Corrosion Engineering

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Chapter 1

Corrosion

Corrosion is the disintegration of an engineered material into its constituent atoms due to chemical reactions with its surroundings. In the most common use of the word, this means electrochemical oxidation of metals in reaction with an oxidant such as oxygen. Formation of an oxide of iron due to oxidation of the iron atoms in solid solution is a well-known example of electrochemical corrosion, commonly known as rusting. This type of damage typically produces oxide(s) and/or salt(s) of the original metal. Corrosion can also refer to other materials than metals, such as ceramics or polymers, although in this context, the term degradation is more common.

In other words, corrosion is the wearing away of metals due to a chemical reaction.

Many structural alloys corrode merely from exposure to moisture in the air, but the process can be strongly affected by exposure to certain substances (see below). Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate-conversion, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable.

Rust, the most familiar example of corrosion.

Volcanic gases have sped the corrosion of this abandoned mining machinery.

Corrosion on exposed metal.

Galvanic corrosion

Galvanic corrosion occurs when two different metals electrically contact each other and are immersed in an electrolyte. In order for galvanic corrosion to occur, an electrically conductive path and an ionically conductive path are necessary. This effects a galvanic couple where the more active metal corrodes at an accelerated rate and the more noble metal corrodes at a retarded rate. When immersed, neither metal would normally corrode as quickly without the electrically conductive connection (usually via a wire or direct contact). Galvanic corrosion is often utilized in sacrificial anodes. What type of metal(s) to use is readily determined by following the galvanic series. For example, zinc is often used as a sacrificial anode for steel structures, such as pipelines or docked naval ships. Galvanic corrosion is of major interest to the marine industry and also anywhere water can contact pipes or metal structures.

Factors such as relative size of anode (smaller is generally less desirable), types of metal, and operating conditions (temperature, humidity, salinity, etc.) will affect galvanic corrosion. The surface area ratio of the anode and cathode will directly affect the corrosion rates of the materials.

Galvanic series

In a given sea environment (one standard medium is aerated, room-temperature seawater), one metal will be either more *noble* or more *active* than the next, based on how strongly its ions are bound to the surface. Two metals in electrical contact share the same electrons, so that the tug-of-war at each surface is translated into a competition for free electrons between the two materials. The noble metal will tend to take electrons from the active one, while the electrolyte hosts a flow of ions in the same direction. The resulting mass flow or electrical current can be measured to establish a hierarchy of materials in the medium of interest. This hierarchy is called a *galvanic series*, and can be a very useful in predicting and understanding corrosion.

Resistance to corrosion

Some metals are more intrinsically resistant to corrosion than others, either due to the fundamental nature of the electrochemical processes involved or due to the details of how reaction products form. If a more susceptible material is used, many techniques can be applied during an item's manufacture and use to protect its materials from damage.

Intrinsic chemistry

Gold nuggets do not naturally corrode, even on a geological time scale.

The materials most resistant to corrosion are those for which corrosion is thermodynamically unfavorable. Any corrosion products of gold or platinum tend to decompose spontaneously into pure metal, which is why these elements can be found in metallic form on Earth, and is a large part of their intrinsic value. More common "base" metals can only be protected by more temporary means.

Some metals have naturally slow reaction kinetics, even though their corrosion is thermodynamically favorable. These include such metals as zinc, magnesium, and cadmium. While corrosion of these metals is continuous and ongoing, it happens at an acceptably slow rate. An extreme example is graphite, which releases large amounts of energy upon oxidation, but has such slow kinetics that it is effectively immune to electrochemical corrosion under normal conditions.

Passivation

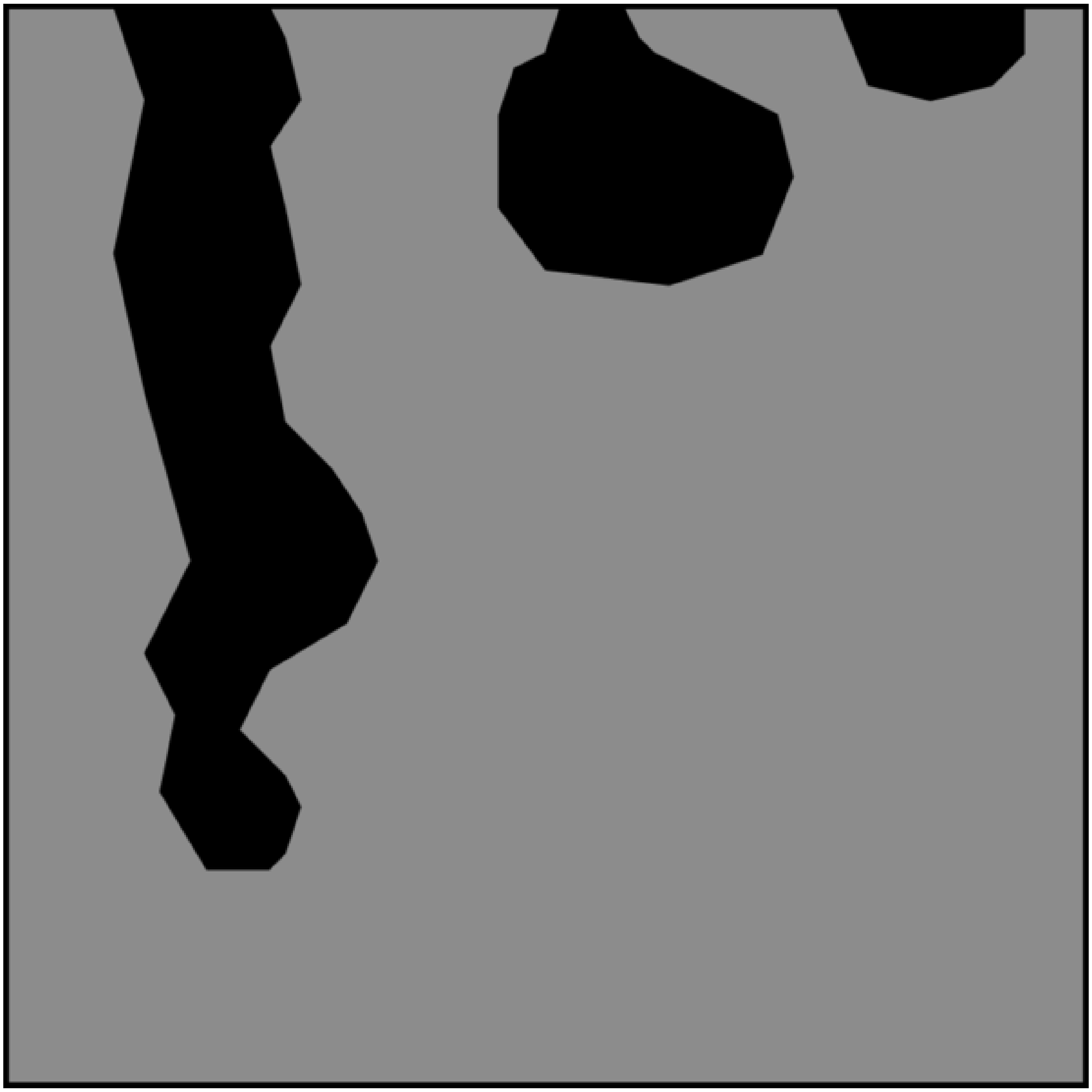
Given the right conditions, a thin film of corrosion products can form on a metal's surface spontaneously, acting as a barrier to further oxidation. When this layer stops growing at less than a micrometre thick under the conditions that a material will be used in, the phenomenon is known as passivation (rust, for example, usually grows to be much thicker, and so is not considered passivation, because this mixed oxidized layer is not protective). While this effect is in some sense a property of the material, it serves as an indirect kinetic barrier: the reaction is often quite rapid unless and until an impermeable layer forms. Passivation in air and water at moderate pH is seen in such materials as aluminium, stainless steel, titanium, and silicon.

These conditions required for passivation are specific to the material. The effect of pH is recorded using Pourbaix diagrams, but many other factors are influential. Some conditions that inhibit passivation include: high pH for aluminium, low pH or the presence of chloride ions for stainless steel, high temperature for titanium (in which case the oxide dissolves into the metal, rather than the electrolyte) and fluoride ions for silicon. On the other hand, sometimes unusual conditions can bring on passivation in materials that are normally unprotected, as the alkaline environment of concrete does for steel rebar. Exposure to a liquid metal such as mercury or hot solder can often circumvent passivation mechanisms.

Corrosion in passivated materials

Passivation is extremely useful in alleviating corrosion damage, but care must be taken not to trust it too thoroughly. Even a high-quality alloy will corrode if its ability to form a passivating film is hindered. Because the resulting modes of corrosion are more exotic and their immediate results are less visible than rust and other bulk corrosion, they often escape notice and cause problems among those who are not familiar with them.

Pitting corrosion



The scheme of pitting corrosion

Certain conditions, such as low concentrations of oxygen or high concentrations of species such as chloride which compete as anions, can interfere with a given alloy's ability to re-form a passivating film. In the worst case, almost all of the surface will remain protected, but tiny local fluctuations will degrade the oxide film in a few critical points. Corrosion at these points will be greatly amplified, and can cause *corrosion pits* of several types, depending upon conditions. While the corrosion pits only nucleate under fairly extreme circumstances, they can continue to grow even when conditions return to normal, since the interior of a pit is naturally deprived of oxygen and locally the pH decreases to very low values and the corrosion rate increases due to an auto-catalytic process. In extreme cases, the sharp tips of extremely long and narrow corrosion pits can cause stress concentration to the point that otherwise tough alloys can shatter; a thin film pierced by an invisibly small hole can hide a thumb sized pit from view. These problems are especially dangerous because they are difficult to detect before a part or structure fails. Pitting remains among the most common and damaging forms of corrosion in passivated alloys, but it can be prevented by control of the alloy's environment.

Weld decay and knifeline attack

Stainless steel can pose special corrosion challenges, since its passivating behavior relies on the presence of a minor alloying component (Chromium, typically only 18%). Due to the elevated temperatures of welding or during improper heat treatment, chromium carbides can form in the grain boundaries of stainless alloys. This chemical reaction robs the material of chromium in the zone near the grain boundary, making those areas much less resistant to corrosion. This creates a galvanic couple with the well-protected alloy nearby, which leads to *weld decay* (corrosion of the grain boundaries near welds) in highly corrosive environments. Special alloys, either with low carbon content or with added carbon "getters" such as titanium and niobium (in types 321 and 347, respectively), can prevent this effect, but the latter require special heat treatment after welding to prevent the similar phenomenon of *knifeline attack*. As its name applies, this is limited to a small zone, often only a few micrometres across, which causes it to proceed more rapidly. This zone is very near the weld, making it even less noticeable[1].

Crevice corrosion

Crevice corrosion is a localized form of corrosion occurring in spaces to which the access of the working fluid from the environment is limited and a concentration cell, areas with different oxygen concentration, will take place with consequent high corrosion rate . These spaces are generally called crevices. Examples of crevices are gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, spaces filled with deposits and under sludge piles.

Microbial corrosion

Microbial corrosion, or bacterial corrosion, is a corrosion caused or promoted by microorganisms, usually chemoautotrophs. It can apply to both metals and non-metallic materials, in both the presence and lack of oxygen. Sulfate-reducing bacteria are common in lack of oxygen; they produce hydrogen sulfide, causing sulfide stress cracking. In presence of oxygen, some bacteria directly oxidize iron to iron oxides and hydroxides, other bacteria oxidize sulfur and produce sulfuric acid causing biogenic sulfide corrosion. Concentration cells can form in the deposits of corrosion products, causing and enhancing galvanic corrosion.

Accelerated Low Water Corrosion (ALWC) is a particularly aggressive form of MIC that affects steel piles in seawater near the low water tide mark. It is characterised by an orange sludge, which smells of Hydrogen Sulphide when treated with acid. Corrosion rates can be very high and design corrosion allowances can soon be exceeded leading to premature failure of the steel pile. Piles that have been coating and have cathodic protection installed at the time of construction are not susceptible to ALWC. For unprotected piles, sacrificial anodes can be installed local to the affected areas to inhibit the corrosion or a complete retrofitted sacrificial anode system can be installed. Affected areas can also be treated electrochemically by using an electrode to first produce chlorine to kill the bacteria, and then to produced a calcareous deposit, which will help shield the metal from further attack.

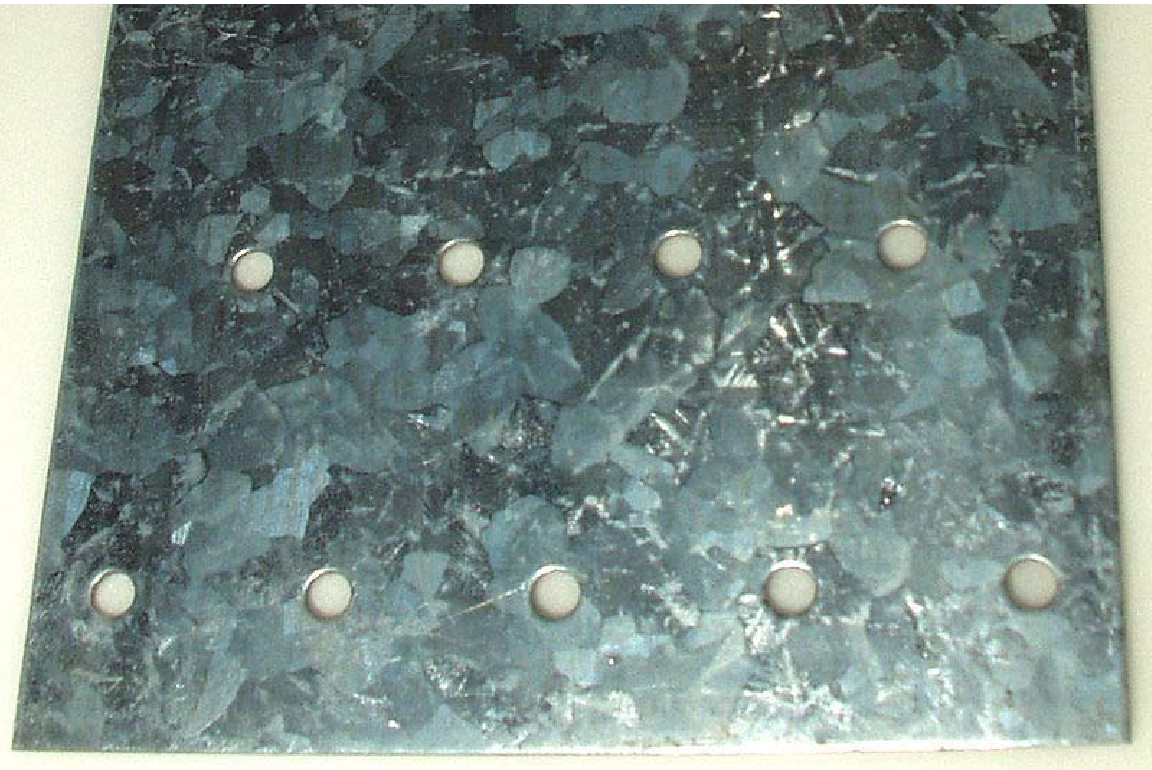
High temperature corrosion

High temperature corrosion is chemical deterioration of a material (typically a metal) under very high temperature conditions. This non-galvanic form of corrosion can occur when a metal is subject to a high temperature atmosphere containing oxygen, sulfur or other compounds capable of oxidising (or assisting the oxidation of) the material concerned. For example, materials used in aerospace, power generation and even in car engines have to resist sustained periods at high temperature in which they may be exposed to an atmosphere containing potentially highly corrosive products of combustion.

The products of high temperature corrosion can potentially be turned to the advantage of the engineer. The formation of oxides on stainless steels, for example, can provide a protective layer preventing further atmospheric attack, allowing for a material to be used for sustained periods at both room and high temperature in hostile conditions. Such high temperature corrosion products in the form of compacted oxide layer glazes have also been shown to prevent or reduce wear during high temperature sliding contact of metallic (or metallic and ceramic) surfaces.

Methods of protection from corrosion

Surface treatments



Galvanized surface

Applied coatings

Plating, painting, and the application of enamel are the most common anti-corrosion treatments. They work by providing a barrier of corrosion-resistant material between the damaging environment and the (often cheaper, tougher, and/or easier-to-process) structural material. Aside from cosmetic and manufacturing issues, there are tradeoffs in mechanical flexibility versus resistance to abrasion and high temperature. Platings usually fail only in small sections, and if the plating is more noble than the substrate (for example, chromium on steel), a galvanic couple will cause any exposed area to corrode much more rapidly than an unplated surface would. For this reason, it is often wise to plate with a more active metal such as zinc or cadmium. Painting either by roller or brush is more desirable for tight spaces; spray would be better for larger coating areas such as steel decks and waterfront applications. Flexible polyurethane coatings, like Durabak-M26 for example, can provide an anti-corrosive seal with a highly durable slip resistant membrane. Painted coatings are relatively easy to apply and have fast drying times although temperature and humidity may cause dry times to vary.

Reactive coatings

If the environment is controlled (especially in recirculating systems), corrosion inhibitors can often be added to it. These form an electrically insulating and/or chemically impermeable coating on exposed metal surfaces, to suppress electrochemical reactions. Such methods obviously make the system less sensitive to scratches or defects in the coating, since extra inhibitors can be made available wherever metal becomes exposed. Chemicals that inhibit corrosion include some of the salts in hard water (Roman water systems are famous for their mineral deposits), chromates, phosphates, polyaniline, other conducting polymers and a wide range of specially-designed chemicals that resemble surfactants (i.e. long-chain organic molecules with ionic end groups).

This figure-8 descender is annodized with a yellow finish. Climbing equipment is available in a wide range of anodized colors.

Anodization

Aluminium alloys often undergo a surface treatment. Electrochemical conditions in the bath are carefully adjusted so that uniform pores several nanometers wide appear in the metal's oxide film. These pores allow the oxide to grow much thicker than passivating conditions would allow. At the end of the treatment, the pores are allowed to seal, forming a harder-than-usual surface layer. If this coating is scratched, normal passivation processes take over to protect the damaged area. Anodizing is very resilient to weathering and corrosion, so it is commonly used for building facades and other areas that the surface will come into regular contact with the elements. Whilst being resilient, it must be cleaned frequently. If left without cleaning Panel Edge Staining will naturally occur.

Controlled permeability formwork

Controlled permeability formwork (CPF) is a method of preventing the corrosion of reinforcement by naturally enhancing the durability of the cover during concrete placement, . CPF has been used in environments to combat the effects of carbonation, chlorides, frost and abrasion.

Cathodic protection

Cathodic protection (CP) is a technique to control the corrosion of a metal surface by making that surface the cathode of an electrochemical cell. Cathodic protection systems are most commonly used to protect steel, water, and fuel pipelines and tanks; steel pier piles, ships, and offshore oil platforms.

Sacrificial anode protection

Sacrificial anode in the hull of a ship.

For effective CP, the potential of the steel surface is polarized (pushed) more negative until the metal surface has a uniform potential. With a uniform potential, the driving force for the corrosion reaction is halted. For galvanic CP systems, the anode material corrodes under the influence of the steel, and eventually it must be replaced. The polarization is caused by the current flow from the anode to the cathode, driven by the difference in electrochemical potential between the anode and the cathode.

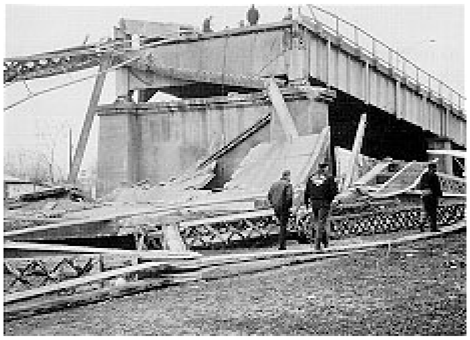
Impressed current cathodic protection

For larger structures, galvanic anodes cannot economically deliver enough current to provide complete protection. Impressed Current Cathodic Protection (ICCP) systems use anodes connected to a DC power source (such as a cathodic protection rectifier). Anodes for ICCP systems are tubular and solid rod shapes of various specialized materials. These include high silicon cast iron, graphite, mixed metal oxide or platinum coated titanium or niobium coated rod and wires.

Anodic protection

Anodic protection impresses anodic current on the structure to be protected (opposite to the cathodic protection). It is appropriate for metals that exhibit passivity (e.g., stainless steel) and suitably small passive current over a wide range of potentials. It is used in aggressive environments, e.g., solutions of sulfuric acid.

Economic impact



The collapsed Silver Bridge, as seen from the Ohio side

The US Federal Highway Administration released a study, entitled *Corrosion Costs and Preventive Strategies in the United States,* in 2002 on the direct costs associated with metallic corrosion in nearly every U.S. industry sector. The study showed that for 1998 the total annual estimated direct cost of corrosion in the U.S. was approximately $276 billion (approximately 3.2% of the US gross domestic product).

Rust is one of the most common causes of bridge accidents. As rust has a much higher volume than the originating mass of iron, its build-up can also cause failure by forcing apart adjacent parts. It was the cause of the collapse of the Mianus river bridge in 1983, when the bearings rusted internally and pushed one corner of the road slab off its support.

Three drivers on the roadway at the time died as the slab fell into the river below. The following NTSB investigation showed that a drain in the road had been blocked for road re-surfacing, and had not been unblocked so that runoff water penetrated the support hangers. It was also difficult for maintenance engineers to see the bearings from the inspection walkway. Rust was also an important factor in the Silver Bridge disaster of 1967 in West Virginia, when a steel suspension bridge collapsed in less than a minute, killing 46 drivers and passengers on the bridge at the time.

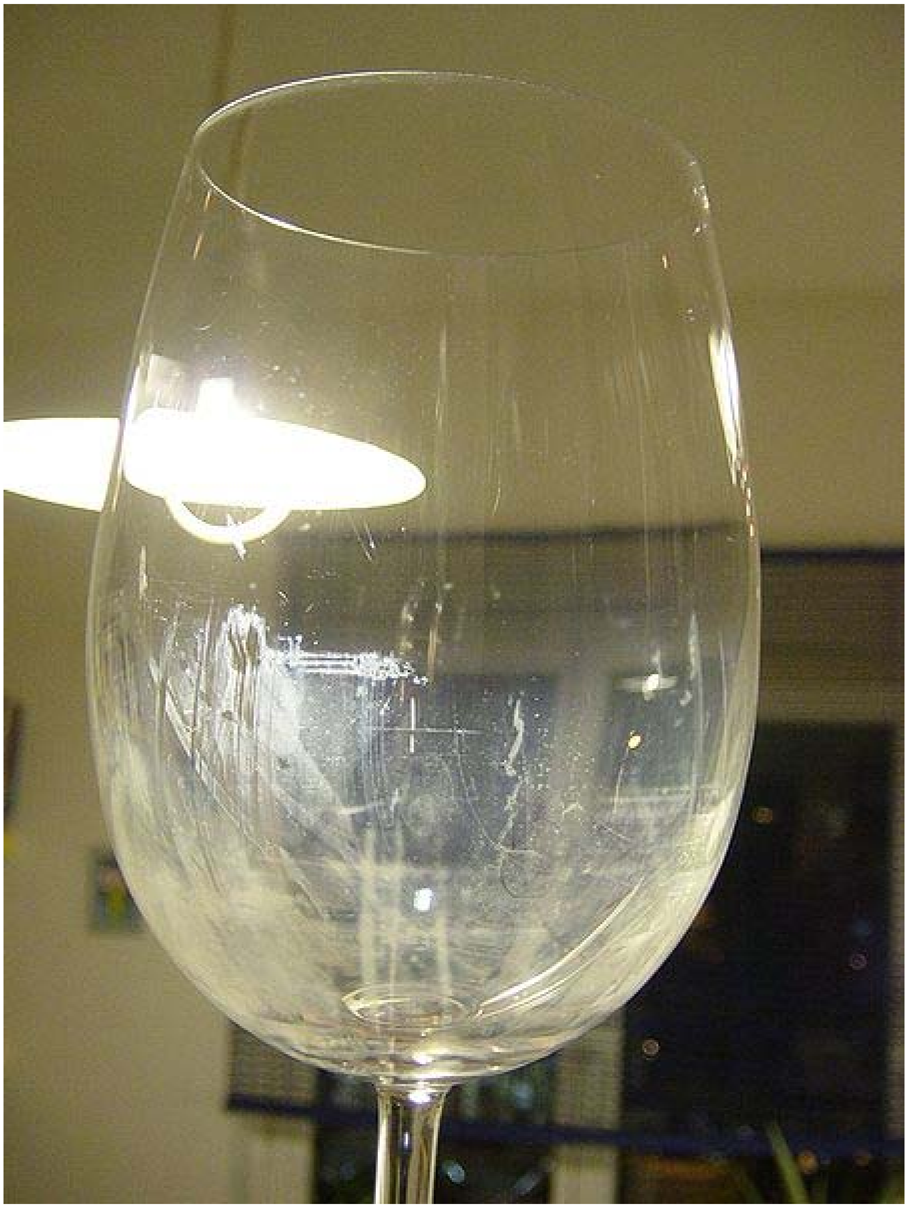
Similarly corrosion of concrete-covered steel and iron can cause the concrete to spall, creating severe structural problems. It is one of the most common failure modes of reinforced concrete bridges. Measuring instruments based on the half-cell potential are able to detect the potential corrosion spots before total failure of the concrete structure is reached.

Corrosion in nonmetals

Most ceramic materials are almost entirely immune to corrosion. The strong ionic and/or covalent bonds that hold them together leave very little free chemical energy in the structure; they can be thought of as already corroded. When corrosion does occur, it is almost always a simple dissolution of the material or chemical reaction, rather than an electrochemical process. A common example of corrosion protection in ceramics is the lime added to soda-lime glass to reduce its solubility in water; though it is not nearly as soluble as pure sodium silicate, normal glass does form sub-microscopic flaws when exposed to moisture. Due to its brittleness, such flaws cause a dramatic reduction in the strength of a glass object during its first few hours at room temperature.

Polymer degradation is due to a wide array of complex and often poorly-understood physiochemical processes. These are strikingly different from the other processes discussed here, and so the term "corrosion" is only applied to them in a loose sense of the word. Because of their large molecular weight, very little entropy can be gained by mixing a given mass of polymer with another substance, making them generally quite difficult to dissolve. While dissolution is a problem in some polymer applications, it is relatively simple to design against. A more common and related problem is *swelling*, where small molecules infiltrate the structure, reducing strength and stiffness and causing a volume change. Conversely, many polymers (notably flexible vinyl) are intentionally swelled with plasticizers, which can be leached out of the structure, causing brittleness or other undesirable changes. The most common form of degradation, however, is a decrease in polymer chain length. Mechanisms which break polymer chains are familiar to biologists because of their effect on DNA: ionizing radiation (most commonly ultraviolet light), free radicals, and oxidizers such as oxygen, ozone, and chlorine. Additives can slow these process very effectively, and can be as simple as a UV-absorbing pigment (i.e., titanium dioxide or carbon black). Plastic shopping bags often do not include these additives so that they break down more easily as litter.

