups (ethoxy groups or, more frequently in industrial practice, chlorine atoms) may be polymerized by condensation in a two-step reaction to form a linear polymer whose chemical name is **polysiloxane** but is better known as **silicone**.

In the first step, the reactive groups are transformed into hydroxyl groups by hydrolysis.

Figure 7.11

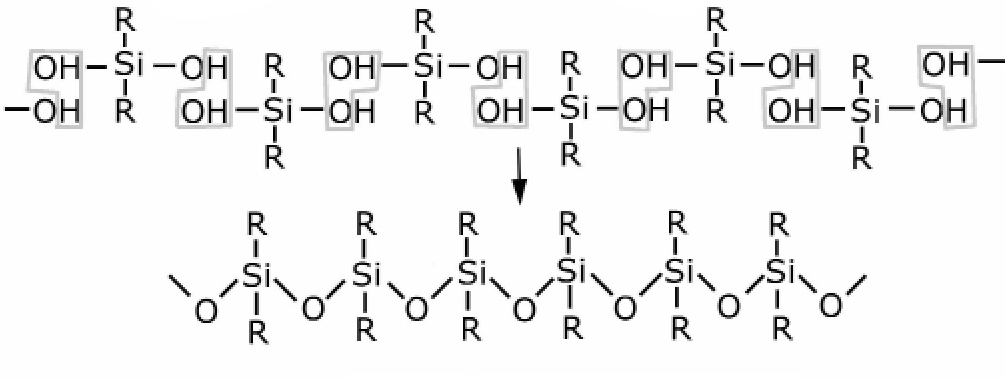


$$C_2H_5O-\overset{R}{\underset{R}{Si}}-OC_2H_5 + 2H_2O \longrightarrow OH-\overset{R}{\underset{R}{Si}}-OH + 2C_2H_5OH$$

synthesis of silicones, step 1

The linear polymer is formed in the second step by a poly-condensation reaction.

Figure 7.12



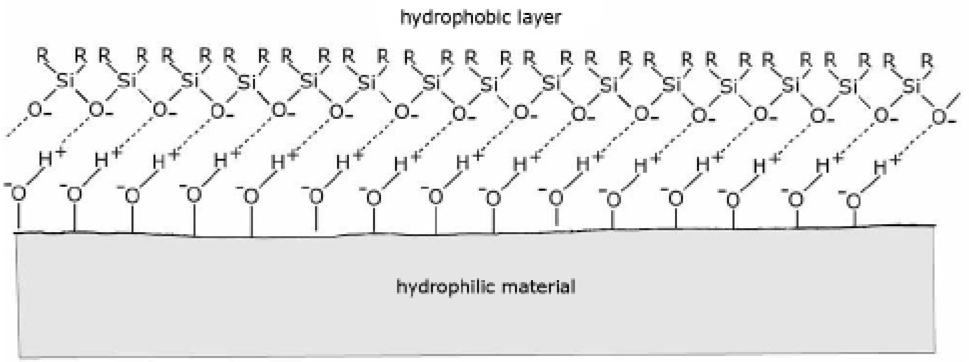
synthesis of silicones, step 2

The number of connected units is not very high, between 50 and 200, so the polymers are not solids but more or less viscous liquids.

Silicones are quite different from the other synthetic polymers because the **backbone** of the long molecule is not a chain of carbon atoms but a **sequence of silicon-oxygen bonds** whose chemical name is **polysiloxane**. As a consequence, the fundamental structure of the silicones is inorganic and rather polar while the side chains are organic and non-polar.

The inorganic backbone ensures a good resistance to heat up to 200°C, and its polar character provides electrical attraction forces that allow the molecules to adhere to the surface of hydrophilic materials.

Figure 7.13



silicone molecule on a hydrophilic surface

When a silicone molecule is tied to a polar surface, all the organic, non-polar side chains are forced to line up on the other side, facing air; as a consequence, a solution of silicone molecules applied on a hydrophilic material creates a water-repellent coating.

The minimal thickness of the coating produces no optical effect; actually, the presence of a silicone on a surface is detectable only when some water is poured over it because the treated area remains dry.

Actually, the hydrophobic layer is not a continuous film but rather a sort of microscopic network; liquid water drops are unable to penetrate it, but single water molecules (i.e., water vapor) can, thus allowing a wet material to dry through the film without excessive interference.

The permeability to water vapor of a silicone-treated stone is about 50% of that of the untreated material. This is normally considered a positive quality because, as architects often say, silicones allow stones "to breathe," meaning that silicones avoid the danger of accumulation of water behind an impervious film, e.g., by internal condensation of water vapor in cold climates.

