

CHEMISTRY - COURSE 224**A REVIEW OF 424**

GOAL

To review the chemical technology addressed in 424.

OBJECTIVES AND TESTS

Since this is a review lesson, there are no formal objectives.

The objectives for 424 are an appropriate study guide.

TOPICS

This lesson will review the topics listed below and will briefly indicate their importance within the CANDU system:

- pH
- Conductivity
- Radiolysis
- Recombination Units
- Activation
- IX Columns Operation
- Filtration
- Corrosion Principles
- Types of Corrosion:
 - Uniform Corrosion
 - Galvanic Corrosion
 - Pitting and Crevice Corrosion
 - Stress Corrosion Cracking (SCC)
 - Corrosion Fatigue
 - Microbiologically Induced Corrosion (MIC)
 - Erosion Corrosion
- Minimizing Corrosion

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pH

All aqueous solutions contain both hydrogen ions $[H^+]$ and hydroxyl or hydroxide ions $[OH^-]$. The concentration of $[H^+]$ multiplied by the concentration of $[OH^-]$ equals 10^{-14} at $25^\circ C$. The relative proportion of hydrogen and hydroxyl ions determines whether the solution is acidic, neutral, or basic (alkaline):

- If $[H^+]$ and $[OH^-]$ ion concentrations are both 10^{-7} moles/litre, the solution is neutral.
- If $[H^+]$ ion concentration $< 10^{-7}$ moles/litre then the $[OH^-]$ ion concentration is $> 10^{-7}$ moles per litre, and the solution is alkaline or basic. The term caustic may be used to indicate a very strongly alkaline solution.
- If $[H^+]$ concentration $> 10^{-7}$ moles/litre then the $[OH^-]$ ion concentration is $< 10^{-7}$ moles per litre, and the solution is acidic.

The conventional definition of pH is **the negative logarithm of the hydrogen ion concentration, in moles per litre at 25 C.**

pH is used to indicate the relative acidity or alkalinity of a solution, as shown in Figure 1. Since the pH scale is logarithmic, a unit change in pH reflects a factor of ten change in $[H^+]$ concentration.

Recall that 10^{-6} is greater than 10^{-7} :

$$\begin{array}{l} 10^{-6} \rightarrow \text{pH } 6 \\ 10^{-7} \rightarrow \text{pH } 7 \\ 10^{-8} \rightarrow \text{pH } 8 \end{array} \quad \begin{array}{l} 10^{-6} = \underline{10} \times 10^{-7} \\ 10^{-8} = \underline{100} \times 10^{-8} \end{array}$$

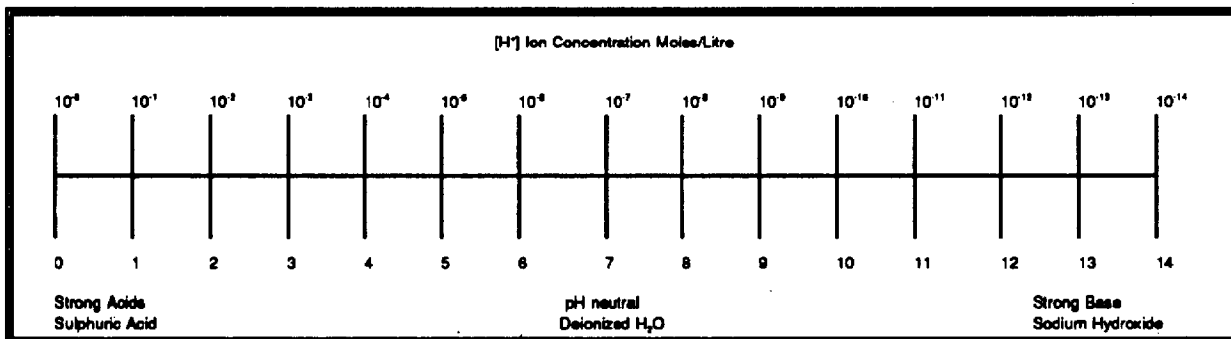


Figure 1: Relationship of the pH scale (25°C) and $[H^+]$ Ion Concentration

Examples of the Importance of pH Measurements

Monitoring pH, ie, $[H^+]$ ion concentration, is an important aspect of chemical control in CANDU systems. For example:

- Acid attack results in corrosion of metals and is a consequence of $[H^+]$ ions in solution. Minimizing this attack is commonly a matter of pH control.
- If the pH of the moderator system rises significantly above 7, any gadolinium nitrate poison in solution in the moderator will precipitate out as gadolinium.
- The HTS pH is held at 10.3 - 10.7 to minimize corrosion by $[D^+]$ and $[OD^-]$ and to maintain a protective magnetite layer on the carbon steel.
- Very low levels of $[H^+]$ and the corresponding very high $[OH^-]$ levels, ie, a high pH, can be a concern if they cause metal wastage or promote caustic embrittlement which is a form of stress corrosion cracking in an alkaline medium.

Summary

- All aqueous solutions contain both $[H^+]$ and $[OH^-]$ ions.
- pH is a measure of $[H^+]$ ion concentration.
- $[H^+]$ concentration determines whether a solution is acidic ($pH < 7$), neutral ($pH = 7$ at $25^\circ C$) or basic ($pH > 7$).
- pH is an important monitoring and control parameter in CANDU systems.