Corrosion of glasses



Glass corrosion

Glass disease is the corrosion of silicate glasses in aqueous solutions. It is governed by two mechanisms: diffusion-controlled leaching (ion exchange) and glass network hydrolytic dissolution. Both corrosion mechanisms strongly depend on the pH of contacting solution: the rate of ion exchange decreases with pH as $10^{-0.5pH}$ whereas the rate of hydrolytic dissolution increases with pH as $10^{0.5pH}$

Mathematically, corrosion rates of glasses are characterised by normalised corrosion rates of elements NR_i (g/cm^2 d) which are determined as the ratio of total amount of released species into the water M_i (g) to the water-contacting surface area S (cm^2), time of contact t (days) and weight fraction content of the element in the glass f_i:

$$NR_i = \frac{M_i}{Sf_it}.$$

The overall corrosion rate is a sum of contributions from both mechanisms (leaching + dissolution) $NR_i=Nrx_i+NRh$. Diffusion-controlled leaching (ion exchange) is characteristic of the initial phase of corrosion and involves replacement of alkali ions in the glass by a hydronium (H_3O^+) ion from the solution. It causes an ion-selective depletion of near surface layers of glasses and gives an inverse square root dependence of corrosion rate with exposure time. The diffusion controlled normalised leaching rate of cations from glasses (g/cm^2 d) is given by:

$$NRx_i = 2\rho\sqrt{\frac{D_i}{\pi t}},$$

where t is time, D_i is the i-th cation effective diffusion coefficient (cm^2/d), which depends on pH of contacting water as $D_i = D_{i0}\cdot 10^{-pH}$, and ρ is the density of the glass (g/cm^3).

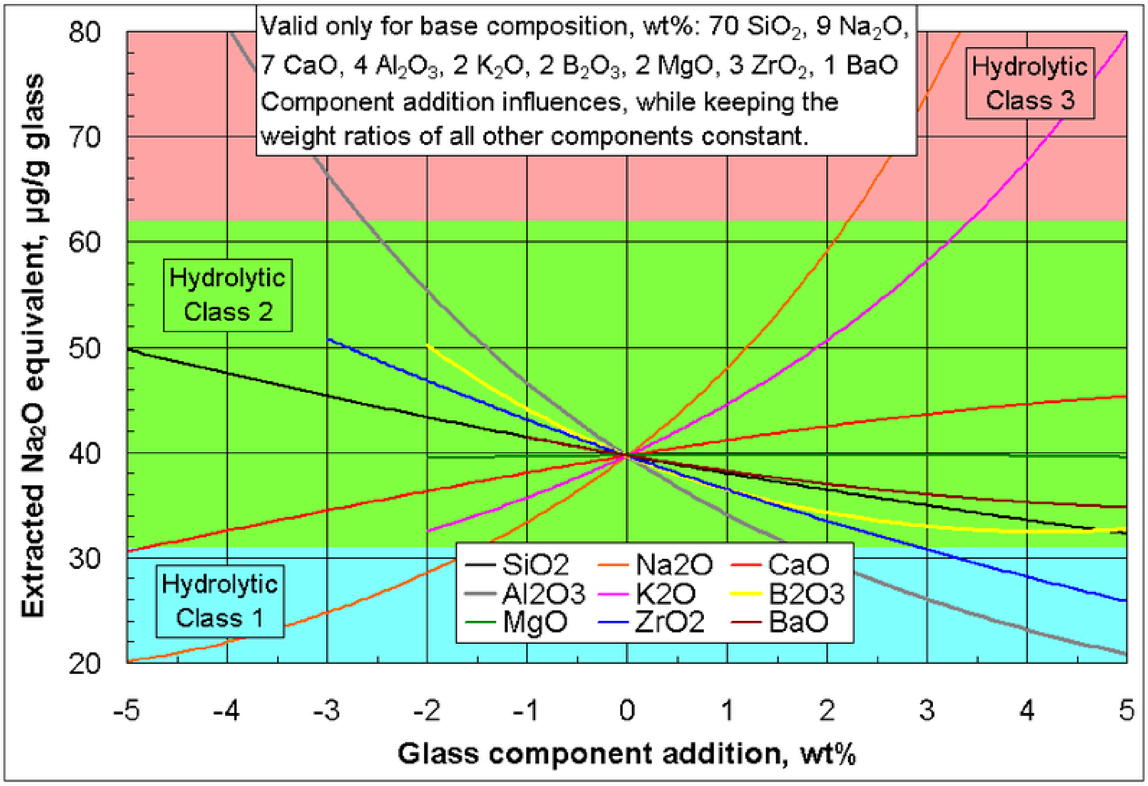
Glass network dissolution is characteristic of the later phases of corrosion and causes a congruent release of ions into the water solution at a time-independent rate in dilute solutions (g/cm^2 d):

$$NRh = \rho r_h,$$

where r_h is the stationary hydrolysis (dissolution) rate of the glass (cm/d). In closed systems the consumption of protons from the aqueous phase increases the pH and causes a fast transition to hydrolysis. However further silica saturation of solution impedes hydrolysis and causes the glass to return to an ion-exchange, e.g. diffusion-controlled regime of corrosion.

In typical natural conditions normalised corrosion rates of silicate glasses are very low and are of the order of 10^{-7} - 10^{-5} g/cm^2 d. The very high durability of silicate glasses in water makes them suitable for hazardous and nuclear waste immobilisation.

Glass corrosion tests



Influences of selected glass component additions on the chemical durability against water corrosion of a specific base glass (corrosion test ISO 719).

There exist numerous standardized procedures for measuring the corrosion (also called **chemical durability**) of glasses in neutral, basic, and acidic environments, under simulated environmental conditions, in simulated body fluid, at high temperature and pressure, and under other conditions.

In the standard procedure ISO 719 a test of the extraction of water soluble basic compounds under neutral conditions is described: 2 g glass, particle size 300-500 µm, is kept for 60 min in 50 ml de-ionized water of grade 2 at 98°C. 25 ml of the obtained solution is titrated against 0.01 mol/l HCl solution. The volume of HCl needed for neutralization is recorded and classified following the values in the table below.

0.01M HCl needed to neutralize extracted basic oxides, ml	**Extracted Na_2O equivalent, µg**	**Hydrolytic class**
to 0.1	to 31	1
above 0.1 to 0.2	above 31 to 62	2
above 0.2 to 0.85	above 62 to 264	3
above 0.85 to 2.0	above 264 to 620	4
above 2.0 to 3.5	above 620 to 1085	5

above 3.5	above 1085	>5

Chapter 2

Corrosion Fatigue

Corrosion fatigue is fatigue in a corrosive environment. It is the mechanical degradation of a material under the joint action of corrosion and cyclic loading. Nearly all engineering structures experience some form of alternating stress and are exposed to harmful environments during their service life. The environment plays a significant role in the fatigue of high strength structural materials like steels, aluminum alloys and titanium alloys. Materials with high specific strength are being developed to meet the requirements of advancing technology. However,their usefulness depends to a large extent on the extent to which they resist corrosion fatigue. Effects of corrosive environments on fatigue behavior of metallic materials have been studied as early as 1930 (1). The phenomenon is not to be confused with stress corrosion cracking, where corrosion such as pitting attack leads to development of brittle cracks, growth and failure. The only requirement is that the sample is under tensile stress.

Effect of corrosion on S-N diagram

Effect of corrosion on smooth specimen S-N diagram is shown schematically in Fig.1. In this figure, curve A shows the fatigue behavior of a material tested in air. A fatigue threshold or limit is seen in A corresponding to the horizontal part of the curve. Curves B and C represent the fatigue behavior of the same material in two corrosive environments. In curve B, the fatigue failure at high stress levels is retarded and the fatigue limit is eliminated. In curve C, the whole curve is shifted to the left indicating a general lowering in the fatigue strength, accelerated initiation at higher stresses and elimination of a fatigue limit. To meet the needs of advancing technology, higher strength materials are developed through heat treatments or alloying. Such higher strength materials generally exhibit higher fatigue limits and thus can be used at higher service stress levels even under fatigue loading. However, presence of corrosive environments during fatigue loading eliminates this stress advantage, as the fatigue limit becomes almost insensitive to the strength level for a particular group of alloys (2). This effect is schematically shown, for the case of several steels, in Fig.2. This figure brings out the debilitating effect of corrosive environments on the functionality of high strength materials under fatigue.

Corrosion fatigue in aqueous media is an electrochemical behavior. Fractures are initiated either by pitting or at persistent slip bands (3). Corrosion fatigue can hence be reduced by alloy additions, inhibition, and cathodic protection all of which reduce pitting (4) Since corrosion fatigue cracks initiate at the metal surface, surface treatments like plating, cladding, nitriding and shot-peening were found to improve the materials' resistance to this phenomenon (5).

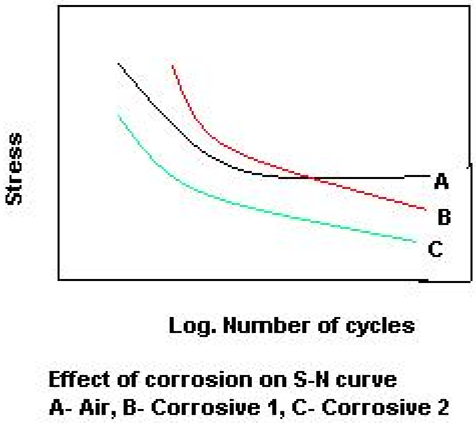


Fig.1 Effect of corrosion on S-N diagram

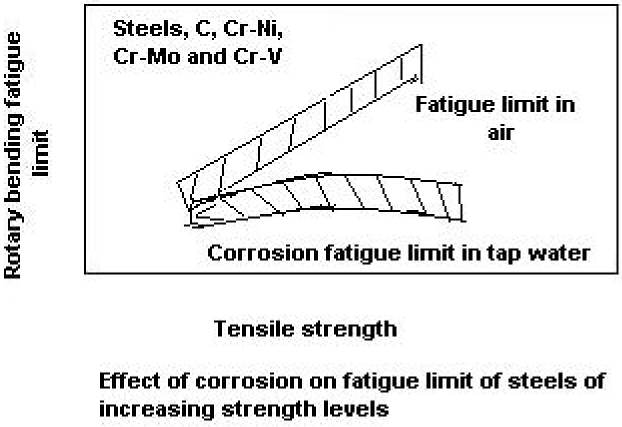


Fig.2 Effect of corrosion on fatigue limits of steels

Crack propagation studies in corrosion fatigue

In normal fatigue testing of smooth specimens, about 90% of the life is spent in crack nucleation and only the remaining 10 % in crack propagation. However,in corrosion fatigue,crack nucleation is facilitated by corrosion and typically about 10 % of life is sufficient for this stage. The rest, 90 % of life is spent in crack propagation. Thus it is much more informative to evaluate the crack propagation behavior during corrosion fatigue. Fracture mechanics uses pre-cracked specimens and effectively measures crack propagation behavior. Hence considerable emphasis is being given to crack propagation velocity measurements using fracture mechanics to study corrosion fatigue. Since fatigue crack grows in a stable fashion below the critical stress intensity factor for fracture (fracture toughness), the process is called sub-critical crack growth. Fig.3 shows a typical fatigue crack growth behavior.

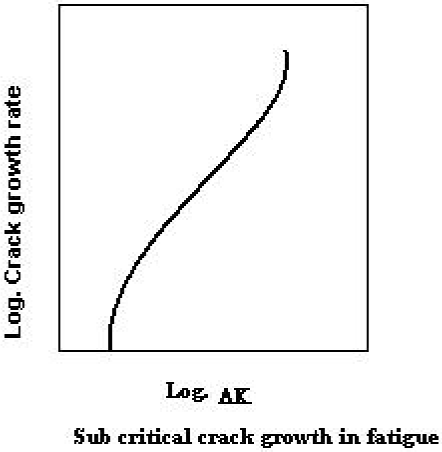


Fig.3. Typical fatigue crack growth behavior(Schematic)

In this log-log plot,the crack propagation velocity is plotted against the applied stress intensity range. Generally there is threshold stress intensity range below which the crack propagation velocity is insignificantly low. Three stages may be visualized in this plot. Near the threshold,crack propagation velocity increases considerably with increasing stress intensity range, a second region where the curve is nearly linear and follows the Paris' law(6), and the third region where crack propagation velocity increases rapidly with stress intensity range leading to fracture at the fracture toughness value.

Crack propagation under corrosion fatigue may be classified in to i) true corrosion fatigue, ii) stress corrosion fatigue and iii) a combination of true, and stress, corrosion fatigues.

True corrosion fatigue

In true corrosion fatigue, the fatigue crack growth rate is enhanced by corrosion and this effect is seen in all the three regions of the fatigue crack growth rate diagram. Fig.4 shows a schematic diagram of crack growth rate under true corrosion fatigue. It is seen from this figure that the whole curve is shifted to lower stress intensity factor range in the corrosive environment. The threshold is lower and the crack growth velocities are higher at all stress intensity factors. The fracture of the specimen occurs when the stress intensity factor range is equal to the applicable threshold stress intensity factor for stress corrosion cracking.

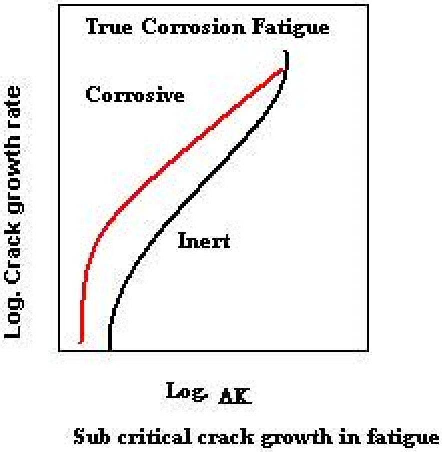


Fig.4 Crack growth behavior under true corrosion fatigue

When attempting to analyze the effects of corrosion fatigue on crack growth in a particular, both corrosion type and fatigue load levels can each affect the crack growth to varying degrees. Common corrosion types include crevice, pitting, filiform, exfoliation, intergranular—each will affect crack growth in a particular material in a distinct way. For instance, pitting corrosion will often be the most damaging type of corrosion, degrading a material's performance (that it, speeds up crack growth rates) more than any of the other kinds of corrosion; even pits the order of a material's grain size can substantially degrade a material. The degree to which corrosion can affect crack growth rates can also be depending on fatigue load levels; for instance, corrosion can cause much greater increase in crack growth rates at low loads than it does at high loads (7).

Stress corrosion fatigue

In materials where the maximum applied stress intensity factor exceeds the stress corrosion cracking threshold value, stress corrosion will also add to the crack growth velocity. This is shown schematically in Fig.5. In the corrosive environment, the crack grows due to cyclic loading at lower stress intensity ranges,but above the threshold stress intensity for scc, additional crack growth (red line) occurs due to stress corrosion cracking. The lower stress intensity regions are not affected and the threshold stress intensity range for fatigue crack propagation is unchanged in the corrosive environment.

In the most general case, corrosion fatigue crack growth may exhibit both of the above effects and the crack growth behavior is represented schematically in Fig.6.

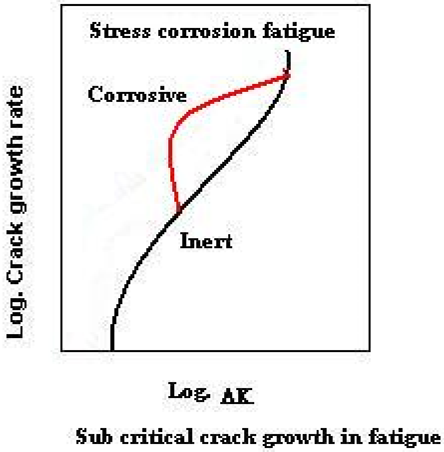


Fig.5 Crack growth behavior under stress corrosion fatigue

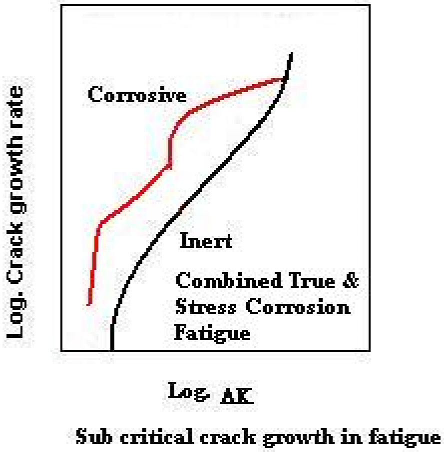


Fig.6. Combined true corrosion fatigue and stress corrosion fatigue.

Chapter 3

Concrete Degradation

Concrete degradation may have various causes. Concrete can be damaged by fire, aggregate expansion, sea water effects, bacterial corrosion, calcium leaching, physical damage and chemical damage (from carbonation, chlorides, sulfates and distilled water). This process adversely affects concrete exposed to these damaging stimuli.

Aggregate expansion

Typical crack pattern associated to the alkali-silica reaction affecting a concrete step barrier on an US motorway (photograph, courtesy of the Federal Highway Administration (US Department of Transportation).

Various types of aggregate undergo chemical reactions in concrete, leading to damaging expansive phenomena. The most common are those containing reactive silica, that can react (in the presence of water) with the alkalis in concrete (K_2O and Na_2O, coming principally from cement). Among the more reactive mineral components of some aggregates are opal, chalcedony, flint and strained quartz. Following the alkali-silica reaction (ASR), an expansive gel forms, that creates extensive cracks and damage on structural members. On the surface of concrete pavements the ASR can cause pop-outs, i.e. the expulsion of small cones (up to 3 cm about in diameter) in correspondence of aggregate particles. When some aggregates containing dolomite are used, a dedolomitization reaction occurs where the magnesium carbonate compound reacts with hydroxyl ions and yields magnesium hydroxide and a carbonate ion. The resulting expansion may cause destruction of the material. Far less common are pop-outs caused by the presence of pyrite, an iron sulfide that generates expansion by forming iron oxide and ettringite. Other reactions and recrystallizations, e.g. hydration of clay minerals in some aggregates, may lead to destructive expansion as well.

Corrosion of reinforcement bars

The expansion of the corrosion products (iron oxides) of carbon steel reinforcement structures may induce mechanical stress that can cause the formation of cracks and disrupt the concrete structure. If the rebars have been poorly installed and are located too close to the concrete surface in contact with the air, spalling can easily occur: flat fragments of concrete are detached from the concrete mass by the rebars corrosion and may fall down.

Chemical damage

Carbonation

Carbonation-initiated deterioration of concrete at Hippodrome Wellington, Belgium.

Carbon dioxide from air can react with the calcium hydroxide in concrete to form calcium carbonate. This process is called carbonation, which is essentially the reversal of the chemical process of calcination of lime taking place in a cement kiln. Carbonation of concrete is a slow and continuous process progressing from the outer surface inward, but slows down with increasing diffusion depth. Carbonation has two effects: it increases mechanical strength of concrete, but it also decreases alkalinity, which is essential for corrosion prevention of the reinforcement steel. Below a pH of 10, the steel's thin layer of surface passivation dissolves and corrosion is promoted. For the latter reason, carbonation is an unwanted process in concrete chemistry. Carbonation can be tested by applying Phenolphthalein solution, a pH indicator, over a fresh fracture surface, which indicates non-carbonated and thus alkaline areas with a violet color.

Chlorides

Chlorides, particularly calcium chloride, have been used to shorten the setting time of concrete. However, calcium chloride and (to a lesser extent) sodium chloride have been shown to leach calcium hydroxide and cause chemical changes in Portland cement, leading to loss of strength, as well as attacking the steel reinforcement present in most concrete.

Sulfates

Sulfates in solution in contact with concrete can cause chemical changes to the cement, which can cause significant microstructural effects leading to the weakening of the cement binder.

Leaching

When water flows through cracks present in concrete, water may dissolve various minerals present in the hardened cement paste or in the aggregates, if the solution is unsaturated with respect to them. Dissolved ions, such as calcium (Ca^{2+}), are leached out and transported in solution on a some distance. If the physico-chemical conditions prevailing in the seeping water evolve with distance along the water path and water becomes supersaturated with respect to certain minerals, they can further precipitate, making deposits or efflorescences inside the cracks, or at the concrete outer surface. This process can cause the self-healing of fractures in particular conditions.

Decalcification

Distilled water can wash out calcium content in concrete, leaving the concrete in brittle condition. A common source of distilled water can be condensed steam. Distilled water leaches out the calcium better because undistilled water contains some calcium ions already, and does not dissolve them.

Sea water

Concrete exposed to seawater is susceptible to its corrosive effects. The effects are more pronounced above the tidal zone than where the concrete is permanently submerged. In the submerged zone, magnesium and hydrogen carbonate ions precipitate a layer of brucite, about 30 micrometers thick, on which a slower deposition of calcium carbonate as aragonite occurs. These layers somewhat protect the concrete from other processes, which include attack by magnesium, chloride and sulfate ions and carbonation. Above the water surface, mechanical damage may occur by erosion by waves themselves or sand and gravel they carry, and by crystallization of salts from water soaking into the concrete pores and then drying up. Pozzolanic cements and cements using more than 60% of slag as aggregate are more resistant to sea water than pure Portland cement. Sea water corrosion contains elements of both chloride and sulfate corrosion.

Bacterial corrosion

Bacteria themselves do not have noticeable effect on concrete. However, anaerobic bacteria (*Thiobacillus*) in untreated sewage tend to produce hydrogen sulfide, which is then oxidized by aerobic bacteria present in biofilm on the concrete surface above the water level to sulfuric acid. The sulfuric acid dissolves the carbonates in the cured cement and causes strength loss, as well as producing sulfates which are harmful to concrete. Concrete floors lying on ground that contains pyrite (iron(II) sulfide) are also at risk. Using limestone as the aggregate makes the concrete more resistant to acids, and the sewage may be pretreated by ways increasing pH or oxidizing or precipitating the sulfides in order to inhibit the activity of sulfide utilizing bacteria.

Physical damage

Damage can occur during the casting and de-shuttering processes. For instance, the corners of beams can be damaged during the removal of shuttering because they are less effectively compacted by means of vibration (improved by using form-vibrators). Other physical damage can be caused by the use of steel shuttering without base plates. The steel shuttering pinches the top surface of a concrete slab due to the weight of the next slab being constructed.

Thermal damage

Due to its low thermal conductivity, a layer of concrete is frequently used for fireproofing of steel structures. However, concrete itself may be damaged by fire.

Up to about 300 °C, the concrete undergoes normal thermal expansion. Above that temperature, shrinkage occurs due to water loss; however, the aggregate continues expanding, which causes internal stresses. Up to about 500 °C, the major structural changes are carbonation and coarsening of pores. At 573 °C, quartz undergoes rapid expansion due to Phase transition, and at 900 °C calcite starts shrinking due to decomposition. At 450-550 °C the cement hydrate decomposes, yielding calcium oxide. Calcium carbonate decomposes at about 600 °C. Rehydration of the calcium oxide on cooling of the structure causes expansion, which can cause damage to material which withstood fire without falling apart. Concrete in buildings that experienced a fire and were left standing for several years shows extensive degree of carbonation from carbon dioxide which is reabsorbed.

Concrete exposed to up to 100 °C is normally considered as healthy. The parts of a concrete structure that is exposed to temperatures above approximately 300 °C (dependent of water/cement ratio) will most likely get a pink color. Over approximately 600 °C the concrete will turn light grey, and over approximately 1000 °C it turns yellow-brown. One rule of thumb is to consider all pink colored concrete as damaged that should be removed.

Fire will expose the concrete to gases and liquids that can be harmful to the concrete, among other salts and acids that occur when gases produced by a fire come into contact with water.

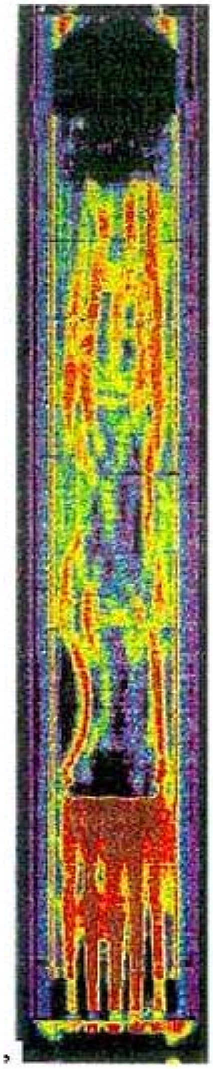
Radiation damages

Exposure of concrete structures to neutrons and gamma radiations in nuclear power plants and high-flux material testing reactor can induce radiation damages in their concrete structures. Paramagnetic defects and optical centers are easily formed, but very high fluxes are necessary to displace a sufficiently high number of atoms in the crystal lattice of minerals present in concrete before significant mechanical damages are observed.

Chapter 4

Behavior of Nuclear Fuel during a Reactor Accident

This is devoted to a discussion of how uranium dioxide nuclear fuel behaves during both normal nuclear reactor operation and under reactor accident conditions such as overheating. Work in this area is often very expensive to conduct, and so has often been performed on a collaborative basis between groups of countries, usually under the aegis of the CSNI.



This is a false colour tomography picture of a bundle (FPT1) of 18 irradiated fuel rods (23 GWd/tU mean burn-up) degraded under steam as part of the PHEBUS set of experiments. The black and blue is for areas of low density while red is an area of high density. It can be seen that the fuel has failed mechanically and has formed a pool near the bottom of the bundle. The bottom of the bundle did not melt.

Swelling

Cladding

Both the fuel can swell and the cladding which covers the fuel to form a fuel pin can be deformed. It is normal to fill the gap between the fuel and the cladding with helium gas to permit better thermal contact between the fuel and the cladding. During use the amount of gas inside the fuel pin can increase because of the formation of noble gases (krypton and xenon) by the fission process. If a Loss-of-coolant accident (LOCA) (e.g. Three Mile Island) or a Reactivity Initiated Accident (RIA) (e.g. Chernobyl or SL-1) occurs then the temperature of this gas can increase. As the fuel pin is sealed the pressure of the gas will increase ($PV = nRT$) and it is possible to deform and burst the cladding. It has been noticed that both corrosion and irradiation can alter the properties of the zirconium alloy commonly used as cladding, making it brittle. As a result the experiments using unirradated zirconium alloy tubes can be misleading.

According to one paper the following difference between the cladding failure mode of unused and used fuel was seen.

Unirradiated fuel rods were pressurized before being placed in a special reactor at the Japanese Nuclear Safety Research Reactor (NSRR) where they were subjected to a simulated RIA transient. These rods failed after ballooning late in the transient when the cladding temperature was high. The failure of the cladding in these tests was ductile, and it was a burst opening.