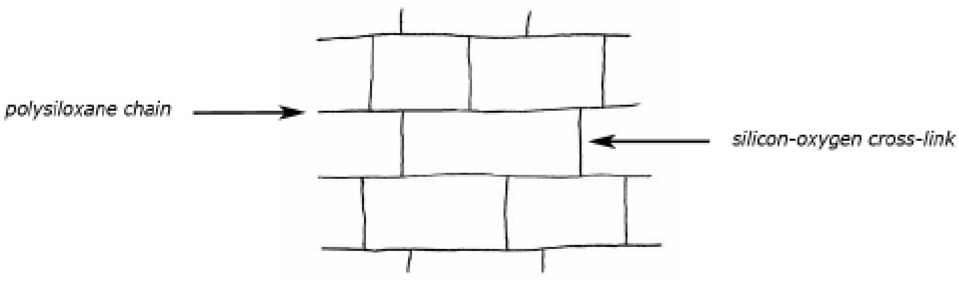
Permeability to gases, however, becomes a negative factor when stone must be protected against acid gases present in the atmosphere as single molecules are allowed to reach the surface of reactive materials (e.g., calcareous stones). In general, silicones, as protective films in polluted atmospheres, perform far better over siliceous stones than over calcareous ones (e.g., white marble).

7.3.2 Cross-linked silicones

Cross-linked polymers based on the polysiloxane chain may be prepared by adding to the bi-functional monomer, which would form a linear chain if polymerized alone, a controlled amount of another monomer provided with three reactive points.

Silicone resins are synthesized in this way, e.g., starting from a mix of some tri-ethoxy- (or tri-chloro-) silane with di-ethoxy- (or di-chloro-) silane. The amount of cross-linking that is obtained depends upon the proportions of the two components.

Figure 7.14



rigid cross-links in silicone resins

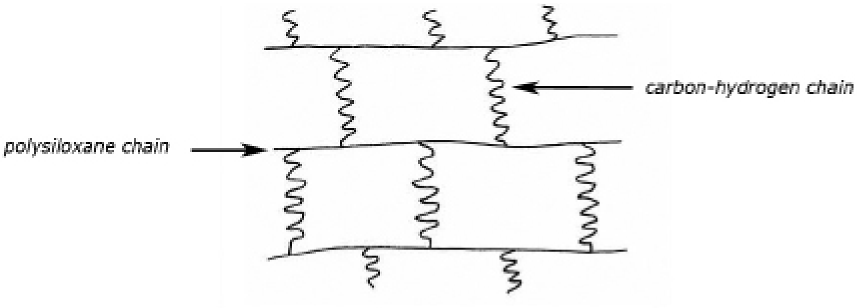
Cross-links thus formed are made of rigid silicon-oxygen bonds; therefore, as their number increases, the resulting polymer becomes stiffer and less flexible.

A different kind of cross-link is created to synthesize **silicone rubbers**. The synthesis is done in two steps: a linear polymer is prepared first, including in the monomer mix some silanes that contain double bonds in the organic radicals attached to the silicon atoms.

After the polymerization by poly-condensation, the double bonds are still present in the long molecules and the linear polymer, blended with appropriate fillers, is marketed together with a catalyst that can activate the double bonds.

The second step is carried out by the users, who mix the components in the right proportion; a reaction of polymerization by addition (see section 6.4.1.1) then follows and produces the rubber-like material. The cross-links are formed by flexible chains of carbon-hydrogen groups that allow a very large elastic deformation, acting like springs between the long chains of the polymer.

Figure 7.15



flexible cross-links in silicone rubber

7.3.3 Aging of silicones

The organic radicals undergo an oxidation reaction (see chapter 6.6) when silicones are exposed to air and light; this results in the progressive loss of the hydrophobic property of the very thin layers that are applied on the surface of hydrophilic materials.

As a consequence, the service life of silicones as hydrophobic protective agents is limited, five to ten years being estimated now for the best commercial types. Impurities in the polymers, or even in the solvents used for their application, may even accelerate the loss of hydrophobicity and cause discoloration (which normally is rather light).

The large organic radicals (e.g., amyl or phenyl) initially produce the best hydrophobic properties, but the smallest ones (methyl groups) show a better resistance to oxidation.

The recent introduction of fluorine atoms in the organic radicals of silicones is aimed at increasing the resistance to oxidation, but it is not yet possible to assess the actual improvement of service life that is thus achieved.

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