The used fuel (61 GW days/tonne of uranium) failed early in the transient with a brittle fracture which was a longitudinal crack.

If was found that hydrided zirconium tube is weaker and the bursting pressure is lower.

The common failure process of fuel in the water cooled reactors is a transition to film boiling and subsequent ignition of zirconium cladding in the steam. The effects of the intense hot hydrogen reaction product flow on the fuel pellets and on the bundle's wall well represented on the sidebar picture.

Fuel

The nuclear fuel can swell during use, this is because of effects such as bubble formation in the fuel and the damage which occurs to the lattice of the solid. The swelling of the fuel can impose mechanical stresses upon the cladding which covers the fuel. A document on the subject of the swelling of the fuel can be downloaded from the NASA web site.

Fission gas release

As the fuel is degraded or heated the more volatile fission products which are trapped within the uranium dioxide may become free. For example see.

A report on the release of ^{85}Kr, ^{106}Ru and ^{137}Cs from uranium when air is present has been written. It was found that uranium dioxide was converted to U_3O_8 between about 300 and 500 °C in air. They report that this process requires some time to start, after the induction time the sample gains mass. The authors report that a layer of U_3O_7 was present on the uranium dioxide surface during this induction time. They report that 3 to 8% of the krypton-85 was released, and that much less of the ruthenium (0.5%) and caesium (2.6×10^{-3}%) occurred during the oxidation of the uranium dioxide.

Heat transfer between the cladding and the water

In a water cooled power reactor (or in a water filled used fuel store cooling pond), if a power surge occurs as a result of a reactivity initiated accident, an understanding of the transfer of heat from the surface of the cladding to the water is very useful. In a French study, metal pipe immersed in water (both under typical PWR and pond conditions), was electrically heated to simulate the generation of heat within a fuel pin by nuclear processes. The temperature of the pipe was monitored by thermocouples and for the tests conducted under PWR conditions the water entering the larger pipe (14.2 mm diameter) holding the test metal pipe (9.5 mm outside diameter and 600 mm long) was at 280 ^{o}C and 15 MPa. The water was flowing past the inner pipe at *circa* 4 ms^{-1} and the cladding was subjected to heating at 2200 to 4900 °C s^{-1} to simulate an RIA. It was found that as the temperature of the cladding increased the rate of heat transfer from the surface of the cladding increased at first as the water boiled at nucleation sites. When the heat flux is greater than the critical heat flux a boiling crisis occurs. This occurs as the temperature of the fuel cladding surface increases so that the surface of the metal was too hot (surface dries out) for nucleation boiling. When the surface dries out the rate of heat transfer decreases, after a further increase in the temperature of the metal surface the boiling resumes but it is now film boiling.

Corrosion and other changes to materials in the reactor

Corrosion on the inside of the cladding

Zirconium alloys can undergo stress corrosion cracking when exposed to iodine, the iodine is formed as a fission product which depending on the nature of the fuel can escape from the pellet. It has been shown that iodine causes the rate of cracking in pressurised zircaloy-4 tubing to increase.

Graphite moderated reactors

In the cases of carbon dioxide cooled graphite moderated reactors such as magnox and AGR power reactors an important corrosion reaction is the reaction of a molecule of carbon dioxide with graphite (carbon) to form two molecules of carbon monoxide. This is one of the processes which limits the working life of this type of reactor.

Water cooled reactors

Corrosion

In an water cooled reactor the action of radiation on the water (radiolysis) forms hydrogen peroxide and oxygen. These can cause stress corrosion cracking of metal parts which include fuel cladding and other pipework. To mitigate this hydrazine and hydrogen are injected into a BWR or PWR primary cooling circuit as corrosion inhibitors to adjust the redox properties of the system. A review of recent developments on this topic has been published.

Thermal stresses upon quenching

In a loss-of-coolant accident (LOCA) it is thought that the surface of the cladding could reach a temperature between 800 and 1400 K, and the cladding will be exposed to steam for some time before water is reintroduced into the reactor to cool the fuel. During this time when the hot cladding is exposed to steam some oxidation of the zirconium will occur to form a zirconium oxide which is more zirconium rich than zirconia. This Zr(O) phase is the α-phase, further oxidation forms zirconia. The longer the cladding is exposed to steam the less ductile it will be. One measure of the ductility is to compress a ring along a diameter (at a constant rate of displacement, in this case 2 mm min^{-1}) until the first crack occurs, then the ring will start to fail. The elongation which occurs between when the maximum force is applied and when the mechanical load is declined to 80% of the load required to induce the first crack is the $L_{0.8}$ value in mm. The more ductile a sample is the greater this $L_{0.8}$ value will be.

In one experiment the zirconium is heated in steam to 1473 K, the sample is slowly cooled in steam to 1173 K before being quenched in water. As the heating time at 1473 K is increased the zirconium becomes more brittle and the $L_{0.8}$ value declines.

Aging of steels

Irradiation causes the properties of steels to become poorer, for instance SS316 becomes less ductile and less tough. Also creep and stress corrosion cracking become worse. Papers on this effect continue to be published.

Cracking and overheating of the fuel

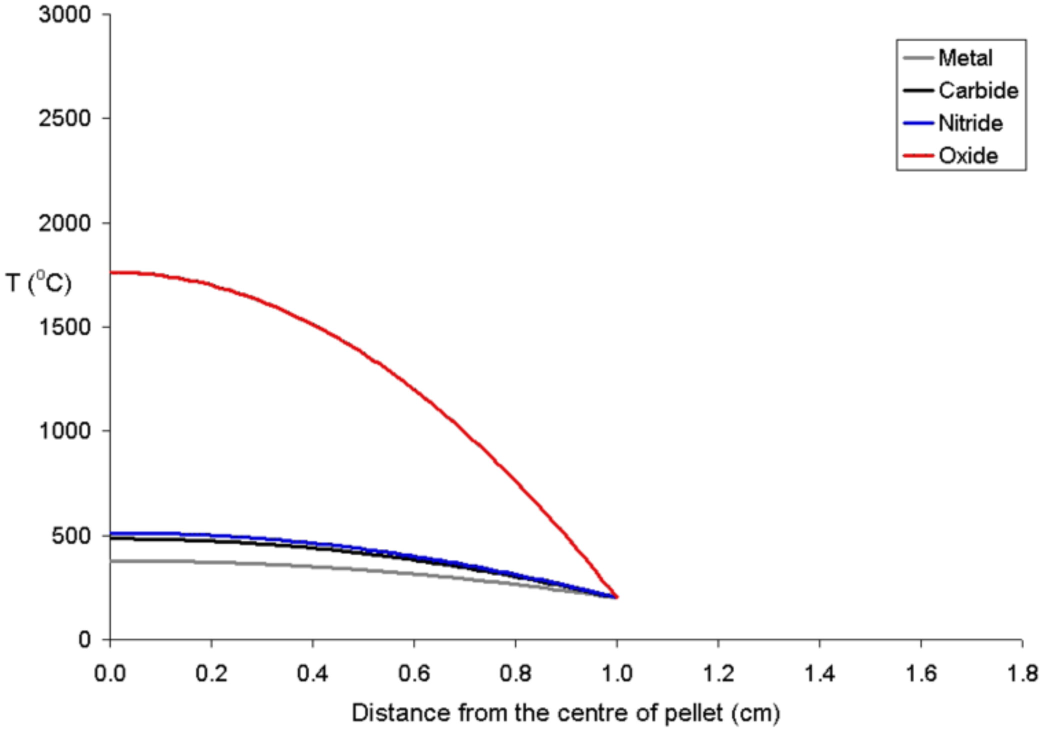
This is due to the fact that as the fuel expands on heating, the core of the pellet expands more than the rim. Because of the thermal stress thus formed the fuel cracks, the cracks tend to go from the center to the edge in a star shaped pattern. A PhD thesis on the subject has been published by a student at the Royal Institute of Technology in Stockholm (Sweden).

The cracking of the fuel has an effect on the release of radioactivity from fuel both under accident conditions and also when the spent fuel is used as the final disposal form. The cracking increases the surface area of the fuel which increases the rate at which fission products can leave the fuel.

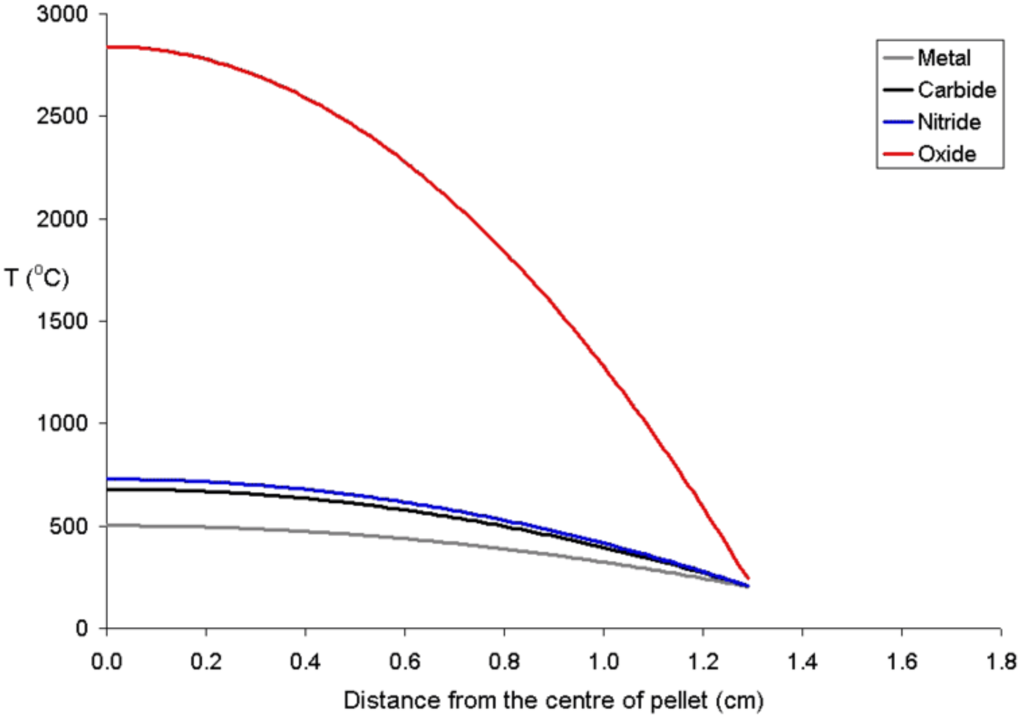
The temperature of the fuel varies as a function of the distance from the center to the rim. At distance x from the center the temperature (T_x) is described by the equation where ρ is the power density ($W\ m^{-3}$) and K_f is the thermal conductivity.

$$T_x = T_{Rim} + \rho\,(r_{pellet}^2 - x^2)\,(4\,K_f)^{-1}$$

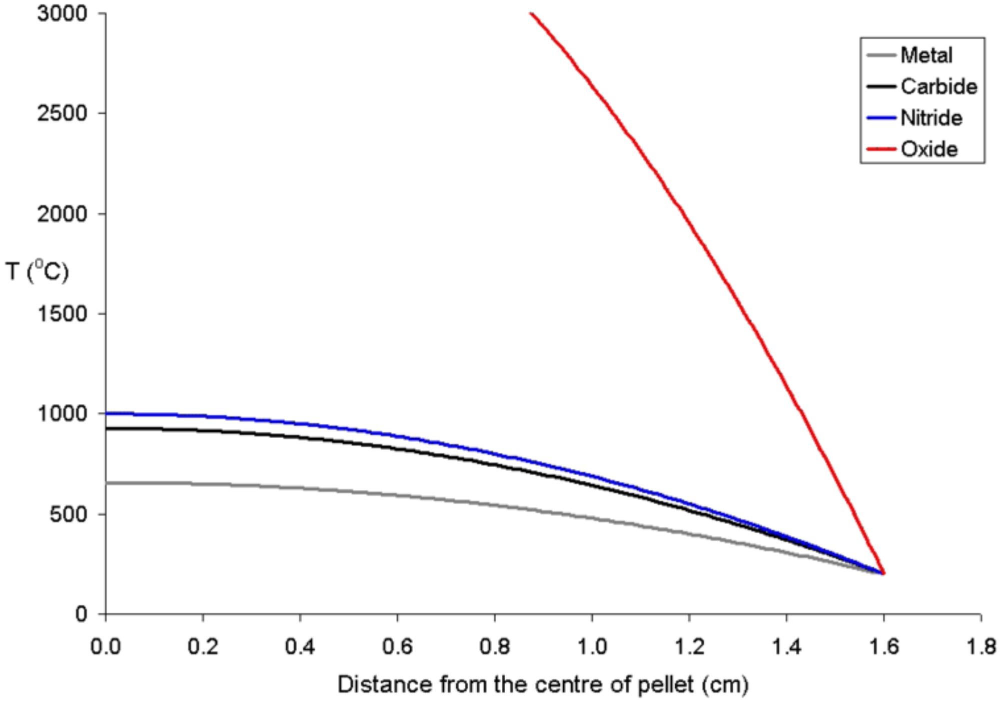
To explain this a for a series of fuel pellets being used with a rim temperature of 200 °C (typical for a BWR) with different diameters and power densities of 250 Wm^{-3} have been modeled using the above equation. These fuel pellets are rather large; it is normal to use oxide pellets which are about 10 mm in diameter.



Temperature profile for a 20 mm diameter fuel pellet with a power density of 250 W per cubic meter. The central temperature is very different for the different fuel solids.

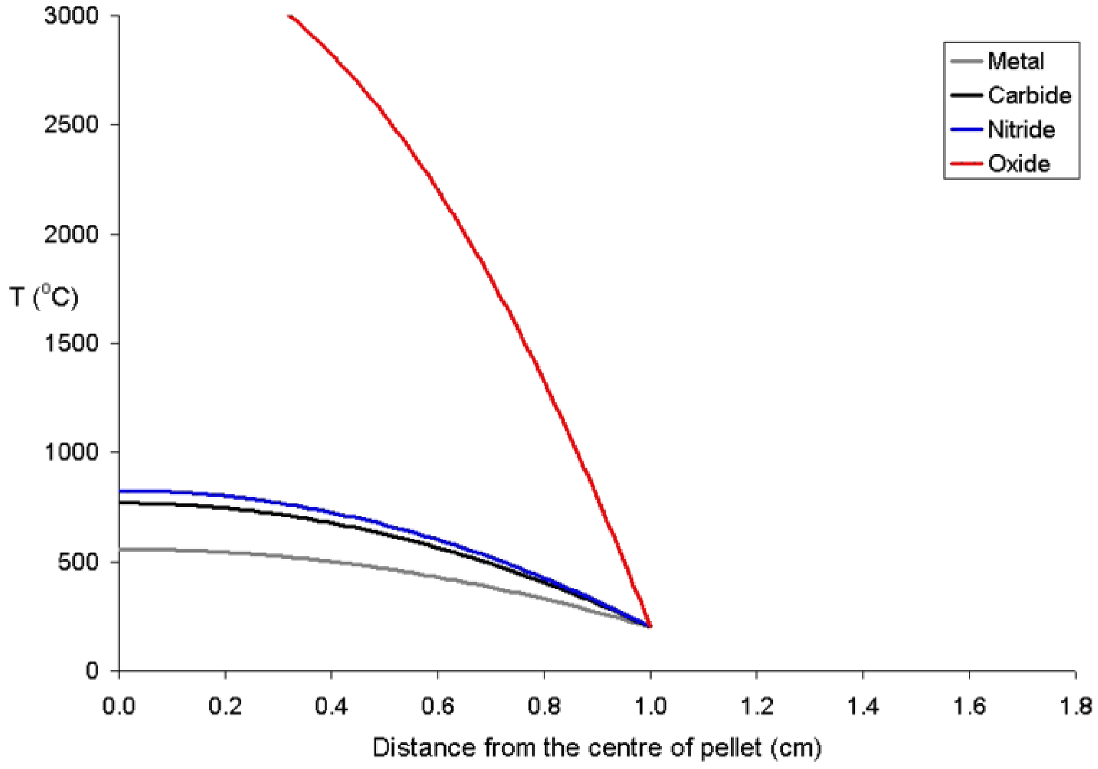


Temperature profile for a 26 mm diameter fuel pellet with a power density of 250 W per cubic meter.

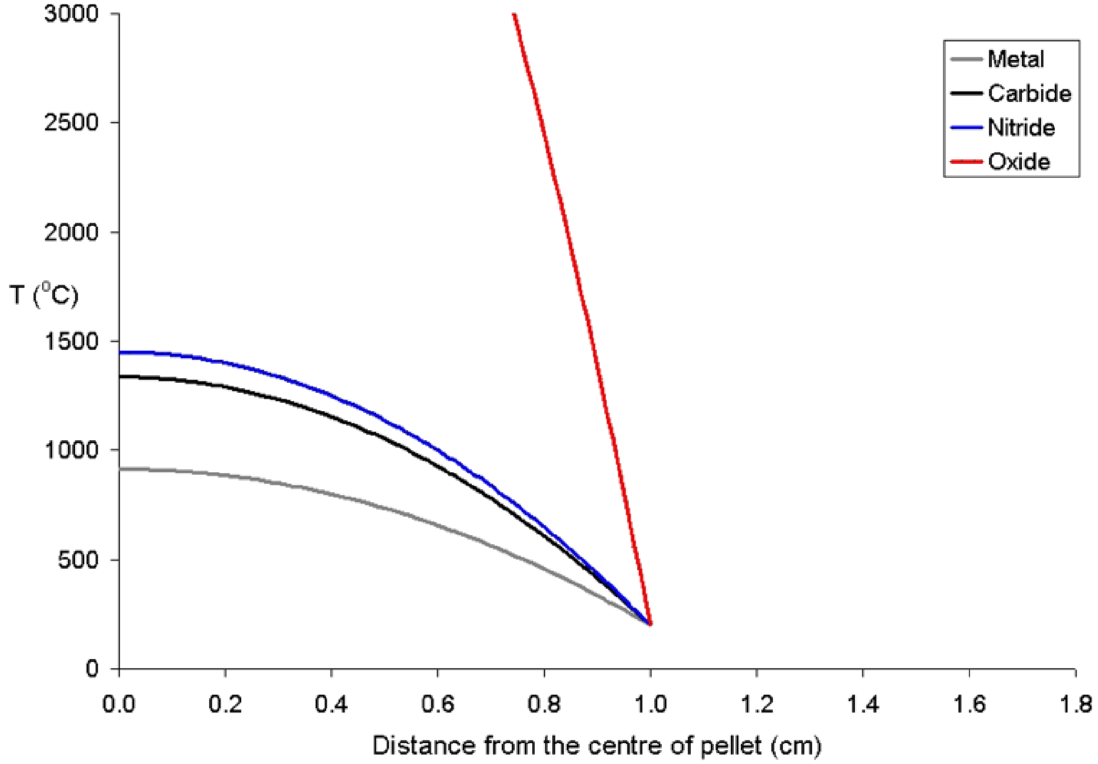


Temperature profile for a 32 mm diameter fuel pellet with a power density of 250 W per cubic meter.

To show the effects of different power densities on the centerline temperatures two graphs for 20 mm pellets at different power levels are shown below. It is clear that for all pellets (and most true of uranium dioxide) that for a given sized pellet that a limit must be set on the power density. It is likely that the maths used for these calculations would be used to explain how electrical fuses function and also it could be used to predict the centerline temperature in any system where heat is released throughout a cylinder shaped object.



Temperature profile for a 20 mm diameter fuel pellet with a power density of 500 W per cubic meter. Because the melting point of uranium dioxide is about 3300 K, it is clear that uranium oxide fuel is overheating at the center



Temperature profile for a 20 mm diameter fuel pellet with a power density of 1000 W per cubic meter. The fuels other than uranium dioxide are not compromised.

Loss of volatile fission products from pellets

The heating of pellets can result in some of the fission products being lost from the core of the pellet. If the xenon can rapidly leave the pellet then the amount of ^{134}Cs and ^{137}Cs which is present in the gap between the cladding and the fuel will increase. As a result if the zircaloy tubes holding the pellet are broken then a greater release of radioactive caesium from the fuel will occur. It is important to understand that the ^{134}Cs and ^{137}Cs are formed in different ways, and hence as a result the two caesium isotopes can be found at different pats of a fuel pin.

It is clear that the volatile iodine and xenon isotopes have minutes in which they can diffuse out of the pellet and into the gap between the fuel and the cladding. Here the xenon can decay to the long lived caesium isotope.

Genesis of ^{137}Cs

Formation of ^{137}Cs from its precursors

Element	Isotope	decay mode	half life	direct fission yield
Sn	137	β	very short (<1 s)	0.00%
Sb	137	β	very short (<1 s)	0.03%

Te	137	β	2.5 seconds	0.19%
I	137	β	24.5 seconds	1.40%
Xe	137	β	3.8 minutes	1.44%
Cs	137	β	30 years	0.08%

These fission yields were calculated for ^{235}U assuming thermal neutrons (0.0253 eV) using data from the chart of the nuclides.

Genesis of ^{134}Cs

In the case of ^{134}Cs the precursor to this isotope is stable ^{133}Cs which is formed by the decay of much longer lived xenon and iodine isotopes. No ^{134}Cs is formed without neutron activation as ^{134}Xe is a stable isotope. As a result of this different mode of formation the physical location of ^{134}Cs can differ from that of ^{137}Cs.

Formation of ^{134}Cs and its decay products (daughters)

Element	Isotope	decay mode	half life	direct fission yield
In	133	β	0.18 seconds	0.00%
Sn	133	β	1.45 seconds	0.07%
Sb	133	β	2.5 minutes	1.11%
Te	133m	β (82.5%)	55.4 minutes	0.49%
Te	133	β	12.5 minutes	0.15%
I	133	β	20.8 hours	1.22%
Xe	133	β	5.2 days	0.00%
Cs	133	–	stable (undergoes neutron activation in the core)	0.00%
Cs	134	β	2.1 years	6.4 x 10^{-6}%

These fission yields were calculated for ^{235}U assuming thermal neutrons (0.0253 eV) using data from the chart of the nuclides.

An example of a recent PIE study

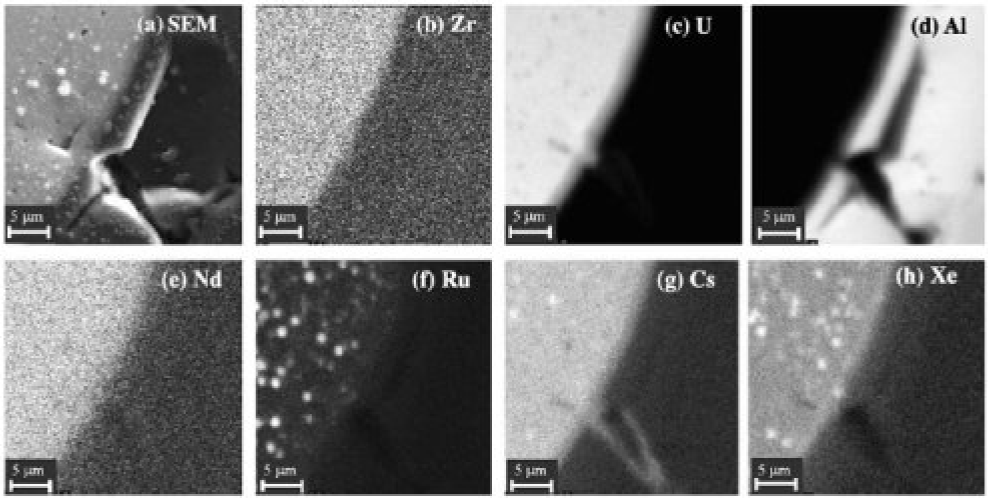
In a recent study, used 20% enriched uranium dispersed in a range of different matrices was examined to determine the physical locations of different isotopes and chemical elements.

- A solid solution of urania in yttria-stabilized zirconia (YSZ) {Y:Zr atom ratio of 1:4}).
- Urania particles in an inert matrix formed by a mixture of YSZ and spinel ($MgAl_2O_4$).

- Urania particles dispersed in the inert matrix formed by a mixture of YSZ and alumina.

The fuels varied in their ability to retain the fission xenon; the first of the three fuels retained 97% of the ^{133}Xe, the second retained 94% while the last fuel only retained 76% of this xenon isotope. The ^{133}Xe is a long-lived radioactive isotope which can diffuse slowly out of the pellet before being neutron activated to form ^{134}Cs. The more short-lived ^{137}Xe was less able to leach out of the pellets; 99%, 98% and 95% of the ^{137}Xe was retained within the pellets. It was also found that the ^{137}Cs concentration in the core of the pellet was much lower than the concentration in the rim of the pellet, while the less volatile ^{106}Ru was spread more evenly throughout the pellets.

The following fuel is particles of solid solution of urania in yttria-stabilized zirconia dispersed in alumina which had burnt up to 105 GW-days per cubic meter. The scanning electron microscope (SEM) is of the interface between the alumina and a fuel particle. It can be seen that the fission products are well confined to within the fuel, little of the fission products have entered the alumina matrix. The neodymium is spread throughout the fuel in a uniform manner, while the caesium is almost homogenously spread out throughout the fuel. The caesium concentration is slightly higher at two points where xenon bubbles are present. Much of the xenon is present in bubbles, while almost all of the ruthenium is present in the form of nanoparticles. The ruthenium nanoparticles are not always colocated with the xenon bubbles.



Used fuel which has been examined with a scanning electron microscope using electron microprobe attachment. The lighter the pixel in the right hand side the higher the element content of the material at that spot

Release of fission products into coolant water in a Three Mile Island type accident

At Three Mile Island a recently SCRAMed core was starved of cooling water, as a result of the decay heat the core dried out and the fuel was damaged. Attempts were made to recool the core using water. According to the International Atomic Energy Agency for a 3,000 MW(t) PWR the normal coolant radioactivity levels are shown below in the table, and the coolant activities for reactors which have been allowed to dry out (and over heat) before being recovered with water. In a gap release the activity in the fuel/cladding gap has been released while in the core melt release the core was melted before being recovered by water.

The levels of radioactivity in the coolant of a typical PWR under different conditions (MBq L^{-1})

Isotope	Normal	>20% Gap release	>10% Core melt
^{131}I	2	200000	700000
^{134}Cs	0.3	10000	60000
^{137}Cs	0.3	6000	30000
^{140}Ba	0.5	–	100000

Chernobyl release

The release of radioactivity from the used fuel is greatly controlled by the volatility of the elements. At Chernobyl much of the xenon and iodine was released while much less of the zirconium was released. The fact that only the more volatile fission products are released with ease will greatly retard the release of radioactivity in the event of an accident which causes serious damage to the core. Using two sources of data it is possible to see that the elements which were in the form of gases, volatile compounds or semi-volatile compounds (such as CsI) were released at Chernobyl while the less volatile elements which form solid solutions with the fuel remained inside the reactor fuel.

According to the OECD NEA report on Chernobyl (ten years on), the following proportions of the core inventory were released. The physical and chemical forms of the release included gases, aerosols and finely fragmented solid fuel. According to some research the ruthenium is very mobile when the nuclear fuel is heated with air.

Some work has been done on TRISO fuel under similar conditions.

Table of chemical data

Chemical forms of fission products in uranium dioxide, the percentage release at Chernobyl and the temperatures according to Colle *et al.* required to release 10% of an element from either unoxidized or oxidized fuel. When data from one element is assumed to apply to another element the enery is in *Italics*.

Element	Gas	Metal	Oxide	Solid solution	Radioisotopes	Release at Chernobyl	T required for 10% release from UO_2	T required for 10% release from U_3O_8
Br	Yes	–	–	–	–	–	–	–
Kr	Yes	–	–	–	*^{85}Kr*	*100%*	–	–
Rb	Yes	–	Yes	–	–	–	–	–

Sr	–	–	Yes	Yes	^{89}Sr and ^{90}Sr	4–6%	1950 K	–
Y	–	–	–	Yes	–	*3.5%*	–	–
Zr	–	–	Yes	Yes	^{95}Zr	3.5%	2600 K	–
Nb	–	–	Yes	–	–	–	–	–
Mo	–	Yes	Yes	–	^{99}Mo	>3.5%	–	1200 K
Tc	–	Yes	–	–	–	–	–	1300 K
Ru	–	Yes	–	–	^{103}Ru and ^{106}Ru	>3.5%	–	–
Rh	–	Yes	–	–	–	–	–	–
Pd	–	Yes	–	–	–	–	–	–
Ag	–	Yes	–	–	–	–	–	–
Cd	–	Yes	–	–	–	–	–	–
In	–	Yes	–	–	–	–	–	–
Sn	–	Yes	–	–	–	–	–	–
Sb	–	Yes	–	–	–	–	–	–
Te	Yes	Yes	Yes	Yes	^{132}Te	25–60%	1400 K	1200 K
I	Yes	–	–	–	^{131}I	50–60%	1300 K	1100 K
Xe	Yes	–	–	–	^{133}Xe	100%	1450 K	–
Cs	Yes	–	Yes	–	^{134}Cs and ^{137}Cs	20–40%	1300 K	1200 to 1300 K
Ba	–	–	Yes	Yes	^{140}Ba	4–6%	1850 K	1300 K
La	–	–	–	Yes	–	*3.5%*	*2300 K*	–
Ce	–	–	–	Yes	^{141}Ce and ^{144}Ce	3.5%	*2300 K*	–
Pr	–	–	–	Yes	–	*3.5%*	*2300 K*	–
Nd	–	–	–	Yes	–	*3.5%*	2300 K	–
Pm	–	–	–	Yes	–	*3.5%*	*2300 K*	–
Sm	–	–	–	Yes	–	*3.5%*	*2300 K*	–
Eu	–	–	–	Yes	–	*3.5%*	*2300 K*	–

The releases of fission products and uranium from uranium dioxide (from spent BWR fuel, burnup was 65 GWd t^{-1}) which was heated in a Knudsen cell has been repeated. Fuel was heated in the Knudsen cell both with and without preoxidation in oxygen at *c* 650 K. It was found even for the noble gases that a high temperature was required to liberate them from the uranium oxide solid. For unoxidized fuel 2300 K was required to release 10% of the uranium while oxidized fuel only requires 1700 K to release 10% of the uranium.

According to the report on Chernobyl used in the above table 3.5% of the following isotopes in the core were released ^{239}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Cm.

Degradation of the whole fuel element

Water and zirconium can react violently at 1200 °C, at the same temperature the zircaloy cladding can react with uranium dioxide to form zirconium oxide and a uranium/zirconium alloy melt.

PHEBUS

In France a facility exists in which a fuel melting incident can be made to happen under strictly controlled conditions. In the PHEBUS research program fuels have been allowed to heat up to temperatures in excess of the normal operating temperatures, the fuel in question is in a special channel which is in a toroidal nuclear reactor. The nuclear reactor is used as a *driver core* to irradate the test fuel. While the reactor is cooled as normal by its own cooling system the test fuel has its own cooling system, which is fitted with filters and equipment to study the release of radioactivity from the damaged fuel. Already the release of radioisotopes from fuel under different conditions has been studied. After the fuel has been used in the experiment it is subject to a detailed examination (PIE), In the 2004 annual report from the ITU some results of the PIE on PHEBUS (FPT2) fuel are reported in section 3.6.

LOFT

The **Loss of Fluid Tests (LOFT)** were an early attempt to scope the response of real nuclear fuel to conditions under a loss-of-coolant accident, funded by USNRC. The facility was built at Idaho National Laboratory, and was essentially a scale-model of a commercial PWR. ('Power/volume scaling' was used between the LOFT model, with a 50MWth core, and a commercial plant of 3000MWth).

The original intention (1963–1975) was to study only one or two major (large break) LOCA, since these had been the main concern of US 'rule-making' hearings in the late 1960s and early 1970s. These rules had focussed around a rather stylised large-break accident, and a set of criteria (e.g. for extent of fuel-clad oxidation) set out in 'Appendix K' of 10CFR50 (Code of Federal Regulations). Following the accident at Three Mile Island, detailed modelling of much smaller LOCA became of equal concern.

38 LOFT tests were eventually performed and their scope was broadened to study a wide spectrum of breach sizes. These tests were used to help validate a series of computer codes (such as RELAP-4, RELAP-5 and TRAC) then being developed to calculate the thermal-hydraulics of LOCA.

Contact of molten fuel with water and concrete

Water

Extensive work was done from 1970 to 1990 on the possibility of a steam explosion or FCI when molten 'corium' contacted water. Many experiments suggested quite low conversion of thermal to mechanical energy, whereas the theoretical models available appeared to suggest that much higher efficiencies were possible. A NEA/OECD report was written on the subject in 2000 which states that a steam explosion caused by contact of corium with water has four stages.

- Premixing

  - As the jet of corium enters the water, it breaks up into droplets. During this stage the thermal contact between the corium and the water is not good because a vapor film surrounds the droplets of corium and this insulates the two from each other. It is possible for this *meta*-stable state to quench without an explosion or it can trigger in the next step

- Triggering
  - A externally or internally generated trigger (such as a pressure wave) causes a collapse of the vapor film between the corium and the water.

- Propagation
  - The local increase in pressure due to the increased heating of the water can generate enhanced heat transfer (usually due to rapid fragmentation of the hot fluid within the colder more volatile one) and a greater pressure wave, this process can be self-sustained. (The mechanics of this stage would then be similar to those in a classical ZND detonation wave).

- Expansion
  - This process leads to the whole of the water being suddenly heated to boiling. This causes an increase in pressure which can result in damage to the plant.

Recent work

Some work has been done in Japan where uranium dioxide and zirconium dioxide was melted in a crucible before being added to water. The fragmentation of the fuel which results is reported in the *Journal of Nuclear Science and Technology*.

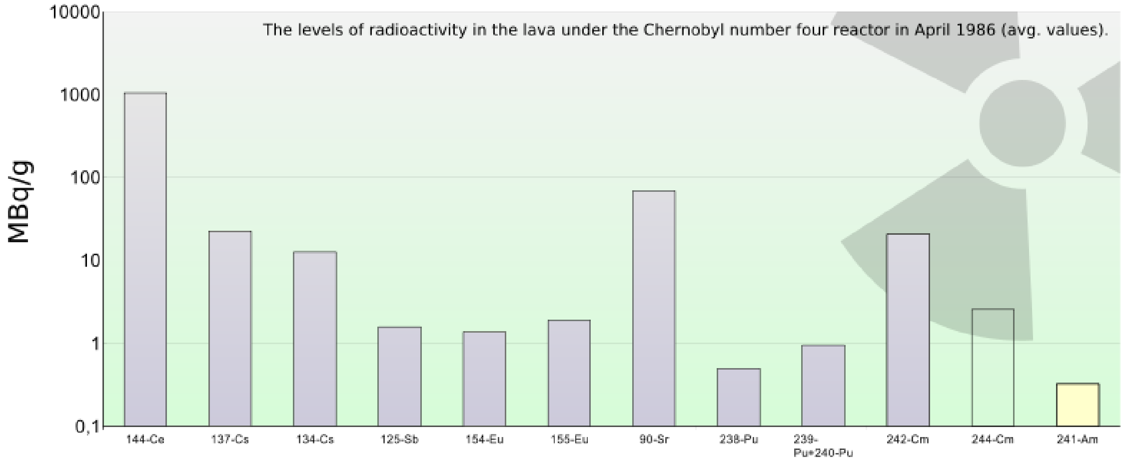
Concrete

A review of the subject can be read at and work on the subject continues to this day; in Germany at the FZK some work has been done on the effect of thermite on concrete, this is a simulation of the effect of the molten core of a reactor breaking through the bottom of the pressure vessel into the containment building.

Lava flows from corium

It is possible to see in the photo shown below that the corium (molten core) will cool and change to a solid with time. It is thought that the solid is weathering with time. The solid can be described as *Fuel Containing Mass*, it is a mixture of sand, zirconium and uranium dioxide which had been heated at a very high temperature until it has melted. The chemical nature of this *FCM* has been the subject of some research. The amount of fuel left in this form within the plant has been considered. A silicone polymer has been used to fix the contamination.

The Chernobyl melt was a silicate melt which did contain inclusions of Zr/U phases, molten steel and high uranium zirconium silicate. The lava flow consists of more than one type of material—a brown lava and a porous ceramic material have been found. The uranium to zirconium for different parts of the solid differs a lot, in the brown lava a uranium rich phase with a U:Zr ratio of 19:3 to about 38:10 is found. The uranium poor phase in the brown lava has a U:Zr ratio of about 1:10. It is possible from the examination of the Zr/U phases to know the thermal history of the mixture, it can be shown that before the explosion that in part of the core the temperature was higher than 2000 °C. While in some areas the temperature was over 2400–2600 °C.



Source: http://www.kiae.ru/rus/inf/chnpp/pr_fcm.htm

The radioactivity levels of different isotopes in the FCM, this has been back calculated by Russian workers to April 1986, note that the levels of radioactivity have decayed a great deal by now

Spent fuel corrosion

Uranium dioxide films

Uranium dioxide films can be deposited by reactive sputtering using an argon and oxygen mixture at a low pressure. This has been used to make a layer of the uranium oxide on a gold surface which was then studied with AC impedance spectroscopy.

Noble metal nanoparticles and hydrogen

According to the work of the corrosion electrochemist Shoesmith the nanoparticles of Mo-Tc-Ru-Pd have a strong effect on the corrosion of uranium dioxide fuel. For instance his work suggests that when the hydrogen (H_2) concentration is high (due to the anaerobic corrosion of the steel waste can) the oxidation of hydrogen at the nanoparticles will exert a protective effect on the uranium dioxide. This effect can be thought of as an example of protection by a sacrificial anode where instead of a metal anode reacting and dissolving it is the hydrogen gas which is consumed.

Chapter 5

Erosion Corrosion of Copper Water Tubes

Erosion corrosion, also known as impingement damage, is the combined effect of corrosion and erosion caused by rapid flowing turbulent water. It is probably the second most common cause of copper tube failures behind Type 1 pitting which is also known as Cold Water Pitting of Copper Tube.

Copper water tubes

Copper tubes have been used to distribute drinking water within buildings for many years, and hundreds of miles are installed throughout Europe every year. The long life of copper when exposed to natural waters is a result of its thermodynamic stability, its high resistance to reacting with the environment, and the formation of insoluble corrosion products that insulate the metal from the environment. The corrosion rate of copper in most drinkable waters is less than 25 µm/year, at this rate a 15 mm tube with a wall thickness of 0.7 mm would last for about 280 years. In some soft waters the general corrosion rate may increase to 125 µm/year, but even at this rate it would take over 50 years to perforate the same tube.

Occurrence

If the general water speed or the degree of local turbulence in an installation is high, the protective film that would normally be formed on a copper tube as a result of slight initial corrosion, may be torn off the surface locally, permitting further corrosion to take place at that point. If this process continues it can produce deep localised attack of the type known as erosion-corrosion or impingement damage. The actual attack on the metal is by the corrosive action of the water to which it is exposed while the erosive factor is the mechanical removal of the corrosion product from the surface.

Impingement attack produces highly characteristic water-swept pits, which are often horseshoe shaped, or it can produce broader areas of attack. The leading edge of the pit is frequently undercut by the swirling action of the water. Usually, the surface of the metal within the pits or areas of attack is smooth and carries no substantial corrosion product. Erosion-corrosion is known to occur in pumped-circulation hot water distribution systems, and even in cold water distribution systems, if the water velocities are too high. The factors influencing the attack include the chemical character of the water passing through the system, the temperature, the average water velocity in the system and the presence of any local features likely to induce turbulence in the water stream.

It is unusual for the general water velocity in a system to be so high that impingement attack occurs throughout the whole of the copper pipework. More commonly, the velocity is just sufficiently low for satisfactory protective films to be formed and to remain in position on most of the system, with impingement damage more likely to occur where there is an abrupt change in the direction of water flow giving rise to a high degree of turbulence, such as at tee pieces and elbow fittings. It is not generally realised how great an effect small obstructions can have on the flow pattern of water in a pipe-work system and the extent to which they can induce turbulence and cause corrosion-erosion. For example, it is most important, as far as possible, to ensure that copper tubes cut with a tube cutter are deburred before making the joint. Also a gap between the tube end and the stop in the fitting, due to the tube not having been cut to the correct length and fully inserted into the socket of the fitting, can also induce turbulence in the water stream.

Recommendations

The rate of impingement attack on copper also depends to some extent on the temperature of the water. The maximum velocities for fresh waters at different temperatures recommended in Sweden are given in the table below. These figures are for aerated waters of pH not less than about 7.

Recommended Maximum Water Velocities at Different Temperatures for Copper (m/s)

	10°C	**50°C**	**70°C**	**90°C**
For pipes that can be replaced:	4.0	3.0	2.5	2.0
For pipes that cannot be replaced:	2.0	1.5	1.3	1.0
For short connections to taps, etc§:	16.0	12.0	10.0	8.0

§ These velocities give a risk of impingement attack and are acceptable only for small bore connections to taps, flushing cisterns etc., through which water flow is intermittent.

BS 6700 gives the following maximum water velocities although it does note that these are currently under investigation and the velocities specified will be amended if the results of this investigation so require.

Water Temperature °C	**Maximum Water Velocity (m/s)**
10	3.0

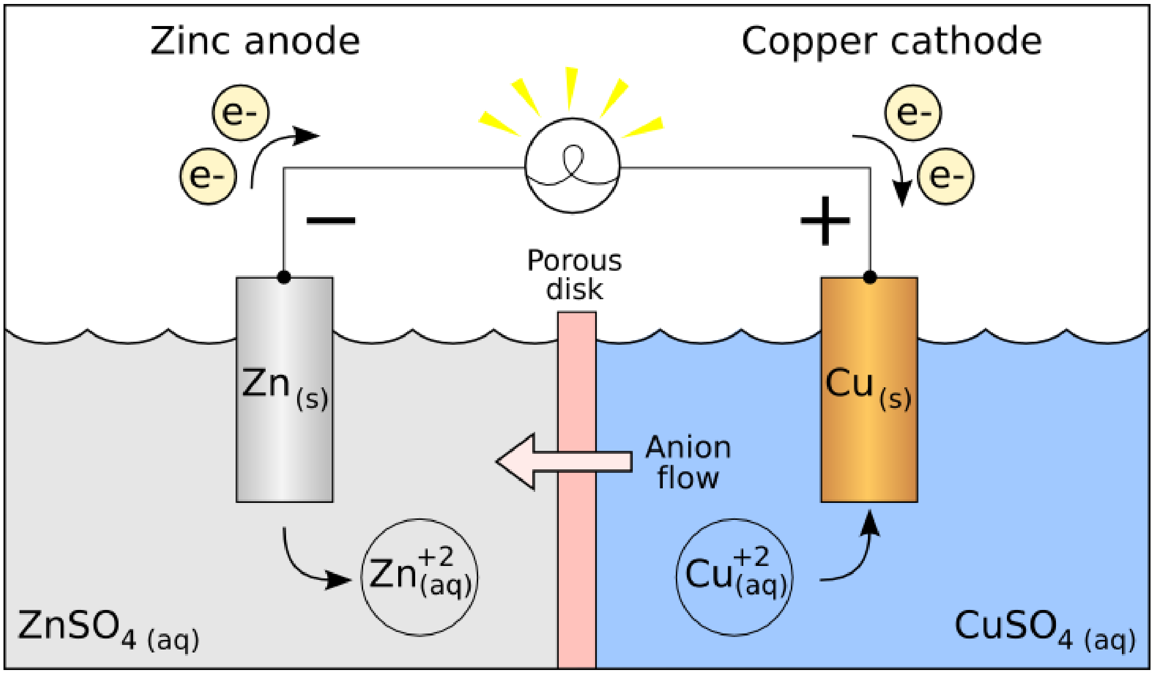
50	3.0
70	2.5
90	2.0

The minimum water speed at which copper pipes suffer impingement attack depends also to some extent on water composition. Aggressive waters that tend to be cupro-solvent are the most likely to give rise to impingement attack. Installations in large buildings where flow rates may be high and water is in continuous circulation are much more susceptible to attack than ordinary domestic installations. A high mineral content or a pH below 7 is likely to increase the possibility of corrosion-erosion occurring while a positive Langelier Index and consequent tendency to deposit a calcium carbonate scale is generally beneficial. The presence or absence of colloidal organic matter is also probably of some importance.

Remedial measures for impingement attack include modifications to the system to reduce the average water velocity, e.g. by using larger diameter tubes or, if appropriate, to lower the pump speed, and/or to redesign the part of the installation concerned to eliminate the cause of local turbulence, e.g. by using slow or swept bends and tee fittings rather than elbows and square tees. It is important to minimise the possibility of any local turbulence occurring by ensuring that the ends of tubes cut with a tube cutter are deburred and that the tubes are inserted fully to the stops in the fitting before the joints are made. In some cases, where the above approaches are not possible, the length of copper tube affected can sometimes be replaced by materials more resistant to corrosion-erosion, e.g. 90/10 copper-nickel (BS Designation CN102) using appropriate fittings, or stainless steel to BS 4127:1994.

Chapter 6

Galvanic Cell



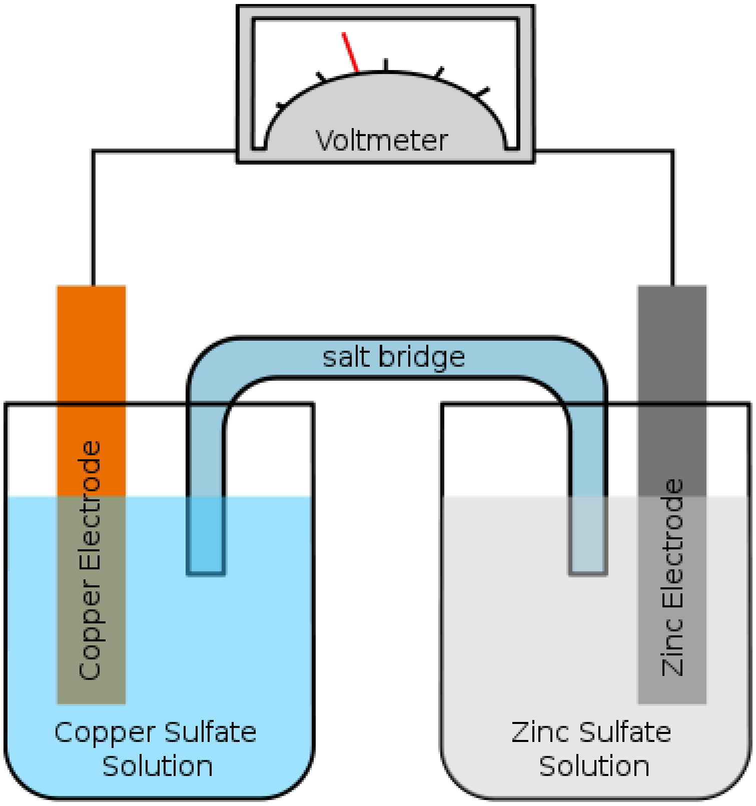
A **Galvanic cell**, or **Voltaic cell**, named after Luigi Galvani, or Alessandro Volta respectively, is an electrochemical cell that derives electrical energy from chemical reactions taking place within the cell. It generally consists of two different metals connected by a salt bridge, or individual half-cells separated by a porous membrane.

Volta was the inventor of the voltaic pile, the first electrical battery. In common usage, the word "battery" has come to include a single Galvanic cell, but a battery properly consists of multiple cells.

History

In 1780, Luigi Galvani discovered that when two different metals (copper and zinc for example) were connected together and then both touched to different parts of a nerve of a frog leg at the same time, they made the leg contract. He called this "animal electricity". The voltaic pile invented by Alessandro Volta in the 1800s is similar to the galvanic cell. These discoveries paved the way for electrical batteries.

Description



Schematic of Zn-Cu galvanic cell

A Galvanic cell consists of two half-cells. In its simplest form, each half-cell consists of a metal and a solution of a salt of the metal. The salt solution contains a cation of the metal and an anion to balance the charge on the cation. In essence the half-cell contains the metal in two oxidation states and the chemical reaction in the half-cell is an oxidation-reduction (redox) reaction, written symbolically in reduction direction as

$$M^{n+} \text{ (oxidized species)} + n\, e^{-} \rightleftharpoons M \text{ (reduced species)}$$

In a galvanic cell one metal is able to reduce the cation of the other and, conversely, the other cation can oxidize the first metal. The two half-cells must be physically separated so that the solutions do not mix together. A salt bridge or porous plate is used to separate the two solutions yet keep the respective charges of the solutions from separating, which would stop the chemical reactions.

The number of electrons transferred in both directions must be the same, so the two half-cells are combined to give the whole-cell electrochemical reaction. For two metals A and B:

$$A^{n+} + n\,e^{-} \rightleftharpoons A$$
$$B^{m+} + m\,e^{-} \rightleftharpoons B$$
$$m\,A + n\,B^{m+} \rightleftharpoons n\,B + m\,A^{n+}$$

This is not the whole story as anions must also be transferred from one half-cell to the other. When a metal in one half-cell is oxidized, anions must be transferred into that half-cell to balance the electrical charge of the cation produced. The anions are released from the other half-cell where a cation is reduced to the metallic state. Thus, the salt bridge or porous membrane serves both to keep the solutions apart and to allow the flow of anions in the direction opposite to the flow of electrons in the wire connecting the electrodes.

The voltage of the Galvanic cell is the sum of the voltages of the two half-cells. It is measured by connecting a voltmeter to the two electrodes. The voltmeter has very high resistance, so the current flow is effectively negligible. When a device such as an electric motor is attached to the electrodes, a current flows and redox reactions occur in both half-cells. This will continue until the concentration of the cations that are being reduced goes to zero.

For the Daniell cell, depicted in the figure, the two metals are zinc and copper and the two salts are sulfates of the respective metal. Zinc is the oxidized metal so when a device is connected to the electrodes, the electrochemical reaction is

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

The zinc electrode is dissolved and copper is deposited on the copper electrode (as copper ions become reduced to copper metal). By definition, the cathode is the electrode where reduction (gain of electrons) takes place, so the copper electrode is the cathode. The cathode attracts cations, so has a negative charge when current is discharging. In this case, copper is the cathode and zinc the anode.

Galvanic cells are typically used as a source of electrical power. By their nature they produce direct current. For example, a lead-acid battery contains a number of galvanic cells. The two electrodes are effectively lead and lead oxide.

The Weston cell was adopted as an International Standard for voltage in 1911. The anode is a cadmium mercury amalgam, the cathode is made of pure mercury, the electrolyte is a (saturated) solution of cadmium sulfate and the depolarizer is a paste of mercurous sulfate. When the electrolyte solution is saturated the voltage of the cell is very reproducible, hence its use as a standard.

Cell voltage

The standard electrical potential of a cell can be determined by use of a standard potential table for the two half cells involved. The first step is to identify the two metals reacting in the cell. Then one looks up the standard electrode potential, E^0, in volts, for each of the two half reactions. The standard potential for the cell is equal to the more positive E^0 value minus the more negative E^0 value.

For example, in the figure above the solutions are $CuSO_4$ and $ZnSO_4$. Each solution has a corresponding metal strip in it, and a salt bridge or porous disk connecting the two solutions and allowing SO_4^{2-} ions to flow freely between the copper and zinc solutions. In order to calculate the standard potential one looks up copper and zinc's half reactions and finds:

$Cu^{2+} + 2\,e^- \rightleftharpoons Cu$: $E^0 = +0.34$ V
$Zn^{2+} + 2\,e^- \rightleftharpoons Zn$: $E^0 = -0.76$ V

Thus the overall reaction is:

$Cu^{2+} + Zn \rightleftharpoons Cu + Zn^{2+}$

The standard potential for the reaction is then +0.34 V − (−0.76 V) = 1.10 V. The polarity of the cell is determined as follows. Zinc metal is more strongly reducing than copper metal as shown by the fact that the standard (reduction) potential for zinc is more negative than that of copper. Thus, zinc metal will lose electrons to copper ions and develop a positive electrical charge. The equilibrium constant, K, for the cell is given by

$$\ln K = \frac{nFE^0}{RT}$$

where F is the Faraday constant, R is the gas constant and T is the temperature in kelvins. For the Daniell cell K is approximately equal to 1.5×10^{37}. Thus, at equilibrium, a few electrons are transferred, enough to cause the electrodes to be charged.

Actual half-cell potentials must be calculated by using the Nernst equation as the solutes are unlikely to be in their standard states,

$$E_{\textbf{half-cell}} = E^0 - \frac{RT}{nF}\ln_e Q$$

where Q is the reaction quotient. This simplifies to

$$E_{\textbf{half-cell}} = E^0 + 2.303\frac{RT}{nF}\log_{10}\{M^{n+}\}$$

where $\{M^{n+}\}$ is the activity of the metal ion in solution. The metal electrode is in its standard state so by definition has unit activity. In practice concentration is used in place of activity. The potential of the whole cell is obtained by combining the potentials for the two half-cells, so it depends on the concentrations of both dissolved metal ions.

The value of $2.303R/F$ is 0.19845×10^{-3} V/K, so at 25 °C (298.15 K) the half-cell potential will change by $0.05918V / n$ if the concentration of a metal ion is increased or decreased by a factor of 10.

$$E_{\textbf{half-cell}} = E^0 + \frac{0.05918V}{n} \log_{10}[M^{n+}]$$

These calculations are based on the assumption that all chemical reactions are in equilibrium. When a current flows in the circuit, equilibrium conditions are not achieved and the cell potential will usually be reduced by various mechanisms, such as the development of overpotentials. Also, since chemical reactions occur when the cell is producing power, the electrolyte concentrations change and the cell voltage is reduced. A consequence of the temperature dependency of standard potentials is that the voltage produced by a galvanic cell is also temperature dependent.

Galvanic corrosion

Galvanic corrosion is a process that degrades metals electrochemically. This corrosion occurs when two dissimilar metals are placed in contact with each other in the presence of an electrolyte, such as salt water, forming a galvanic cell. A cell can also be formed if the same metal is exposed to two different concentrations of electrolyte. The resulting electrochemical potential then develops an electric current that electrolytically dissolves the less noble material.

Chapter 7

Hydrogen Embrittlement & Hydrogen Damage

Hydrogen Embrittlement

Hydrogen embrittlement is the process by which various metals, most importantly high-strength steel, become brittle and fracture following exposure to hydrogen. Hydrogen embrittlement is often the result of unintentional introduction of hydrogen into susceptible metals during forming or finishing operations.

Hydrogen embrittlement is also used to describe the formation of zircaloy hydride. Use of the term in this context is common in the nuclear industry.

Process

The mechanism starts with lone hydrogen atoms diffusing through the metal. At high temperatures, the elevated solubility of hydrogen allows hydrogen to diffuse into the metal (or the hydrogen can diffuse in at a low temperature, assisted by a concentration gradient). When these hydrogen atoms re-combine in minuscule voids of the metal matrix to form hydrogen molecules, they create pressure from inside the cavity they are in. This pressure can increase to levels where the metal has reduced ductility and tensile strength up to the point where it cracks open (*hydrogen induced cracking*, or HIC). High-strength and low-alloy steels, nickel and titanium alloys are most susceptible. Austempered iron is also susceptible. Steel with an ultimate tensile strength of less than 1000 MPa or hardness of less than 30 HRC are not generally considered susceptible to hydrogen embrittlement. Jewett *et al.* reports the results of tensile tests carried out on several structural metals under high-pressure molecular hydrogen environment. These tests have shown that austenitic stainless steels, aluminum (including alloys), copper (including alloys, e.g. beryllium copper) are not susceptible to hydrogen embrittlement along with few other metals. For example of a severe embrittlement measured by Jewett, the elongation at failure of 17-4PH precipitation hardened stainless steel was measured to drop from 17% to only 1.7% when smooth specimens were exposed to high-pressure hydrogen.

Hydrogen embrittlement can occur during various manufacturing operations or operational use - anywhere that the metal comes into contact with atomic or molecular hydrogen. Processes that can lead to this include cathodic protection, phosphating, pickling, and electroplating. A special case is arc welding, in which the hydrogen is released from moisture (for example in the coating of the welding electrodes; to minimize this, special low-hydrogen electrodes are used for welding high-strength steels). Other mechanisms of introduction of hydrogen into metal are galvanic corrosion, chemical reactions of metal with acids, or with other chemicals (notably hydrogen sulfide in sulfide stress cracking, or SSC, a process of importance for the oil and gas industries).

Counteractions

If the metal has not yet started to crack, the condition can be reversed by removing the hydrogen source and causing the hydrogen within the metal to diffuse out, possibly at elevated temperatures. Susceptible alloys, after chemical or electrochemical treatments where hydrogen is produced, are often subjected to heat treatment to remove absorbed hydrogen. There is a 4-hour time limit for baking out entrapped hydrogen after acid treating the parts. This is the time between the end of acid exposure and the beginning of the heating cycle in the baking furnace. This per SAE AMS 2759/9 Section 3.3.3.1 which calls out the correct procedure for eliminating entrapped hydrogen.

In the case of welding, often pre- and post-heating the metal is applied to allow the hydrogen to diffuse out before it can cause any damage. This is specifically done with high-strength steels and low alloy steel such as the chrome/molybdenum/vanadium alloys. Due to the time needed to re-combine hydrogen atoms into the harmful hydrogen molecules, hydrogen cracking due to welding can occur over 24 hours after the welding operation is completed.

Products such as ferrosilicates can be used to treat surfaces normally subject to hydrogen embrittlement in order to prevent it from taking place.

Related phenomena

If steel is exposed to hydrogen at high temperatures, hydrogen will diffuse into the alloy and combine with carbon to form tiny pockets of methane at internal surfaces like grain boundaries and voids. This methane does not diffuse out of the metal, and collects in the voids at high pressure and initiates cracks in the steel. This selective leaching process is known as hydrogen attack, or high temperature hydrogen attack and leads to decarburization of the steel and loss of strength and ductility.

Copper alloys which contain oxygen can be embrittled if exposed to hot hydrogen. The hydrogen diffuses through the copper and reacts with inclusions of Cu_2O, forming H_2O (water), which then forms pressurized bubbles at the grain boundaries. This process can cause the grains to literally be forced away from each other, and is known as *steam embrittlement* (because steam is produced, not because exposure to steam causes the problem).

Testing

There are two ASTM standards for testing embrittlement due to hydrogen gas. The standard ASTM F1459-06 Standard Test Method for Determination of the Susceptibility of Metallic Materials to Hydrogen Gas Embrittlement (HGE) Test uses a diaphragm loaded with a differential pressure. The test ASTM G142-98(2004) Standard Test Method for Determination of Susceptibility of Metals to Embrittlement in Hydrogen Containing Environments at High Pressure, High Temperature, or Both uses a cylindrical tensile specimen tested into an enclosure pressurized with hydrogen or helium.

Another ASTM standard exists for quantitatively testing for the Hydrogen Embrittlement threshold stress for the onset of Hydrogen-Induced Cracking due to platings and coatings from Internal Hydrogen Embrittlement (IHE) and Environmental Hydrogen Embrittlement (EHE) - F1624-06 Standard Test Method for Measurement of Hydrogen Embrittlement Threshold in Steel by the Incremental Step Loading Technique. References: ASTM STP 543,"Hydrogen Embrittlement Testing" and ASTM STP 962,"Hydrogen Embrittlement: Prevention and Control."

- NACE TM0284-2003 (NACE International) Resistance to Hydrogen-Induced Cracking
- ISO 11114-4:2005 (ISO)Test methods for selecting metallic materials resistant to hydrogen embrittlement .
- ASTM F1940-07a- Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement in Plated or Coated Fasteners
- ASTM F519-06e2-Standard Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating/Coating Processes and Service Environments

Hydrogen Damage

Hydrogen damage is the generic name given to a large number of metal degradation processes due to interaction with hydrogen.

Hydrogen is present practically everywhere, in the atmosphere, several kilometres above the earth and inside the earth. Engineering materials are exposed to hydrogen and they may interact with it resulting in various kinds of structural damage. Damaging effects of hydrogen in metallic materials have been known since 1875 when W. H. Johnson reported “some remarkable changes produced in iron by the action of hydrogen and acids”. During the intervening years many similar effects have been observed in different structural materials, such as steel, aluminium, titanium, and zirconium. Because of the technological importance of hydrogen damage, many people explored the nature, causes and control measures of hydrogen related degradation of metals. Hardening, embrittlement and internal damage are the main hydrogen damage processes in metals.

Importance

With advancing technology, use of high strength structural materials becomes a necessity. Depletion of fossil fuels and the search for other sources of energy is a current activity of mankind. Hydrogen is believed to be a possible future source of energy (Engineering note: Hydrogen could not be used as a "source" of energy but only as a means to transport energy from one place to another) and a “hydrogen economy” is a strong possibility within the next 50 years. In such a scenario, large scale production, storage, transportation and use of hydrogen becomes necessary. Materials’ problems caused by hydrogen damage could limit the progress of such an economy. Hydrogen may be picked up by metals during melting, casting, shaping and fabrication. They are also exposed to hydrogen during their service life. Materials susceptible to hydrogen damage have ample opportunities to be degraded during all these stages.

Classifications

Hydrogen damage may be of four types: solid solution hardening, creation of internal defects, hydride embrittlement, and hydrogen embrittlement. Each of these may further be classified into the various damaging processes.

Solid solution hardening

Metals like niobium and tantalum dissolve hydrogen and experience hardening and embrittlement at concentrations much below their solid solubility limit. The hardening and embrittlement are enhanced by increased rate of straining.

Hydride embrittlement

In hydride forming metals like titanium, zirconium and vanadium, hydrogen absorption causes severe embrittlement. At low concentrations of hydrogen, below the solid solubility limit, stress-assisted hydride formation causes the embrittlement which is enhanced by slow straining. At hydrogen concentrations above the solubility limit, brittle hydrides are precipitated on slip planes and cause severe embrittlement. This latter kind of embrittlement is encouraged by increased strain-rates, decreased temperature and by the presence of notches in the material.

Creation of internal defects

Hydrogen present in metals can produce several kinds of internal defects like blisters, shatter fracture, flakes, fish-eyes and porosity. Carbon steels exposed to hydrogen at high temperatures experience hydrogen attack which leads to internal decarburization and weakening.

Blistering

Atomic hydrogen diffusing through metals may collect at internal defects like inclusions and laminations and form molecular hydrogen. High pressures may be built up at such locations due to continued absorption of hydrogen leading to blister formation, growth and eventual bursting of the blister. Such hydrogen induced blister cracking has been observed in steels, aluminium alloys, titanium alloys and nuclear structural materials.

Shatter cracks, flakes, fish-eyes and micro perforations

Flakes and shatter cracks are internal fissures seen in large forgings. Hydrogen picked up during melting and casting segregates at internal voids and discontinuities and produces these defects during forging. Fish-eyes are bright patches named for their appearance seen on fracture surfaces, generally of weldments. Hydrogen enters the metal during fusion-welding and produces this defect during subsequent stressing. Steel containment vessels exposed to extremely high hydrogen pressures develop small fissures or micro perforations through which fluids may leak.

Porosity

In metals like iron and steel, aluminium and magnesium whose hydrogen solubilities decrease with decreasing temperature, liberation of excess hydrogen during cooling from the melt, (in ingots and castings) produces gas porosity.

Hydrogen embrittlement

By far, the most damaging effect of hydrogen in structural materials is hydrogen embrittlement. Materials susceptible to this process exhibit a marked decrease in their energy absorption ability before fracture in the presence of hydrogen. This phenomenon is also known as hydrogen-assisted cracking, hydrogen-induced blister cracking. The embrittlement is enhanced by slow strain rates and low temperatures, near room temperature.

Hydrogen stress cracking

Brittle delayed failure of normally ductile materials when hydrogen is present within is called hydrogen stress cracking or internal hydrogen embrittlement. This effect is seen in high strength structural steels, titanium alloys and aluminium alloys.

Hydrogen environment embrittlement

Embrittlement of materials when tensile loaded in contact with gaseous hydrogen is known as hydrogen environment embrittlement or external hydrogen embrittlement. It has been observed in alloy steels and alloys of nickel, titanium, uranium and niobium.

Loss in tensile ductility

Hydrogen lowers tensile ductility in many materials. In ductile materials, like austenitic stainless steels and aluminium alloys, no marked embrittlement may occur, but may exhibit significant lowering in tensile ductility (% elongation or % reduction in area) in tensile tests.

Degradation of other mechanical properties

Hydrogen may also affect the plastic flow behaviour of metals. Increased or decreased yield strengths, serrated yielding, altered work hardening rates as well as lowered fatigue and creep properties have been reported.

Control of hydrogen damage

The best method of controlling hydrogen damage is to control contact between the metal and hydrogen. Many steps can be taken to reduce the entry of hydrogen into metals during critical operations like melting, casting, working (rolling, forging, etc.), welding, surface preparation, like chemical cleaning, electroplating, and corrosion during their service life. Control of the environment and metallurgical control of the material to decrease its susceptibility to hydrogen are the two major approaches to reduce hydrogen damage.

Detection of hydrogen damage

There are various methods of adequately identifying and monitoring hydrogen damage, including ultrasonic echo attenuation method, amplitude-based backscatter, velocity ratio, creeping waves/time-of-flight measurement, pitch-catch mode shear wave velocity, advanced ultrasonic backscatter techniques (AUBT), time of flight diffraction (TOFD), thickness mapping and in-situ metallography – replicas.

To inspect industrial facilities, such as a plant for the possible occurrence of hydrogen damage, an accurate inspection plan has to be made by combining advanced techniques like time of flight diffraction (TOFD), automated backscatter and velocity ratio measurements.

The backscatter technique uses corroscan for the most critical areas, i.e., at highest temperature and/or highest partial hydrogen pressure. In order to discriminate between hydrogen damage and small inclusions, additional measurements are taken with the Velocity Ratio Technique.

Chapter 8

Low Plasticity Burnishing & High Temperature Corrosion

Low Plasticity Burnishing

Low plasticity burnishing (**LPB**) is a method of metal improvement that provides deep, stable surface compressive residual stresses with little cold work for improved damage tolerance and metal fatigue life extension. Improved fretting fatigue and stress corrosion performance has been documented, even at elevated temperatures where the compression from other metal improvement processes relaxes. The resulting deep layer of compressive residual stress has also been shown to improve high cycle fatigue (HCF) and low cycle fatigue (LCF) performance.

History

Unlike LPB, traditional burnishing tools consist of a hard wheel or fixed lubricated ball pressed into the surface of an asymmetrical work piece with sufficient force to deform the surface layers, usually in a lathe. The process does multiple passes over the work pieces, usually under increasing load, to improve surface finish and deliberately cold work the surface. Roller and ball burnishing have been studied in Russia and Japan, and were applied most extensively in the USSR in the 1970s. Various burnishing methods are used, particularly in Eastern Europe, to improve fatigue life. Improvements in HCF, corrosion fatigue and SCC are documented, with fatigue strength enhancement attributed to improved finish, the development of a compressive surface layer, and the increased yield strength of the cold worked surface.

LPB was developed and patented by Lambda Technologies, a small family-owned company from Cincinnati, Ohio, in 1996. Since then, LPB has been developed to produce compression in a wide array of materials to mitigate surface damage, including fretting, corrosion pitting, stress corrosion cracking (SCC), and foreign object damage (FOD), and is being employed by such companies as Delta TechOps and PAS Technologies, as well as NAVAIR, to aid in their daily MRO operations. To this day, LPB is the *only* metal improvement method applied under continuous closed-loop process control and has been successfully applied to turbine engines, piston engines, propellers, aging aircraft structures, landing gear, nuclear waste material containers, biomedical implants and welded joints. The applications involved titanium, iron, nickel and steel-based components and showed improved damage tolerance as well as high and low cycle fatigue performance by an order of magnitude.

How it works

The basic LPB tool is a ball that is supported in a spherical hydrostatic bearing. The tool can be held in any CNC machine or by industrial robots, depending on the application. The machine tool coolant is used to pressurize the bearing with a continuous flow of fluid to support the ball. The ball does not contact the mechanical bearing seat, even under load. The ball is loaded at a normal state to the surface of a component with a hydraulic cylinder that is in the body of the tool. LPB can be performed in conjunction with chip forming machining operations in the same CNC machining tool.

The ball rolls across the surface of a component in a pattern defined in the CNC code, as in any machining operation. The tool path and normal pressure applied are designed to create a distribution of compressive residual stress. The form of the distribution is designed to counter applied stresses and optimize fatigue and stress corrosion performance. Since there is no shear being applied to the ball, it is free to roll in any direction. As the ball rolls over the component, the pressure from the ball causes plastic deformation to occur in the surface of the material under the ball. Since the bulk of the material constrains the deformed area, the deformed zone is left in compression after the ball passes.

Benefits

The LPB process includes a unique and patented way of analyzing, designing, and testing metallic components in order to develop the unique metal treatment necessary to improve performance and reduce metal fatigue, SCC, and corrosion fatigue failures. Lambda designs a new tool for each component to provide the best results possible and to ensure that the apparatus reaches every inch on the component. With this practice of constantly redesigning, along with the closed-loop process control system, LPB has been shown to produce a maximum compression of 12mm, although the average is around 1-7+mm. LPB has even been shown to have the ability to produce through-thickness compression in blades and vanes, greatly increasing their damage tolerance over 10-fold, effectively mitigating most FOD and reducing inspection requirements. No material is removed during this process, even when correcting corrosion damage. LPB smooths surface asperities during machining, leaving an improved, almost mirror-like surface finish that is vastly better looking and better protected than even a newly manufactured component.

Cold working

The cold work produced from this process is typically between 2-5%, a great deal less than shot peening, laser peening, gravity peening or deep rolling. Cold work is particularly important because the higher the cold work at the surface of a component, the more vulnerable to elevated temperatures and mechanical overload that component will be and the easier the beneficial surface residual compression will relax, rendering the treatment pointless. In other words, a component that has been highly cold worked will not hold the compression if it comes into contact with extreme heat, like an engine, and will be just as vulnerable as it was to start. The reason LPB produces such low percentages of cold work is because of the aforementioned closed-loop process control. Other processes have some guesswork involved and are not exact at all, causing the procedure to have to be performed multiple times on one component. For example, shot peening, in order to make sure every spot on the component is treated, typically specifies coverage of between 200% and 400%. This means that each spot was impacted 2-4 times on the component. The problem is that one spot will be hit four times while the one next to it is hit only twice, leaving uneven compression. This uneven compression results in the whole process being easily "undone", as was mentioned above. LPB requires only one pass with the tool and leaves a deep, even, beneficial compressive stress.

The LPB process can be performed on-site in the shop or in situ on aircraft using robots, making it easy to incorporate into everyday maintenance and manufacturing procedures. The method is applied under continuous closed loop process control (CLPC), creating accuracy within 0.1% and alerting the operator and QA immediately if the processing bounds are exceeded. The limitation of this process is that different CNC processing codes need to be developed for each application, just like any other machining task. The other issue is that because of dimensional restrictions, it may not be possible to create the tools necessary to work on certain geometries, although that has yet to be a problem.

High Temperature Corrosion

Hot corrosion is a mechanism of "high temperature corrosion", others include high temperature oxidation, sulfidation and carbonization.

Hot corrosion by sulfates

Two types of sulfate-induced hot corrosion are generally distinguished: Type I takes place above the melting point of sodium sulfate and Type II occurs below the melting point of sodium sulfate but in the presence of small amounts of SO_3.

In Type I the protective oxide scale is dissolved by the molten salt. Sulfur is released from the salt and diffuses into the metal substrate forming discrete grey/blue colored aluminum or chromium sulfides so that, after the salt layer has been removed, the steel cannot rebuilt a new protective oxide layer. Alkali sulfates are formed from sulfur trioxide and sodium-containing compounds. As the formation of vanadates is preferred, sulfates are formed only if the amount of alkali metals is higher than the corresponding amount of vanadium.

The same kind of attack has been observed for potassium and magnesium sulfate.

Hot corrosion by vanadium

Vanadium is present in petroleum, especially from Canada, western United States, Venezuela and the Caribbean region, in the form of porphyrine complexes. These complexes get concentrated on the higher-boiling fractions, which are the base of heavy residual fuel oils. Residues of sodium, primarily from sodium chloride and spent oil treatment chemicals, are also present. More than 100 ppm of sodium and vanadium will yield ash capable of causing **fuel ash corrosion**.

Most fuels contain small traces of vanadium. The vanadium is oxidized to different vanadates. Molten vanadates present as deposits on metal can flux oxide scales and passivation layers. Furthermore, the presence of vanadium accelerates the diffusion of oxygen through the fused salt layer to the metal substrate; vanadates can be present in semiconducting or ionic form, where the semiconducting form has significantly higher corrosivity as the oxygen is transported via oxygen vacancies. Ionic form in contrast transports oxygen by diffusion of the vanadates, which is significantly slower. The semiconducting form is rich on vanadium pentoxide.

At high temperatures or lower availability of oxygen, refractory oxides - vanadium dioxide and vanadium trioxide - form. These do not promote corrosion. However, at conditions most common for burning, vanadium pentoxide gets formed. Together with sodium oxide, vanadates of various composition ratios are formed. Vanadates of composition approximating $Na_2O.6\ V_2O_5$ have the highest corrosion rates at the temperatures between 593 °C and 816 °C; at lower temperatures the vanadate is in solid state, at higher temperatures vanadates with higher proportion of vanadium provide higher corrosion rates.

The solubility of the passivation layer oxides in the molten vanadates depends on the composition of the oxide layer. Iron(III) oxide is readily soluble in vanadates between $Na_2O.6\ V_2O_5$ and $6\ Na_2O.V_2O_5$, at temperatures below 705 °C in amounts up to equal to the mass of the vanadate. This composition range is common for ashes, which aggravates the problem. Chromium(III) oxide, nickel(II) oxide, and cobalt(II) oxide are less soluble in vanadates; they convert the vanadates to less corrosive ionic form and their vanadates are tightly adherent, refractory, and acting as oxygen barriers.

The corrosion rate by vanadates can be lowered by lowering the amount of excess air for combustion (thus forming preferentially the refractory oxides), refractory coatings of the exposed surfaces, or use of high-chromium alloys, e.g. 50% Ni/50% Cr or 40% Ni/60% Cr.

The presence of sodium in a ratio of 1:3 gives the lowest melting point and must be avoided. This melting point of 535 °C can cause problems on the hot spots of the engine like piston crowns, valve seats, and turbochargers.

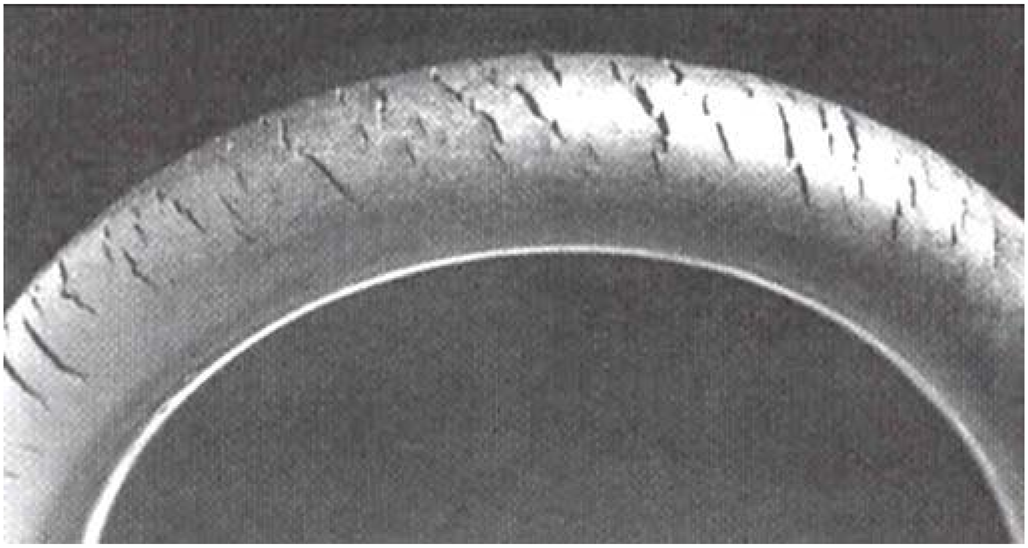
Hot corrosion by lead

Lead can form a low melting slag capable of fluxing protective oxide scales.

Chapter 9

Ozone Cracking & Pitting Corrosion

Ozone Cracking



Ozone cracking in natural rubber tubing

Cracks can be formed in many different elastomers by ozone attack, and the characteristic form of attack of vulnerable rubbers is known as **ozone cracking**. The problem was formerly very common, especially in tires, but is now rarely seen in those products owing to preventive measures.

However, it does occur in many other safety-critical items such as fuel lines and rubber seals, such as gaskets and O-rings, where ozone attack is considered unlikely. Only a trace amount of the gas is needed to initiate cracking, and so these items can also succumb to the problem.

Susceptible elastomers

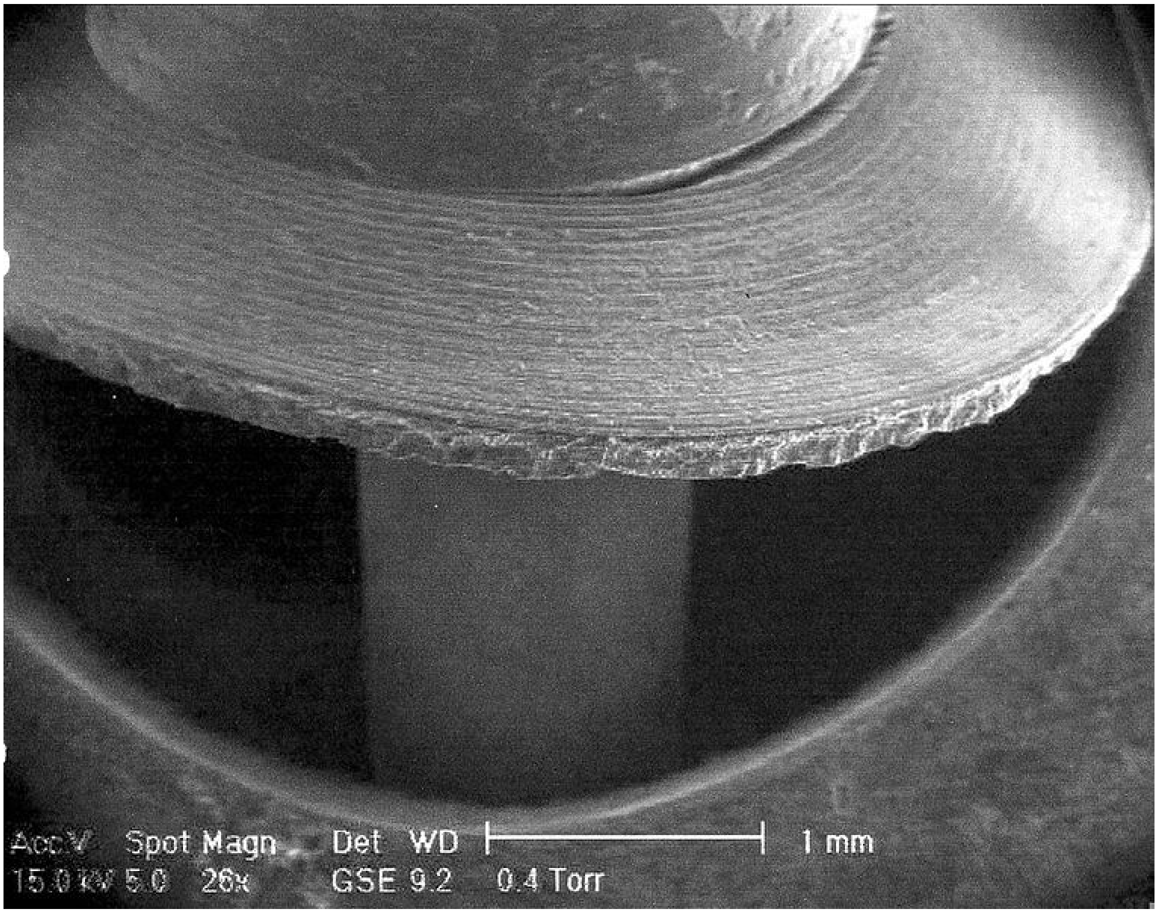
Tiny traces of ozone in the air will attack double bonds in rubber chains, with natural rubber, polybutadiene, styrene-butadiene rubber and nitrile rubber being most sensitive to degradation. Every repeat unit in the first three materials has a double bond, so every unit can be degraded by ozone. Nitrile rubber is a copolymer of butadiene and acrylonitrile units, but the proportion of acrylonitrile is usually lower than butadiene, so attack occurs. Butyl rubber is more resistant but still has a small number of double bonds in its chains, so attack is possible. Exposed surfaces are attacked first, the density of cracks varying with ozone gas concentration. The higher the concentration, the greater the number of cracks formed.

Ozone-resistant elastomers include EPDM, fluoroelastomers like Viton and polychloroprene rubbers like Neoprene. Attack is less likely because double bonds form a very small proportion of the chains, and with the latter, the chlorination reduces the electron density in the double bonds, therefore lowering their propensity to react with ozone. Silicone rubber, Hypalon and polyurethanes are also ozone-resistant.

Form of cracking

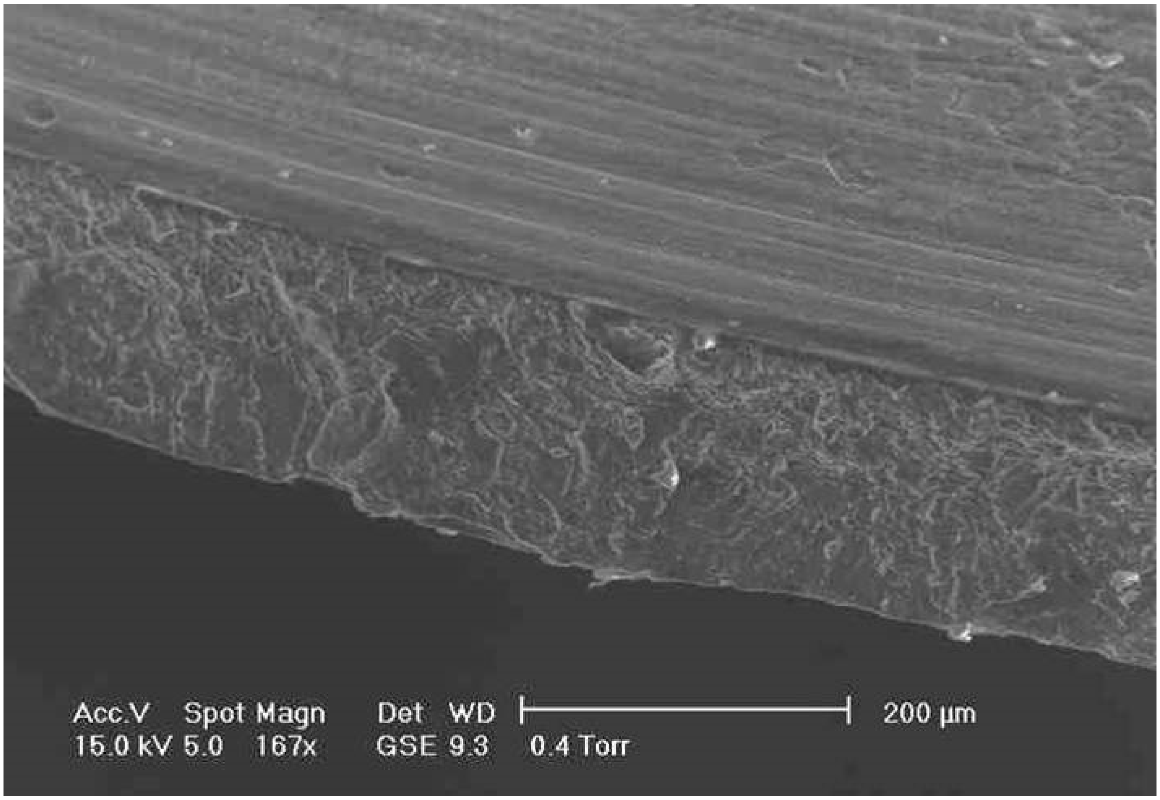
Macrophotograph of ozone cracking in NBR (Nitrile Butadiene Rubber) diaphragm seal

Ozone cracks form in products under tension, but the critical strain is very small. The cracks are always oriented at right angles to the strain axis, so will form around the circumference in a rubber tube bent over. Such cracks are very dangerous when they occur in fuel pipes because the cracks will grow from the outside exposed surfaces into the bore of the pipe, so fuel leakage and fire may follow. Seals are also susceptible to attack, such as diaphragm seals in air lines. Such seals are often critical for the operation of pneumatic controls, and if a crack penetrates the seal, all functions of the system can be lost. Nitrile rubber seals are commonly used in pneumatic systems because of its oil resistance. However, if ozone gas is present, cracking will occur in the seals unless preventative measures are taken.



environmental scanning electron microscope image of ozone cracks in NBR diaphragm seal formed at sharp corners in seal

Ozone attack will occur at the most sensitive zones in a seal, especially sharp corners where the strain is greatest when the seal is flexing in use. The corners represent stress concentrations, so the tension is at a maximum when the diaphragm of the seal is bent under air pressure.

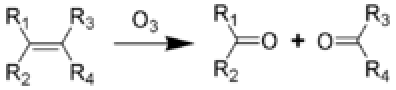


Close-up of ozone crack (using ESEM) in NBR diaphragm seal

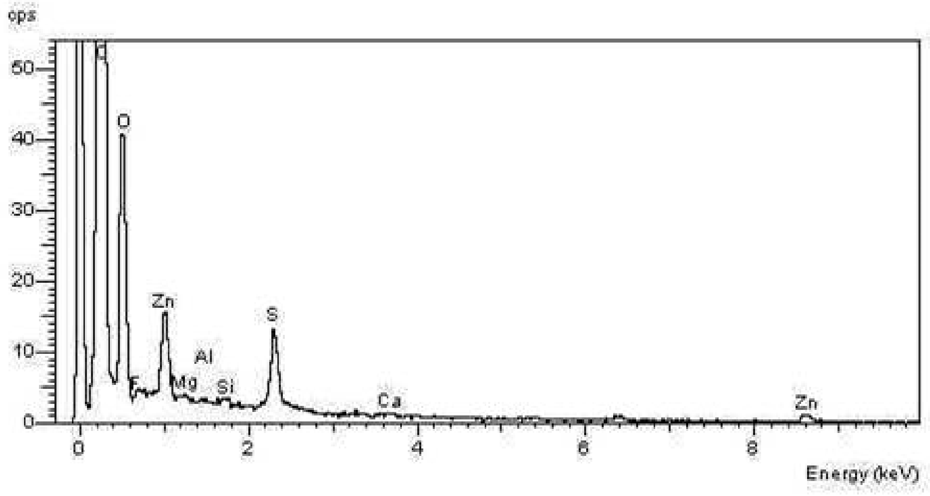
The seal shown at left failed from traces of ozone at circa 1 ppm, and once cracking had started, it continued as long as the gas was present. This particular failure led to loss of production on a semi-conductor fabrication line. The problem was solved by adding effective filters in the air line and by modifying the design to eliminate the very sharp corners. An ozone-resistant elastomer such as Viton was also considered as a replacement for the Nitrile rubber. The pictures were taken using ESEM for maximum resolution.

Ozonolysis

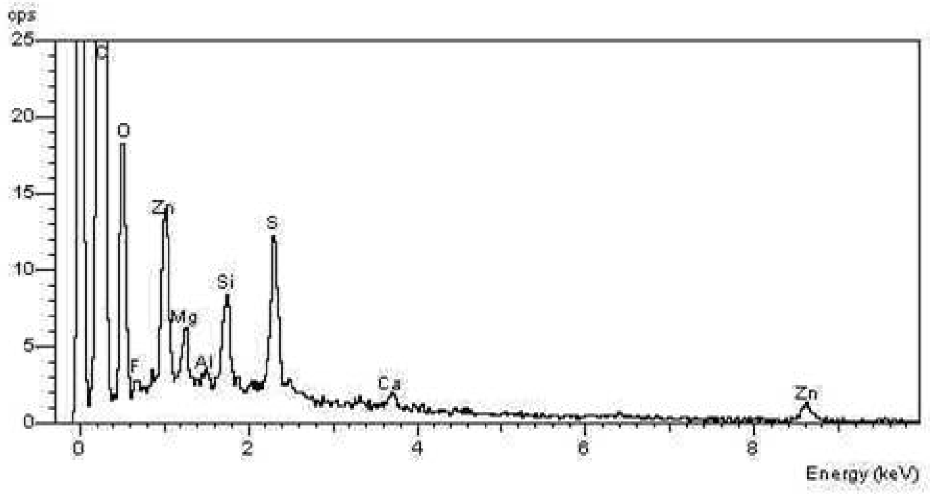
The reaction occurring between double bonds and ozone is known as ozonolysis when one molecule of the gas reacts with the double bond:



The immediate result is formation of an ozonide, which then decomposes rapidly so that the double bond is cleaved. This is the critical step in chain breakage when polymers are attacked. The strength of polymers depends on the chain molecular weight or degree of polymerization, the higher the chain length, the greater the mechanical strength (such as tensile strength). By cleaving the chain, the molecular weight drops rapidly and there comes a point when it has little strength whatsoever, and a crack forms. Further attack occurs in the freshly exposed crack surfaces and the crack grows steadily until it completes a circuit and the product separates or fails. In the case of a seal or a tube, failure occurs when the wall of the device is penetrated.



EDX spectrum of crack surface



EDX spectrum of unaffected rubber surface

The carbonyl end groups which are formed are usually aldehydes or ketones, which can oxidise further to carboxylic acids. The net result is a high concentration of elemental oxygen on the crack surfaces, which can be detected using Energy-dispersive X-ray spectroscopy in the environmental SEM, or ESEM. The spectrum at left shows the high oxygen peak compared with a constant sulfur peak. The spectrum at right shows the unaffected elastomer surface spectrum, with a relatively low oxygen peak compared with the sulfur peak.

Prevention

The problem can be prevented by adding antiozonants to the rubber before vulcanization. Ozone cracks were commonly seen in automobile tire sidewalls, but are now seen rarely thanks to the use of these additives. A common and low cost antiozonant is a wax which bleeds to the surface and forms a protective layer, but other specialist chemicals are also widely used.

On the other hand, the problem does recur in unprotected products such as rubber tubing and seals, where ozone attack is thought to be impossible. Unfortunately, traces of ozone can turn up in the most unexpected situations. Using ozone-resistant rubbers is another way of inhibiting cracking.

For high value equipment where loss of function can cause serious problems, low cost seals may be replaced at frequent intervals so as to preclude failure.

Ozone gas is produced during electric discharge by sparking or corona discharge for example. Static electricity can build up within machines like compressors with moving parts constructed from insulating materials. If those compressors feed pressurised air into a closed pneumatic system, then all seals in the system may be at risk from ozone cracking.

Ozone is also produced by the action of sunlight on volatile organic liquids or VOLs, such as gasoline vapour present in the air of towns and cities, in a problem known as photochemical smog. The ozone formed can drift many miles before it is destroyed by further reactions.

Pitting Corrosion

Pitting corrosion, or **pitting**, is a form of extremely localized corrosion that leads to the creation of small holes in the metal. The driving power for pitting corrosion is the depassivation of a small area, which becomes anodic while an unknown but potentially vast area becomes cathodic, leading to very localized galvanic corrosion. The corrosion penetrates the mass of the metal, with limited diffusion of ions. The mechanism of pitting corrosion is probably the same as crevice corrosion.

Mechanism

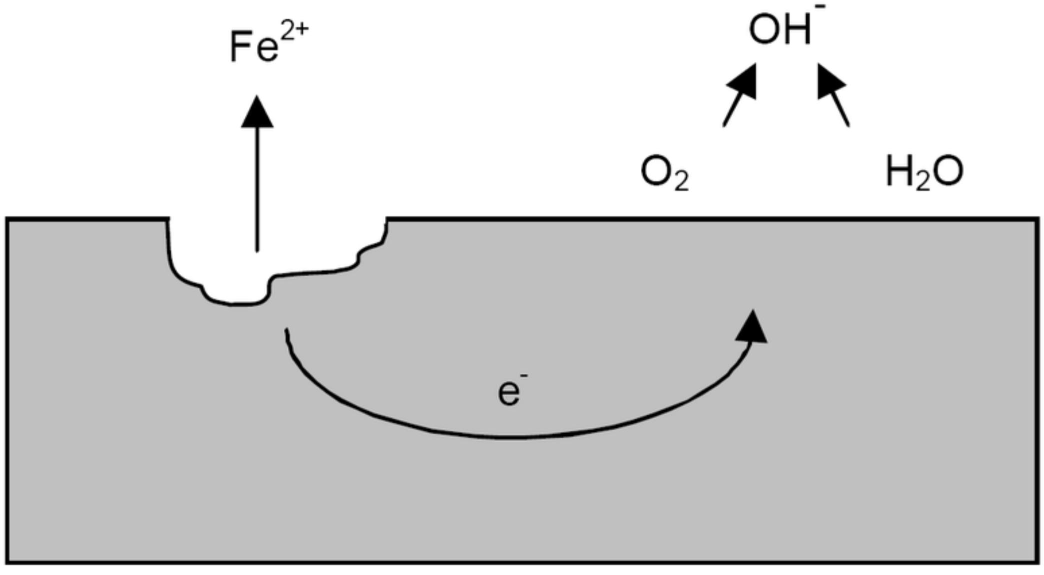


Diagram showing a mechanism of localized corrosion developing on metal in a solution containing oxygen

It is supposed by some that gravitation causes downward-oriented concentration gradient of the dissolved ions in the hole caused by the corrosion, as the concentrated solution is denser. This however is unlikely. The more conventional explanation is that the acidity inside the pit is maintained by the spatial separation of the cathodic and anodic half-reactions, which creates a potential gradient and electromigration of aggressive anions into the pit.

This kind of corrosion is extremely insidious, as it causes little loss of material with small effect on its surface, while it damages the deep structures of the metal. The pits on the surface are often obscured by corrosion products.

Pitting can be initiated by a small surface defect, being a scratch or a local change in composition, or a damage to protective coating. Polished surfaces display higher resistance to pitting.

Susceptible alloys

Alloys most susceptible to pitting corrosion are usually the ones where corrosion resistance is caused by a passivation layer: stainless steels, nickel alloys, aluminum alloys. Metals that are susceptible to uniform corrosion in turn do not tend to suffer from pitting. Thus, a regular carbon steel will corrode uniformly in sea water, while stainless steel will pit. Additions of about 2% of molybdenum increases pitting resistance of stainless steels.

Environment

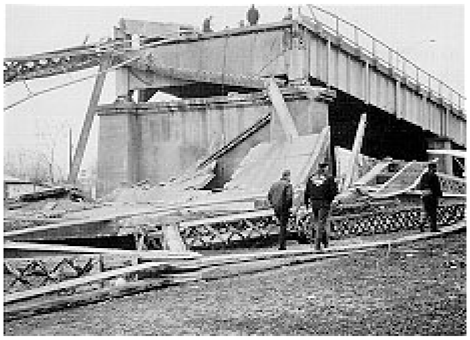
The presence of chlorides, e.g. in sea water, significantly aggravates the conditions for formation and growth of the pits through an autocatalytic process. The pits becomes loaded with positive metal ions through anodic dissociation. The Cl^- ions become concentrated in the pits for charge neutrality and encourage the reaction of positive metal ions with water to form a hydroxide corrosion product and H^+ ions. Now, the pits are weakly acidic, which accelerates the process.

Besides chlorides, other anions implicated in pitting include thiosulfates ($S_2O_3^{2-}$), fluorides and iodides. Stagnant water conditions favour pitting. Thiosulfates are particularly aggressive species and are formed by partial oxidation of pyrite, or partial reduction of sulfate. Thiosulfates are a concern for corrosion in many industries: sulfide ores processing, oil wells and pipelines transporting soured oils, Kraft paper production plants, photographic industry, methionine and lysine factories.

Corrosion inhibitors, when present in sufficient amount, will provide protection against pitting. However, too low level of them can aggravate pitting by forming local anodes.

Examples

A corrosion pit on the outside wall of a pipeline at a coating defect before and after abrasive blasting.



The collapsed Silver Bridge, as seen from the Ohio side

A single pit in a critical point can cause a great deal of damage. One example is the explosion in Guadalajara, Mexico on April 22, 1992, when gasoline fumes accumulated in sewers destroyed kilometers of streets. The vapors originated from a leak of gasoline through a single hole formed by corrosion between a steel gasoline pipe and a zinc-plated water pipe. Firearms can also suffer from pitting, most notably in the bore of the barrel when corrosive ammunition is used and the barrel is not cleaned soon afterward. Deformities in the bore caused by pitting can greatly reduce the firearms accuracy. To prevent pitting in firearm bores, most modern firearms have a bore lined with chromium.

Pitting corrosion can also help initiate stress corrosion cracking, as happened when a single eyebar on the Silver Bridge, West Virginia and killed 46 people on the bridge in December, 1967.

Chapter 10

Polymer Degradation

Polymer degradation is a change in the properties - tensile strength, colour, shape, etc. - of a polymer or polymer-based product under the influence of one or more environmental factors such as heat, light or chemicals such as acids, alkalis and some salts. These changes are usually undesirable, such as cracking and chemical disintegration of products or, more rarely, desirable, as in biodegradation, or deliberately lowering the molecular weight of a polymer for recycling. The changes in properties are often termed "aging".

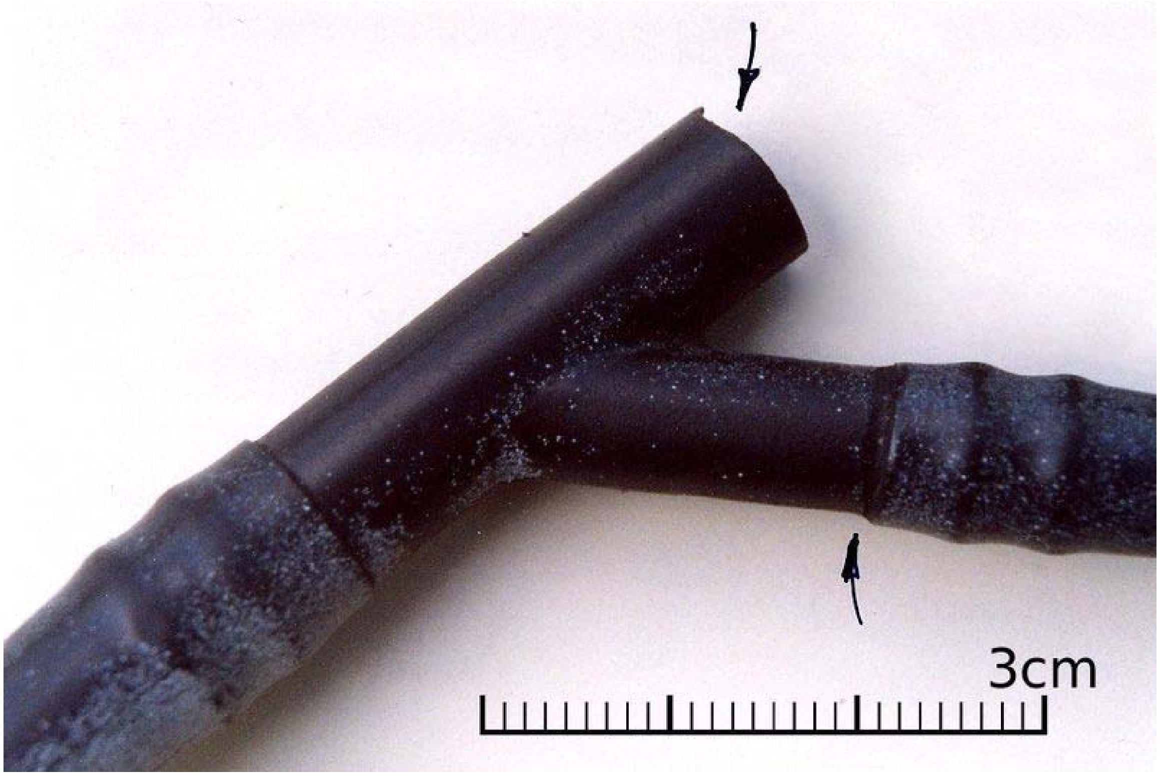
In a finished product such a change is to be prevented or delayed. Degradation can be useful for recycling/reusing the polymer waste to prevent or reduce environmental pollution. Degradation can also be induced deliberately to assist structure determination.

Polymeric molecules are very large (on the molecular scale), and their unique and useful properties are mainly a result of their size. Any loss in chain length lowers tensile strength and is a primary cause of premature cracking.

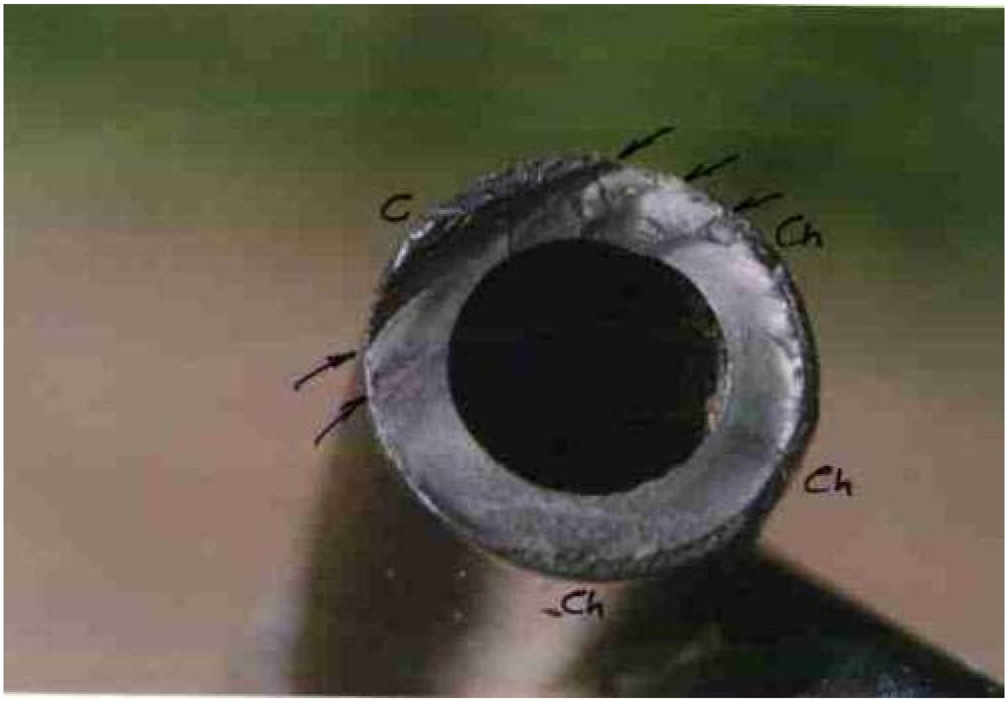
Commodity polymers

Today there are primarily seven commodity polymers in use: polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate or PET, polystyrene, polycarbonate, and poly(methyl methacrylate) (Plexiglass). These make up nearly 98% of all polymers and plastics encountered in daily life. Each of these polymers has its own characteristic modes of degradation and resistances to heat, light and chemicals. Polyethylene, polypropylene, and poly(methyl methacrylate) are sensitive to oxidation and UV radiation, while PVC may discolour at high temperatures due to loss of hydrogen chloride gas, and become very brittle. PET is sensitive to hydrolysis and attack by strong acids, while polycarbonate depolymerizes rapidly when exposed to strong alkalis.

For example, polyethylene usually degrades by *random scission* - that is by a random breakage of the linkages (bonds) that hold the atoms of the polymer together. When this polymer is heated above 450 Celsius it becomes a complex mixture of molecules of various sizes that resemble gasoline. Other polymers - like polyalphamethylstyrene - undergo 'unspecific' chain scission with breakage occurring only at the ends; they literally unzip or depolymerize to become the constituent monomers.



Close-up of broken fuel pipe from road traffic accident



Close-up of broken fuel pipe connector

Photoinduced degradation

Most polymers can be degraded by photolysis to give lower molecular weight molecules. Electromagnetic waves with the energy of visible light or higher, such as ultraviolet light, X-rays and gamma rays are usually involved in such reactions.

Thermal degradation

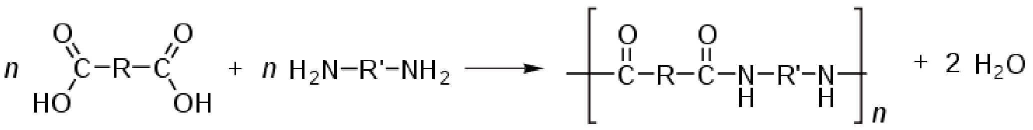
Chain-growth polymers like poly(methyl methacrylate) can be degraded by thermolysis at high temperatures to give monomers, oils, gases and water. The degradation takes place by:

Thermolysis type	**Added material**	**Temperature**	**Pressure**	**Final product**
Pyrolysis		Around 500°C	Reduced pressure	
Hydrogenation	Dihydrogen	Around 450°C	Around 200 bars	
Gasification	Dioxygen and/or water		Under pressure	Carbon monoxide, Carbon dioxide and hydrogen

Chemical degradation

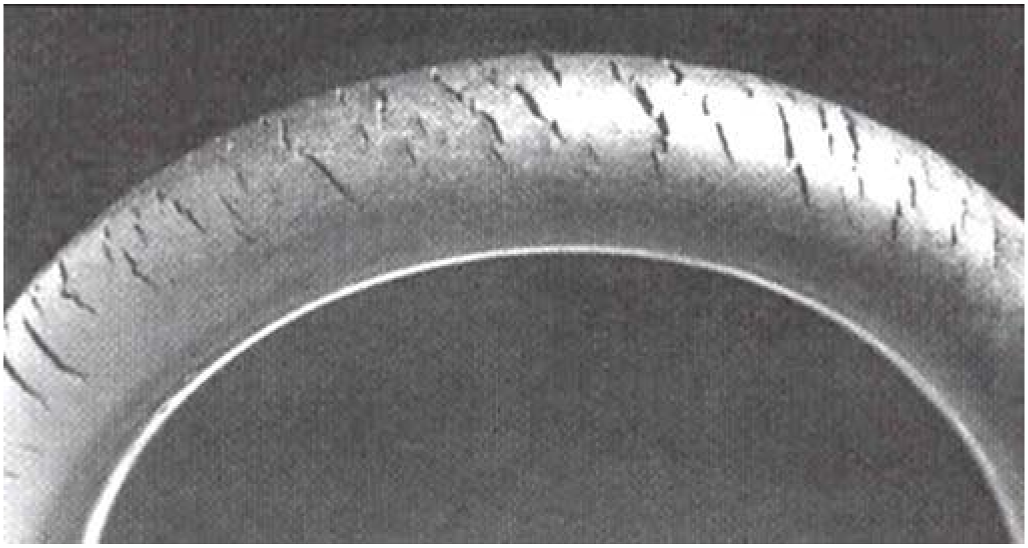
Solvolysis

Step-growth polymers like polyesters, polyamides and polycarbonates can be degraded by solvolysis and mainly hydrolysis to give lower molecular weight molecules. The hydrolysis takes place in the presence of water containing an acid or a base as catalyst. Polyamide is sensitive to degradation by acids and polyamide mouldings will crack when attacked by strong acids. For example, the fracture surface of a fuel connector showed the progressive growth of the crack from acid attack (Ch) to the final cusp (C) of polymer. The problem is known as stress corrosion cracking, and in this case was caused by hydrolysis of the polymer. It was the reverse reaction of the synthesis of the polymer:



$$n\,\mathrm{HOOC{-}R{-}COOH} + n\,\mathrm{H_2N{-}R'{-}NH_2} \longrightarrow \left[\mathrm{{-}\overset{O}{\overset{\|}{C}}{-}R{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}{-}R'{-}\underset{H}{N}{-}}\right]_n + 2\,\mathrm{H_2O}$$

Ozonolysis



Ozone cracking in Natural rubber tubing

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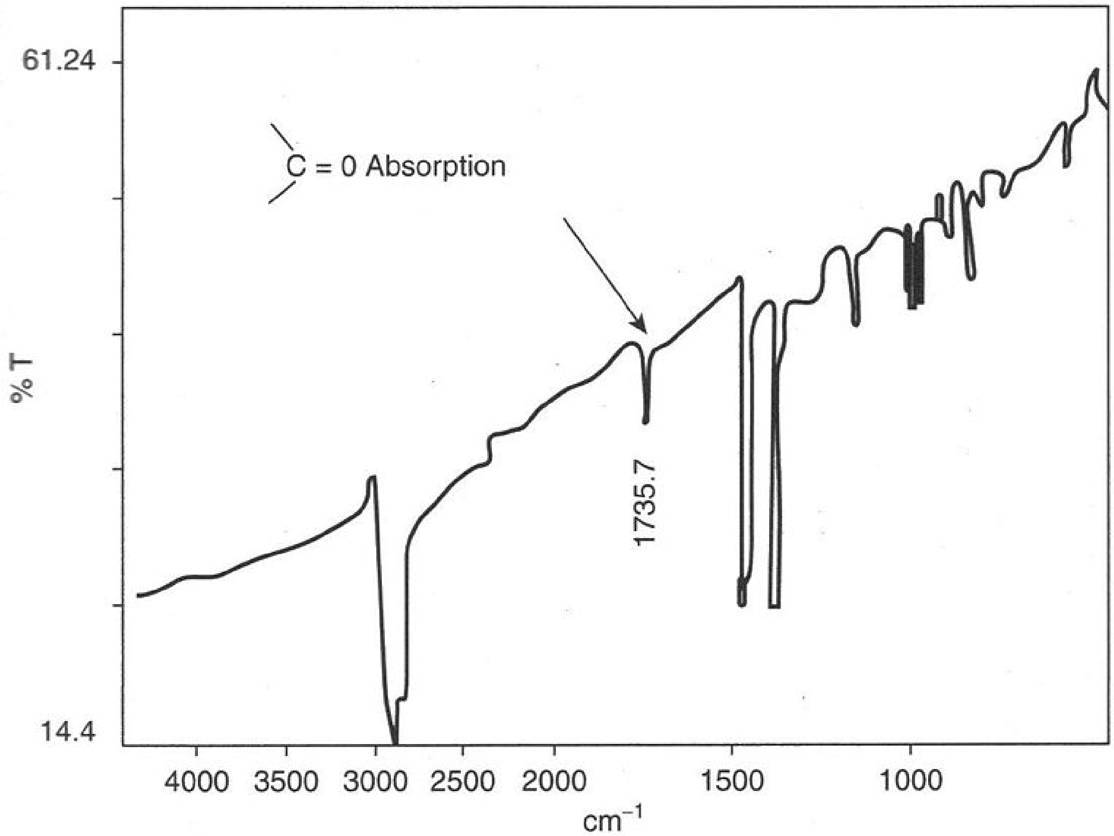
Oxidation



IR spectrum showing carbonyl absorption due to oxidative degradation of polypropylene crutch moulding

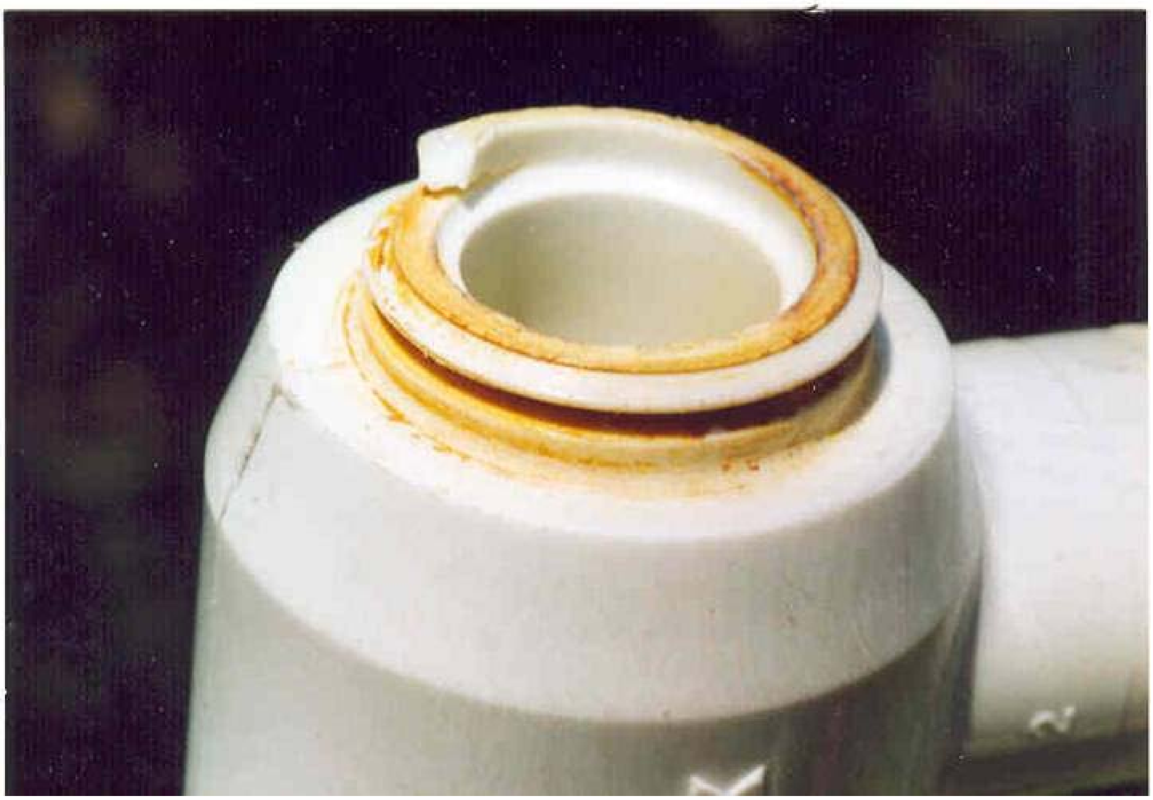
Polymers are susceptible to attack by atmospheric oxygen, especially at elevated temperatures encountered during processing to shape. Many process methods such as extrusion and injection moulding involve pumping molten polymer into tools, and the high temperatures needed for melting may result in oxidation unless precautions are taken. For example, a forearm crutch suddenly snapped and the user was severely injured in the resulting fall. The crutch had fractured across a polypropylene insert within the aluminium tube of the device, and infra-red spectroscopy of the material showed that it had oxidised, possible as a result of poor moulding.

Oxidation is usually relatively easy to detect owing to the strong absorption by the carbonyl group in the spectrum of polyolefins. Polypropylene has a relatively simple spectrum with few peaks at the carbonyl position (like polyethylene). Oxidation tends to start at tertiary carbon atoms because the free radicals formed here are more stable and longer lasting, making them more susceptible to attack by oxygen. The carbonyl group can be further oxidised to break the chain, this weakens the material by lowering its molecular weight, and cracks start to grow in the regions affected.

Galvanic action

Polymer degradation by galvanic action was first described in the technical literature in 1990. This was the discovery that "plastics can corrode", i.e. polymer degradation may occur through galvanic action similar to that of metals under certain conditions. Normally, when two dissimilar metals such as copper (Cu) and iron (Fe) are put into contact and then immersed in salt water, the iron will undergo corrosion, or rust. This is called a galvanic circuit where the copper is the noble metal and the iron is the active metal, i.e., the copper is the cathode or positive (+) electrode and the iron is the anode, or negative (-) electrode. A battery is formed. It follows that plastics are made stronger by impregnating them with thin carbon fibers only a few micrometers in diameter known as carbon fiber reinforced polymers (CFRP). This is to produce materials that are high strength and resistant to high temperatures. The carbon fibers act as a noble metal similar to gold (Au) or platinum (Pt). When put into contact with a more active metal, for example with aluminum (Al) in salt water the aluminum corrodes. However in early 1990, it was reported that imide-linked resins in CFRP composites degrade when bare composite is coupled with an active metal in salt water environments. This is because corrosion not only occurs at the aluminum anode, but also at the carbon fiber cathode in the form of a very strong base with a pH of about 13. This strong base reacts with the polymer chain structure degrading the polymer. Polymers affected include bismaleimides (BMI), condensation polyimides, triazines, and blends thereof. Degradation occurs in the form of dissolved resin and loose fibers. The hydroxyl ions generated at the graphite cathode attack the O-C-N bond in the polyimide structure. Standard corrosion protection procedures were found to prevent polymer degradation under most conditions.

Chlorine-induced cracking



chlorine attack of acetal resin plumbing joint

Another highly reactive gas is chlorine, which will attack susceptible polymers such as acetal resin and polybutylene pipework. There have been many examples of such pipes and acetal fittings failing in properties in the US as a result of chlorine-induced cracking. In essence, the gas attacks sensitive parts of the chain molecules (especially secondary, tertiary, or allylic carbon atoms), oxidizing the chains and ultimately causing chain cleavage. The root cause is traces of chlorine in the water supply, added for its anti-bacterial action, attack occurring even at parts per million traces of the dissolved gas. The chlorine attacks weak parts of a product, and in the case of an acetal resin junction in a water supply system, it is the thread roots that were attacked first, causing a brittle crack to grow. Discolouration on the fracture surface was caused by deposition of carbonates from the hard water supply, so the joint had been in a critical state for many months. The problems in the US also occurred to polybutylene pipework, and led to the material being removed from that market, although it is still used elsewhere in the world.

Biological degradation

Biodegradable plastics can be biologically degraded by microorganisms to give lower molecular weight molecules. To degrade properly biodegradable polymers need to be treated like compost and not just left in a landfill site where degradation is very difficult due to the lack of oxygen and moisture.

Stabilisers

Hindered amine light stabilisers (HALS) stabilise against weathering by scavenging free radicals that are produced by photo-oxidation of the polymer matrix. UV-absorbers stabilises against weathering by absorbing ultraviolet light and converting it into heat. Antioxidants stabilize the polymer by terminating the chain reaction due to the absorption of UV light from sunlight. The chain reaction initiated by photo-oxidation leads to cessation of crosslinking of the polymers and degradation the property of polymers.

Chapter 11

Rust

Colors of rust

Rust is a general term for a series of iron oxides. Colloquially, the term is applied to red oxides, formed by the reaction of iron and oxygen in the presence of water or air moisture. There are also other forms of rust, such as the result of the reaction of iron and chlorine in an environment deprived of oxygen, such as rebar used in underwater concrete pillars, which generates green rust. Several forms of rust are distinguishable visually and by spectroscopy, and form under different circumstances. Rust consists of hydrated iron(III) oxides $Fe_2O_3 \cdot nH_2O$ and iron(III) oxide-hydroxide ($FeO(OH)$, $Fe(OH)_3$). Given sufficient time, oxygen, and water, any iron mass will eventually convert entirely to rust and disintegrate. Surface rust provides no protection to the underlying iron unlike the formation of patina on copper surfaces.

Rusting is the common term for corrosion of iron and its alloys, such as steel. Many other metals undergo equivalent corrosion, but the resulting oxides are not commonly called rust.

Chemical reactions

Heavy rust on the links of a chain near the Golden Gate bridge in San Francisco; it was continuously exposed to moisture and salt-laden spray, causing surface breakdown, cracking, and flaking of the metal.

Oxidation of iron metal

When iron is in contact with water and oxygen, or other strong oxidants and/or acids, it rusts. If salt is present as, for example, in salt water, it tends to rust more quickly, as a result of the electro-chemical reactions. Iron metal is relatively unaffected by pure water or by dry oxygen. As with other metals, like aluminium, a tightly adhering oxide coating, a passivation layer, protects the bulk iron from further oxidation. Thus, the conversion of the passivating iron oxide layer to rust results from the combined action of two agents, usually oxygen and water. Other degrading solutions are sulfur dioxide in water and carbon dioxide in water. Under these corrosive conditions, iron hydroxide species are formed. Unlike iron oxides, the hydroxides do not adhere to the bulk metal. As they form and flake off from the surface, fresh iron is exposed, and the corrosion process continues until all of the iron is either consumed or all of the oxygen, water, carbon dioxide, or sulfur dioxide in the system are removed or consumed.

Associated reactions

A rusted (and dirt-encrusted) bolt; note the surface pitting and gradual shape-deformation, caused by severe oxidation

Rust in pipes can result in brown and black water.

The rusting of iron is an electrochemical process that begins with the transfer of electrons from iron to oxygen. The rate of corrosion is affected by water and accelerated by electrolytes, as illustrated by the effects of road salt on the corrosion of automobiles. The key reaction is the reduction of oxygen:

$$O_2 + 4\ e^- + 2\ H_2O \rightarrow 4\ OH^-$$

Because it forms hydroxide ions, this process is strongly affected by the presence of acid. Indeed, the corrosion of most metals by oxygen is accelerated at low pH. Providing the electrons for the above reaction is the oxidation of iron that may be described as follows:

$$Fe \rightarrow Fe^{2+} + 2\ e^-$$

The following redox reaction also occurs in the presence of water and is crucial to the formation of rust:

$$4\ Fe^{2+} + O_2 \rightarrow 4\ Fe^{3+} + 2\ O^{2-}$$

Additionally, the following multistep acid-base reactions affect the course of rust formation:

$$Fe^{2+} + 2\ H_2O \rightleftharpoons Fe(OH)_2 + 2\ H^+$$
$$Fe^{3+} + 3\ H_2O \rightleftharpoons Fe(OH)_3 + 3\ H^+$$

as do the following dehydration equilibria:

$$Fe(OH)_2 \rightleftharpoons FeO + H_2O$$
$$Fe(OH)_3 \rightleftharpoons FeO(OH) + H_2O$$
$$2\ FeO(OH) \rightleftharpoons Fe_2O_3 + H_2O$$

Rusted pyrite cubes

From the above equations, it is also seen that the corrosion products are dictated by the availability of water and oxygen. With limited dissolved oxygen, iron(II)-containing materials are favoured, including FeO and black lodestone (Fe_3O_4). High oxygen concentrations favour ferric materials with the nominal formulae $Fe(OH)_{3-x}O_{x/2}$. The nature of rust changes with time, reflecting the slow rates of the reactions of solids.

Furthermore, these complex processes are affected by the presence of other ions, such as Ca^{2+}, which both serve as an electrolyte, and thus accelerate rust formation, or combine with the hydroxides and oxides of iron to precipitate a variety of Ca-Fe-O-OH species.

Prevention

Rust is permeable to air and water, therefore the interior iron continues to corrode. Rust prevention thus requires coatings that preclude rust formation. Stainless steel forms a passivation layer of chromium(III) oxide. Similar passivation behavior occurs with magnesium, titanium, zinc, zinc oxides, aluminium, polyaniline, and other electroactive conductive polymers.

Galvanization

An important approach to rust prevention entails galvanization, which typically consists of an application, on the object to be protected, of a layer of zinc by either hot-dip galvanizing or electroplating. Zinc is traditionally used because it is cheap, adheres well to steel and provides a cathodic protection to the steel surface in case of damage of the Zinc layer. In more corrosive environments (such as salt water) cadmium is preferred. Galvanization often fails at seams, holes, and joints, where the coating is pierced. In these cases the coating provides cathodic protection to metal, where it acts as a galvanic anode rusting in preference. More modern coatings add aluminium to the coating as *zinc-alume*, aluminium will migrate to cover scratches and thus provide protection for longer. These approaches rely on the aluminium and zinc oxides protecting the once-scratched surface rather than oxidizing as a sacrificial anode. In some cases, very aggressive environments or long design life, both zinc and a coating are applied to provide corrosion protection.

Cathodic protection

Cathodic protection is a technique used to inhibit corrosion on buried or immersed structures by supplying an electrical charge that suppresses the electro-chemical reaction. If correctly applied, corrosion can be stopped completely. In its simplest form it is achieved by attaching a sacrificial anode thus making the iron or steel the cathode in the cell formed. The sacrificial anode must be made from something with a more negative electrode potential than the iron or steel, commonly zinc, aluminium or magnesium.

Coatings and painting

Flaking paint, exposing a patch of surface rust on sheet-metal

Rust formation can be controlled with coatings, such as paint, that isolate the iron from the environment. Large structures with enclosed box sections, such as ships and modern automobiles, often have a wax-based product (technically a "slushing oil") injected into these sections. Such treatments also contain rust inhibitors. Covering steel with concrete can provide some protection to steel by the high pH environment at the steel-concrete interface. However rusting of steel in concrete can still be a problem.

Plating

Rusting can completely degrade iron. Note the galvanization on the unrusted portions.

- Zinc Plating (Galvanized iron/steel): Iron or steel coated with zinc metal layer. Hot dipped method or zinc blasting method may be used.
- Tin plating : mild steel sheet coated with a tin layer.
- Chrome plating, where a thin layer of chromium is electrolytically applied to the steel, providing both rust protection and a highly polished, bright appearance. Often used on the silver-coloured components of bicycles, motorbikes and automobiles.

Bluing

Bluing is a technique that can provide limited resistance to rusting for small steel items, such as firearms; for it to be successful, water-displacing oil is rubbed onto the blued steel.

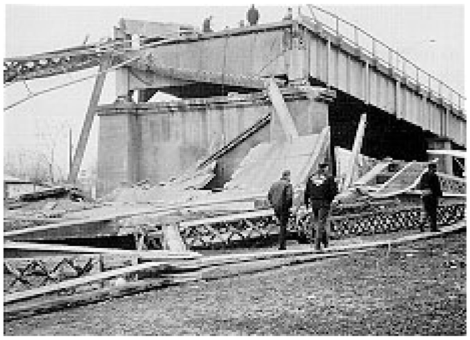
Humidity

Rust can be avoided by controlling the moisture in the atmosphere. An example of this is the use of silica gel.

Inhibitors

Corrosion inhibitors, like gas phase or volatile inhibitors can be used to prevent corrosion in closed systems.

Economic impact



The collapsed Silver Bridge, as seen from the Ohio side

Rust is associated with degradation of iron-based tools and structures. As rust has a much higher volume than the originating mass of iron, its build-up can also cause failure by forcing apart adjacent parts — a phenomenon sometimes known as "rust smacking". It was the cause of the collapse of the Mianus river bridge in 1983, when the bearings rusted internally and pushed one corner of the road slab off its support. Rust was also an important factor in the Silver Bridge disaster of 1967 in West Virginia, when a steel suspension bridge collapsed in less than a minute, killing 46 drivers and passengers on the bridge at the time.

The Kinzua Bridge after it collapsed

Kinzua Bridge in Pennsylvania was blown down by a tornado in 2003 largely because the central base bolts holding the structure to the ground had rusted away, leaving the bridge resting by gravity alone.

Similarly, corrosion of concrete-covered steel and iron can cause the concrete to spall, creating severe structural problems. It is one of the most common failure modes of reinforced concrete bridges.

Chapter 12

Schikorr Reaction

iron(II) hydroxide, $Fe(OH)_2$, the start-reagent of the *Schikorr reaction*.

Magnified crystals of iron(II,III) oxide (Fe_3O_4), the end-product of the *Schikorr reaction* along with hydrogen gas.

The **Schikorr reaction** formally describes the conversion of the iron(II) hydroxide ($Fe(OH)_2$) into iron(II,III) oxide (Fe_3O_4).

The bases of this transformation reaction were first studied by Gerhard Schikorr, a German specialist of iron corrosion, in his early works (~1928-1933) on iron(II) and iron(III) hydroxides. The global reaction that Schikorr proposed to explain his observations onto the iron hydroxides conversion, and which later received his name, can be written as follows:

$$3\ Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2\ H_2O$$

Reaction mechanism

The *Schikorr reaction* involves two distinct processes:

- the anaerobic oxidation of two Fe(II) (Fe^{2+}) into Fe(III) (Fe^{3+}) by the protons of water. The reduction of two water protons is accompanied by the production of molecular hydrogen (H_2), and;
- the loss of two water molecules from the iron(II) and iron(III) hydroxides giving rise to its dehydration and to the formation of a thermodynamically more stable phase iron(II,III) oxide.

The global reaction can thus be decomposed in half redox reactions as follows:

$$2\ (Fe^{2+} \rightarrow Fe^{3+} + e^-)\ \text{(oxidation of 2 iron(II) ions)}$$
$$2\ (H_2O + e^- \rightarrow \tfrac{1}{2}\ H_2 + OH^-)\ \text{(reduction of 2 water protons)}$$

to give:

$$2\ Fe^{2+} + 2\ H_2O \rightarrow 2\ Fe^{3+} + H_2 + 2\ OH^-$$

Adding to this reaction one intact iron(II) ion for each two oxidized iron(II) ions leads to:

$$3\ Fe^{2+} + 2\ H_2O \rightarrow Fe^{2+} + 2\ Fe^{3+} + H_2 + 2\ OH^-$$

Electroneutrality requires the iron cations on both sides of the equation to be counter-balanced by 6 hydroxyl anions (OH^-):

$$3\ Fe^{2+} + 6\ OH^- + 2\ H_2O \rightarrow Fe^{2+} + 2\ Fe^{3+} + H_2 + 8\ OH^-$$
$$3\ Fe(OH)_2 + 2\ H_2O \rightarrow Fe(OH)_2 + 2\ Fe(OH)_3 + H_2$$

For completing the main reaction, two companion reactions have still to be taken into account:

The autoprotolysis of the hydroxyl anions; a proton exchange between two OH^-, like in a classical acid-base reaction:

$OH^{-} + OH^{-} \rightarrow O^{2-} + H_2O$
acid 1 + base 2 → base 1 + acid 2, or also,
$2\ OH^{-} \rightarrow O^{2-} + H_2O$

it is then possible to reorganize the global reaction as:

$3\ Fe(OH)_2 + 2\ H_2O \rightarrow (FeO + H_2O) + (Fe_2O_3 + 3\ H_2O) + H_2$
$3\ Fe(OH)_2 + 2\ H_2O \rightarrow FeO + Fe_2O_3 + 4\ H_2O + H_2$
$3\ Fe(OH)_2 \rightarrow FeO + Fe_2O_3 + 2\ H_2O + H_2$

Considering then the formation reaction of iron(II,III) oxide:

$Fe(II)O + Fe(III)_2O_3 \rightarrow Fe_3O_4$

it is possible to write the balanced global reaction:

$3\ Fe(OH)_2 \rightarrow (FeO{\cdot}Fe_2O_3) + 2\ H_2O + H_2$

in its final form, known as the *Schikorr reaction*:

$3\ Fe(OH)_2 \rightarrow Fe_3O_4 + 2\ H_2O + H_2$

Occurrences

The Schikorr reaction can occur in the process of anaerobic corrosion of iron and carbon steel in various conditions.

Anaerobic corrosion of metallic iron to give iron(II) hydroxide and hydrogen:

$3\ (Fe + 2\ H_2O \rightarrow Fe(OH)_2 + H_2)$

followed by the Schikorr reaction:

$3\ Fe(OH)_2 \rightarrow Fe_3O_4 + 2\ H_2O + H_2$

give the following global reaction:

$3\ Fe + 6\ H_2O \rightarrow Fe_3O_4 + 2\ H_2O + 4\ H_2$
$3\ Fe + 4\ H_2O \rightarrow Fe_3O_4 + 4\ H_2$

At low temperature, the anaerobic corrosion of iron can give rise to the formation of "green rust"(fougerite) an unstable layered double hydroxide (LDH). In function of the geochemical conditions prevailing in the environment of the corroding steel, iron(II) hydroxide and green rust can progressively transform in iron(II,III) oxide, or if bicarbonate ions are present in solution, they can also evolve towards more stable carbonate phases such as iron carbonate ($FeCO_3$), or iron(II) hydroxycarbonate

($Fe_2(OH)_2(CO_3)$, chukanovite) isomorphic to copper(II) hydroxycarbonate ($Cu_2(OH)_2(CO_3)$, malachite) in the copper system.

Application fields

Anaerobic oxidation of iron and steel commonly finds place in oxygen-depleted environments, such as in permanently water-saturated soils, peat bogs or wetlands in which archaeological iron artefacts are often found.

Anaerobic oxidation of carbon steel of canisters and overpacks is also expected to occur in deep geological formations in which high-level radioactive waste (HLW) and spent fuels (SF) should be ultimately disposed. Nowadays, in the frame of the corrosion studies related to HLW disposal, anaerobic corrosion of steel is receiving a renewed and continued attention. Indeed, it is essential to understand this process to guarantee the total containment of HLW waste in an engineered barrier during the first centuries or millennia when the radiotoxicity of the waste is high and when it emits a significant quantity of heat.

The question is also relevant for the corrosion of the reinforcement bars (rebars) in concrete (Aligizaki *et al.*, 2000). This deals then with the service life of concrete structures, amongst others the near-surface vaults intended for hosting low-level radioactive waste.

Hydrogen evolution

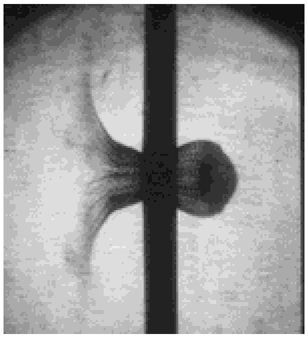
The slow but continuous production of hydrogen in deep low-permeability argillaceous formations could represent a problem for the long-term disposal of radioactive waste (Ortiz *et al.*, 2001; Nagra, 2008; recent Nagra NTB reports). Indeed, a gas pressure build-up could occur if the rate of hydrogen production by the anaerobic corrosion of carbon-steel and by the subsequent transformation of green rust into magnetite should exceed the rate of diffusion of dissolved H_2 in the pore water of the formation. The question is presently the object of many studies (King, 2008; King and Kolar, 2009; Nagra Technical Reports 2000–2009) in the countries (Belgium, Switzerland, France, Canada) envisaging the option of disposal in clay formation.

Hydrogen embrittlement of steel alloys

When nascent hydrogen is produced by anaerobic corrosion of iron by the protons of water, the atomic hydrogen can diffuse into the metal crystal lattice because of the existing concentration gradient. After diffusion, hydrogen atoms can recombine into molecular hydrogen giving rise to the formation of high-pressure micro-bubbles of H_2 in the metallic lattice. The trends to expansion of H_2 bubbles and the resulting tensile stress can generate cracks in the metallic alloys sensitive to this effect also known as hydrogen embrittlement. Several recent studies (Turnbull, 2009; King, 2008; King and Kolar, 2009) address this question in the frame of the radioactive waste disposal in Switzerland and Canada.

Chapter 13

Spall



Very high speed photography of a small projectile striking a thin aluminium plate at 7000 m/s. The impact causes the projectile to disintegrate, and generates a large number of small fragments from the aluminum. This can occur without penetration of the plate.

Spall are flakes of a material that are broken off a larger solid body and can be produced by a variety of mechanisms, including as a result of projectile impact, corrosion, weathering, cavitation, or excessive rolling pressure (as in a ball bearing). **Spalling** and spallation both describe the process of surface failure in which spall is shed.

The terms **spall** and **spalling** have been adopted by particle physicists; in neutron scattering instruments, neutrons are generated by bombarding a uranium target with a stream of atoms. The neutrons that are ejected from the target are known as spall.

Mechanical spalling

Mechanical spalling occurs at high stress contact points, for example, in a ball bearing. Spalling occurs in preference to brinelling where the maximal shear stress occurs not at the surface, but just below, shearing the spall off.

One of the simplest forms of mechanical spalling is plate impact, in which two waves of compression are reflected on the free-surfaces of the plates and then interact to generate a region of high tension stress inside one of the plates.

Spalling can also occur as an effect of cavitation, where fluids are subjected to localized low pressures that cause vapor bubbles to form, typically in pumps, water turbines, vessel propellers, and even piping under some conditions. When such bubbles collapse, a localized high pressure can cause spalling on adjacent surfaces.

Antitank warfare

In anti-tank warfare, spalling through mechanical stress is an intended effect of high explosive squash head (HESH) anti-tank shells and many other munitions which may not be powerful enough to pierce the armor of a target. The relatively soft warhead, containing or made of plastic explosive, flattens against the armor plating on tanks and other armored fighting vehicles (AFVs) and explodes, creating a shock wave that travels through the armor as a compression wave and is reflected at the free surface as a tensile wave breaking (tensile stress/strain fracture) the metal on the inside. The resulting spall is dangerous to crew and equipment, and may result in a partial or complete disablement of a vehicle and/or its crew. Many AFVs are equipped with spall liners inside their armor for protection.

Kinetic energy penetrators, if it can defeat the armor, generally causes spalling within the target as well, which helps to destroy/disable the vehicle and/or its crew.

Spalling in mechanical weathering

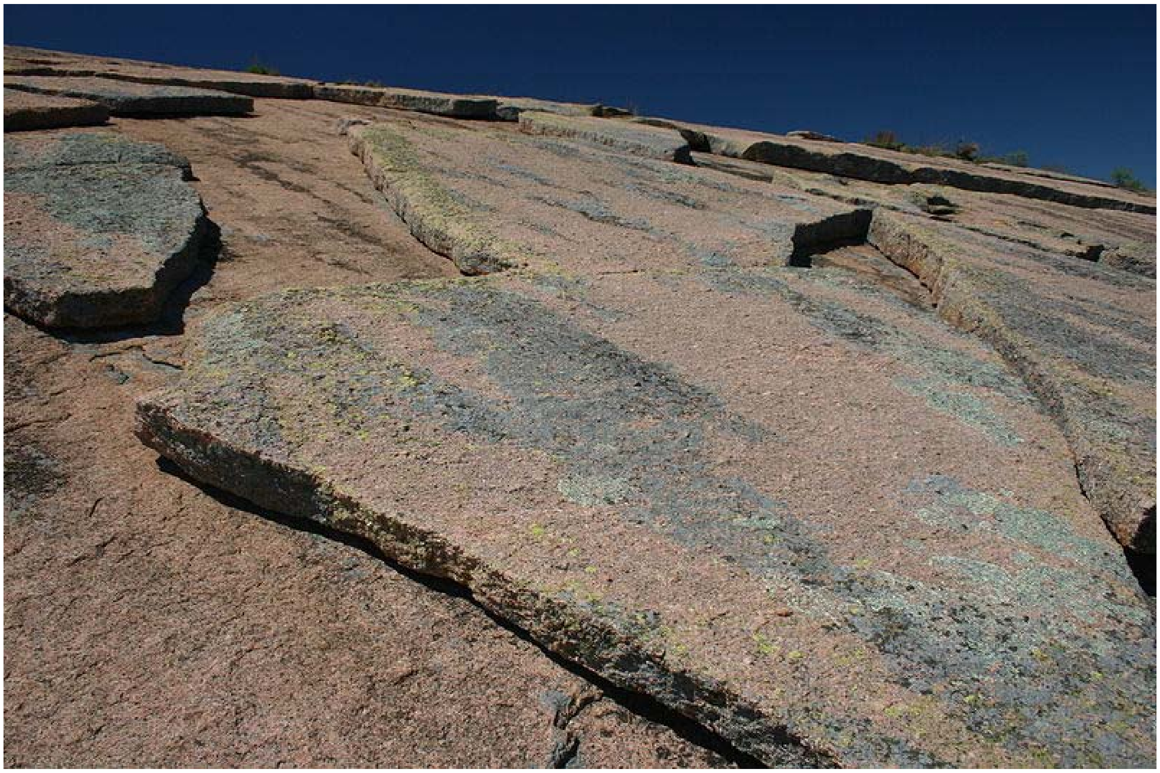
Spalling is a common mechanism of rock weathering, and occurs at the surface of a rock when there are large shear stresses under the surface. This form of Mechanical weathering can be caused by freezing and thawing, unloading, thermal expansion and contraction or salt deposition.

Freeze thaw weathering is caused by moisture freezing inside cracks in rock. Upon freezing its volume expands, causing large forces which cracks spall off the outer surface. As this cycle repeats the outer surface repeatedly undergoes spalling, resulting in weathering.

Some stone and masonry surfaces used as building surfaces will absorb moisture at their surface. If exposed to severe freezing conditions the surface may flake off due to the expansion of the water. This effect can also be seen in terra-cotta surfaces (even if glazed) if there is an entrance for water at the edges.

Unloading is the release of pressure due to the removal of an overburden. When the pressure is reduced rapidly, the rapid expansion of the rock causes high surface stress and spalling.

Exfoliation



Granite dome exfoliation

Exfoliation (or onion skin weathering) is the gradual removing of spall due to the cyclic increase and decrease in the temperature of the surface layers of the rock. Rocks do not conduct heat well, so when they are exposed to extreme heat the outer most layer becomes much hotter than the rock underneath causing different thermal expansion. This differential expansion causes sub-surface shear stress, in turn causing spalling. Extreme temperature change, such as forest fires, can also cause spalling of rock. This mechanism of weathering causes the outer surface of the rock to fall off in thin fragments, sheets or flakes, hence the name exfoliation or onion skin weathering.

Salt spalling

Salt spalling is a specific type of weathering which occurs in porous building materials, such as brick, natural stone, tiles and concrete. Dissolved salt is carried through the material in water and crystallises inside the material near the surface as the water evaporates. As the salt crystals expand this builds up shear stresses which break away spall from the surface.

Some believe that porous building materials can be protected against salt spalling by treatment with penetrating sealants which are hydrophobic (water repellent) and will penetrate deeply enough to keep water with dissolved salts well away from the surface. Great care and expert advice must be taken, though, to ensure that any coating is compatible with the substrate in terms of breathability (ability to allow the release of vapors from inside while preventing water intrusion), or other serious problems can be created.

It must always be assumed that water—possibly even arriving in vapor form from the interior—will collect behind the wall surface, and it must be allowed to both drain and evaporate. Many bricks and stones have been damaged beyond repair by the well-intentioned application of the wrong coating, once the coated masonry has passed through a few freeze-thaw cycles, pipe leaks, etc.

Corrosion

In corrosion, spalling occurs when a substance (metal or concrete) sheds tiny particles of corrosion products as the corrosion reaction progresses. These corrosion products are not soluble or permeable, but, unlike passivation, they do not adhere to the parent material's surface to form a barrier to further corrosion. This happens as the result of a large volume change during the reaction.

In the case of actinide metals (most notably the depleted uranium used in some types of ammunition), the material expands so strongly upon exposure to air that a fine layer of oxide is forcibly expelled from the surface. A slowly oxidised plug of metallic uranium can sometimes resemble an onion subjected to desquamation. The main hazard however arises from the pyrophoric character of actinide metals which can spontaneously ignite when their specific area is high. This property, along with these elements inherent toxicity and (for some to a lesser extent) radioactivity, make them dangerous to handle in metallic form under air. Therefore, they are often handled under an inert atmosphere (nitrogen or argon) inside an anaerobic glovebox.

Chapter 14

Thermal Degradation of Polymers

Thermal degradation of polymers is molecular deterioration as a result of overheating. At high temperatures the components of the long chain backbone of the polymer can begin to separate (molecular scission) and react with one another to change the properties of the polymer. Thermal degradation can present an upper limit to the service temperature of plastics as much as the possibility of mechanical property loss. Indeed unless correctly prevented, significant thermal degradation can occur at temperatures much lower than those at which mechanical failure is likely to occur. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight (and molecular weight distribution) of the polymer and typical property changes include reduced ductility and embrittlement, chalking, color changes, cracking, general reduction in most other desirable physical properties.

The Mechanism of Thermal Degradation

Most types of degradation follow a similar basic pattern. The conventional model for thermal degradation is that of an autoxidation process which involves the major steps of initiation, propagation, branching, and termination.

Initiation

The initiation of thermal degradation involves the loss of a hydrogen atom from the polymer chain as a result of energy input from heat or light. This creates a highly reactive and unstable polymer 'free radical' (R•) and a hydrogen atom with an unpaired electron (H•).

Propagation

The propagation of thermal degradation can involve a variety of reactions and one of these is where the free radical (R•) reacts with an oxygen (O_2) molecule to form a peroxy radical (ROO•) which can then remove a hydrogen atom from another polymer chain to form a hydroperoxide (ROOH) and so regenerate the free radical (R•). The hydroperoxide can then split into two new free radicals, (RO•) + (•OH), which will continue to propagate the reaction to other polymer molecules. The process can therefore accelerate depending on how easy it is to remove the hydrogen from the polymer chain.

Termination

The termination of thermal degradation is achieved by 'mopping up' the free radicals to create inert products. This can occur naturally by combining free radicals or it can be assisted by using stabilizers in the plastic.

The Research Methods of Thermal Degradation of Polymers

TGA

(Thermogravimetric Analysis) (TGA) refers to the techniques where a sample is heated in a controlled atmosphere at a defined heating rate whilst the samples mass is measured. When a polymer sample degrades, its mass decreases due to the production of gaseous products like carbon monoxide, water vapour and carbon dioxide.

DTA and DSC

(Differential thermal analysis) (DTA) and (differential scanning calorimetry) (DSC): Analyzing the heating effect of polymer during the physical changes in terms of glass transition, melting, and so on. These techniques measure the heat flow associated with oxidation.

Ways of Polymer Thermal Degradation

Depolymerisation

Under thermal effect, the end of polymer chain departs, and forms low free radical which has low activity. Then according to the chain reaction mechanism, the polymer loses the monomer one by one. However, the molecular chain doesn't change a lot in a short time. The reaction is shown below. This process is common for polymethymethacrylate (perspex).

$CH_2\text{-}C(CH_3)COOCH_3\text{-}CH_2\text{-}C^*(CH_3)COOCH_3 \rightarrow CH_2\text{-}C^*(CH_3)COOCH_3 + CH_2{=}C(CH_3)COOCH_3$

Random Chain Scission

The backbone will be break down randomly, could be occurred at any position of the backbone. The molecular weight decreases rapidly, and cannot get monomer in this reaction, this is because it forms new free radical which has high activity can occurs intermolecular chain transfer and disproportion termination with the CH2'group.

CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2'→ CH_2-CH_2-CH=CH_2 + CH_3-CH_2-CH_2' or CH_2'+CH_2=CH-CH_2-CH_2-CH_2-CH_3

Side-Group Elimination

Groups that are attached to the side of the backbone are held by bonds which are weaker than the bonds connecting the chain. When the polymer was being heated, the side groups are stripped off from the chain before it is broken into smaller pieces. For example the PVC eliminates HCL, under 100-120^{o}C.

CH_2(Cl)CHCH_2CH(Cl)→CH=CH-CH=CH+2HCl

Oxidation of the polymer

Polyphenylene oxide is well known for oxidation.

Chapter 15

Sulfide & Tribocorrosion

Sulfide

$$S^{2-}$$

sulfide anion

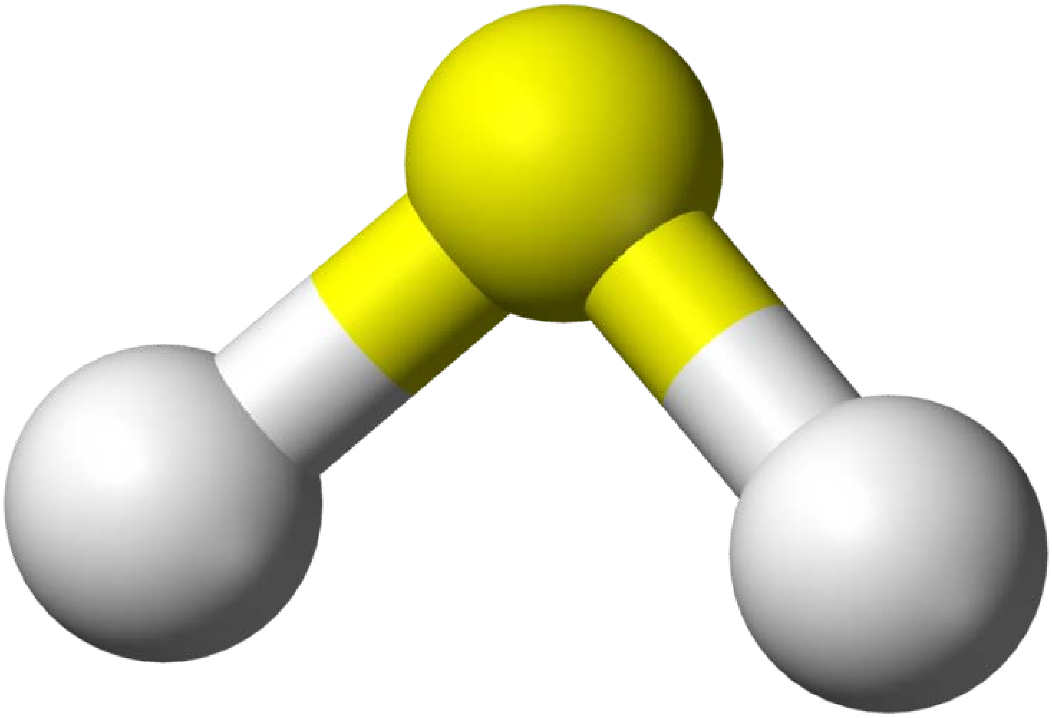
A **sulfide** is an anion of sulfur in its lowest oxidation state of −2. Sulfide is also a slightly archaic term for thioethers, a common type of organosulfur compound that are well known for their bad odors.

Properties

The dianion S^{2-} exists only in strongly alkaline aqueous solutions. Such solutions can form by dissolution of H_2S or alkali metal salts such as Li_2S, Na_2S, and K_2S in the presence of extra hydroxide. The ion S^{2-} is exceptionally basic with a $pK_a > 14$. It does not exist in appreciable concentrations even in highly alkaline water, being undetectable at pH < ~15 (8 M NaOH).

$$^{-}S{-}H$$

Hydrogen sulfide ion



Hydrogen sulfide

Instead, sulfide combines with protons to form HS^-, which is variously called **hydrogen sulfide** ion, **hydrosulfide** ion, **sulfhydryl** ion, or **bisulfide** ion. At still lower pH's (<7), HS^- converts to H_2S, hydrogen sulfide.

Sulfides are moderately strong reducing agents. They react with oxygen in the air in elevated temperatures to form higher-valence sulfur salts, such as sulfates and sulfur dioxide.

Metal derivatives

Aqueous solutions of transition metals cations react with sulfide sources (H_2S, NaHS, Na_2S) to precipitate solid sulfides. Such inorganic sulfides typically have very low solubility in water, and many are related to minerals with the same composition. One famous example is the bright yellow species CdS or "cadmium yellow". The black tarnish formed on sterling silver is Ag_2S. Such species are sometimes referred to as salts. In fact, the bonding in transition metal sulfides is highly covalent, which gives rise to their semiconductor properties, which in turn is related to the deep colors. Several have practical applications as pigments, in solar cells, and as catalysts.

Geology

Many important metal ores are sulfides. Significant examples include: argentite (silver sulfide), cinnabar (mercury), galena (lead sulfide), molybdenite (molybdenum sulfide), pentlandite (nickel sulfide]), realgar (arsenic sulfide), and stibnite (antimony), sphalerite (zinc sulfide), and pyrite (iron disulfide), and chalcopyrite (iron-copper sulfide).

Corrosion induced by sulfide

Dissolved free sulfides (H_2S, HS^- and S^{2-}) are very aggressive species for the corrosion of many metals such as, *e.g.*, steel, stainless steel, and copper. Sulfides present in aqueous solution are responsible for stress corrosion cracking (SCC) of steel, and is also known as sulfide stress cracking. Corrosion is a major concern in many industrial installations processing sulfides: sulfide ore mills, deep oil wells, pipeline transporting soured oil, Kraft paper factories. Microbially-induced corrosion (MIC) or biogenic sulfide corrosion are also caused by sulfate reducing bacteria producing sulfide.

Oxidation of sulfide can also form thiosulfate ($S_2O_3^{2-}$) an intermediate species responsible for severe problems of pitting corrosion of steel and stainless steel while the medium is also acidified by the production of sulfuric acid when oxidation is more advanced.

Organic chemistry

In organic chemistry, "sulfide" usually refers to the linkage C-S-C, although the term thioether is less ambiguous. For example, the thioether dimethyl sulfide is CH_3-S-CH_3. Polyphenylene sulfide (see below) has the empirical formula C_6H_4S. Occasionally, the term sulfide refers to molecules containing the -SH functional group. For example, methyl sulfide can mean CH_3-SH. The preferred descriptor for such SH-containing compounds is thiol or mercaptan, i.e. methanethiol, or methyl mercaptan.

Disulfides

Confusion arises from the different meanings of the term "disulfide". Molybdenum disulfide (MoS_2) consists of separated sulfide centers, in association with molybdenum in the formal 4+ oxidation state (Mo^{4+}). Iron disulfide (pyrite, FeS_2) on the other hand consists of S_2^{2-}, or $^-S–S^-$ dianion, in association with divalent iron in the formal 2+ oxidation state (ferrous ion: Fe^{2+}). Dimethyldisulfide has the chemical binding CH_3-S–S-CH_3, whereas carbon disulfide has no S–S bond, being S=C=S (linear molecule analog to CO_2). Most often in sulfur chemistry and in biochemistry, the disulfide term is commonly ascribed to the sulfur analogue of the peroxide −O–O− bond. The disulfide bond (−S–S−) plays a major role in the conformation of proteins and in the catalytic activity of enzymes.

Examples

Formula		Melting point (°C)	Boiling point (°C)	CAS number
H_2S	Hydrogen sulfide is a very toxic and corrosive gas characterised by a typical odour of "rotten egg".	-85,7	-60,20	7783-06-4
CdS	Cadmium sulfide can be used in photocells.	1750		1306-23-6
	Calcium polysulfide ("lime sulfur") is a traditional fungicide in gardening.			
CS_2	Carbon disulfide is sometimes used as a solvent in industrial chemistry.	-111.6	46	75-15-0
PbS	Lead sulfide is used in infra-red sensors.	1114		1314-87-0
MoS_2	Molybdenum disulfide, the mineral molybdenite, is used as a catalyst to remove sulfur from fossil fuels; also as lubricant for high-temperature and high-pressure applications.			1317-33-5
$Cl\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}Cl$	Mustard Gas, is an organosulfide (thioether) that has been used as a chemical weapon in the first worldwar, the chloride on the molecule acts as a leaving group when in the presence of water and forms a thioether-alcohol and HCl.	13 - 14	217	505-60-2
Ag_2S	Silver sulfide is formed on silver electrical contacts operating in an atmosphere rich in hydrogen sulfide.			21548-73-2
Na_2S	Sodium sulfide is an important industrial chemical, used in manufacture of kraft paper, dyes, leather tanning, crude petroleum processing, treatment of heavy metal pollution, and others.	920	1180	1313-82-2
ZnS	Zinc sulfide is used for lenses and other optical devices in the infrared part of the spectrum. Zinc sulfide doped with silver is used in alpha detectors while zinc sulfide with traces of copper has applications in photoluminescent strips for emergency lighting and luminous watch dials.		1185	1314-98-3

MeS	Several metal sulfides are used as pigments in art, although their use has declined somewhat due to their toxicity. Sulfide pigments include cadmium, mercury, and arsenic.		
C_6H_4S	Polyphenylene sulfide is a polymer commonly called "Sulfar". Its repeating units are bonded together by sulfide (thioether) linkages.		26125-40-6 25212-74-2
SeS_2	Selenium sulfide is an antifungal used in anti-dandruff preparations, such as Selsun Blue. The presence of the highly toxic selenium in healthcare and cosmetics products represents a general health and environmental concern.	<100	7488-56-4
FeS_2	The crystal lattice of pyrite is made of iron disulfide, in which iron is divalent and present as ferrous ion (Fe^{2+}).	600	1317-66-4

Safety

Many metal sulfides are so insoluble in water that they are probably not very toxic. Some metal sulfides, when exposed to a strong mineral acid, including gastric acids, will release toxic hydrogen sulfide.

Organic sulfides are highly flammable. When a sulfide burns to give sulfur dioxide (SO_2) gas.

Hydrogen sulfide, some of its salts, and almost all organic sulfides have a strong and putrid stench; rotting biomass releases these.

Tribocorrosion

Tribocorrosion is a material degradation process due to the combined effect of corrosion and wear. The name tribocorrosion expresses the underlying disciplines of tribology and corrosion. Tribology is concerned with the study of friction, lubrication and wear (its name comes from the Greek "tribo" meaning to rub) and corrosion is concerned with the chemical and electrochemical interactions between a material, normally a metal, and its environment. As a field of research tribocorrosion is relatively new, but tribocorrosion phenomena have been around ever since machines and installations are being used.

Wear is a mechanical material degradation process occurring on rubbing or impacting surfaces, while corrosion involves chemical or electrochemical reactions of the material. Corrosion may accelerate wear and wear may accelerate corrosion. One then speaks of corrosion accelerated wear or wear accelerated corrosion. Both these phenomena, as well as fretting corrosion (which results from small amplitude oscillations between contacting surfaces) fall into the broader category of tribocorrosion. Erosion-corrosion is another tribocorrosion phenomenon involving mechanical and chemical effects: impacting particles or fluids erode a solid surface by abrasion, chipping or fatigue while simultaneously the surface corrodes.

Phenomena in different engineering fields

Tribocorrosion occurs in many engineering fields. It reduces the life-time of pipes, valves and pumps, of waste incinerators, of mining equipment or of medical implants, and it can affect the safety of nuclear reactors or of transport systems. On the other hand, tribocorrosion phenomena can also be applied to good use, for example in the chemical-mechanical planarization of wafers in the electronics industry or in metal grinding and cutting in presence of aqueous emulsions. Keeping this in mind, we may define tribocorrosion in a more general way independently of the notion of usefulness or damage or of the particular type of mechanical interaction: Tribocorrosion concerns the irreversible transformation of materials or of their function as a result of simultaneous mechanical and chemical/electrochemical interactions between surfaces in relative motion.

Biotribocorrosion

Biotribocorrosion covers the science of surface transformations resulting from the interactions of mechanical loading and chemical/electrochemical reactions that occur between elements of a tribological system exposed to biological environments. . It has been studied for aritificial joint prostheses. It is important to understand material degradation processes for joint implants to achieve longer service life and better safety issues for such devices.

Passive metals

While tribocorrosion phenomena may affect many materials, they are most critical for metals, especially the normally corrosion resistant so-called passive metals. The vast majority of corrosion resistant metals and alloys used in engineering (stainless steels, titanium, aluminium etc.) fall into this category. These metals are thermodynamically unstable in the presence of oxygen or water and they derive their corrosion resistance from the presence at the surface of a thin oxide film, called the **passive film**, which acts as a protective barrier between the metal and its environment. Passive films are usually just a few atomic layers thick. Nevertheless, they can provide excellent corrosion protection because if damaged accidentally they spontaneously self-heal by metal oxidation. However, when a metal surface is subjected to severe rubbing or to a stream of impacting particles the passive film damage becomes continuous and extensive. The self-healing process may no longer be effective and in addition it requires a high rate of metal oxidation. In other words, the underlying metal will strongly corrode before the protective passive film is reformed, if at all. In such a case, the total material loss due to tribocorrosion will be much higher than the sum of wear and corrosion one would measure in experiments with the same metal where only wear or only corrosion takes place. The example illustrates the fact that the rate of tribocorrosion is not simply the addition of the rate of wear and the rate of corrosion but it is strongly affected by synergistic and antagonistic effects between mechanical and chemical mechanisms. To study such effects in the laboratory, one most often uses mechanical wear testing rigs which are equipped with an electrochemical cell. This permits one to control independently the mechanical and chemical parameters. For example, by imposing a given potential to the rubbing metal one can simulate the oxidation potential of the environment and in addition, under certain conditions, the current flow is a measure of the instantaneous corrosion rate. For a deeper understanding tribocorrosion experiments are supplemented by detailed microscopic and analytical studies of the contacting surfaces.

At high temperatures, the more rapid generation of oxide due to a combination of temperature and tribological action during sliding wear can generate potentially wear resistant oxide layers known as 'glazes'. Under such circumstances, tribocorrosion can be used potentially in a beneficial way.