CONDUCTIVITY

The conductivity, K° , of a solution is a measure of its ability to conduct an electrical current. The SI unit for conductivity is the millisiemen per metre, mS/m. It is the ions in the solution that allow it to conduct. Figure 2 shows typical conductivities for various aqueous solutions.

The conductivity of a solution is not specific to any one ion but is determined by the total ionic concentration. Note the difference therefore, between pH which is $[H^+]$ -ion specific, and conductivity which is non-ion specific.

A change in the pH of a solution will always change its conductivity, whereas a conductivity change may or may not alter the solution pH. For example, adding common salt, NaCl, to water increases its conductivity but has no effect on its pH.

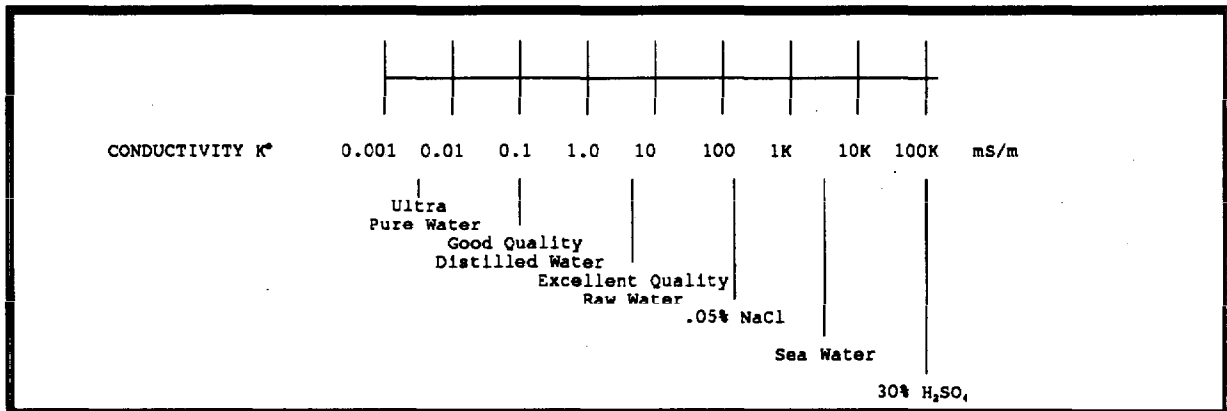


Figure 2: Conductivity of Various Aqueous Solutions

Pure deionized water has a very low conductivity, ie, a high electrical resistance. Any substance that dissociates into ions in water will increase the electrical conductivity of the water.

Solutes

Solutes are substances that are dissolved in a solvent; water is an example of a common solvent. Solutes are often classified according to the electrical conductivity of their aqueous or water solutions. The three categories are **non-electrolytes**, **weak electrolytes** and **strong electrolytes**.

Non-electrolytes are substances which dissolve as molecules producing non-conducting solutions. Common examples are alcohol and sugar.

Weak electrolytes are substances which exist in solution as an equilibrium mixture of ions and molecules. A common NGS example is boric acid. A water solution of boric acid contains a relatively small number of hydrogen and borate ions as compared to the number of boric acid molecules. Other examples are vinegar and household ammonia.

Strong electrolytes are substances which exist in water almost exclusively in the form of ions. Their electrical conductivities even at low concentrations (0.1 molar) are orders of magnitude higher than that of pure water. Common examples encountered in nuclear operations are lithium hydroxide, gadolinium nitrate, caustic soda and sulphuric acid. Ocean water is a strong electrolyte.

The Importance of Electrical Conductivity

The following are examples of the importance of electrical conductivity in the plant:

- Boiler water conductivity measurements may be used to monitor the effectiveness of boiler blowdowns.
- Moderator D₂O conductivity is kept As Low As Reasonably Achievable (ALARA) to minimize radiolysis.
- Corrosion can be an electrochemical process. Water containing dissociated ions can form an electrolyte which promotes corrosion.
- Stator cooling water must have a very low conductivity in order to act as an electrical insulator.
- The conductivity of the effluent from an IX column provides an indication of the state of the resin.

Summary

- The conductivity, K^o, of an aqueous solution is determined by the total ion concentration.
- The SI unit for conductivity is mS/m.
- Solutes are classified as non-electrolytes, weak electrolytes or strong electrolytes.
- Conductivity is an important parameter in the monitoring and control of the chemistry of nuclear station water systems.

RADIOLYSIS

The bonds holding the atoms together in a covalent molecule are produced by the sharing of electron pairs between adjacent atoms. Ionizing radiation is able to transfer energy to these electrons, which destroys the bond between atoms, causing the molecule to break down. (Ionizing radiation is fully described in 427, lesson 2.)

Although the mechanism is different (nucleus interaction), neutron irradiation also causes molecules to break down.

This chemical decomposition caused by radiation is called radiolysis.

Materials affected by radiolysis in the CANDU system include D₂O, air and polymers. The radiolytes (radiolytic fragments) invariably form new compounds.

In $2\text{D}_2\text{O} \xrightarrow{\text{radiolysis}} 2\text{D}_2 + \text{O}_2$, the squiggly arrow signifies the radiolysis reaction. This produces both deuterium and oxygen molecules. Radiolysis of D_2O is increased by many impurities.

Concerns Relating to Radiolysis in the CANDU System

Moderator System

Deuterium and oxygen present an explosion hazard when they migrate to the helium cover gas. Production of these gases is increased by many impurities. Passing the cover gas through recombination units to recombine the D_2 and O_2 into D_2O is required to alleviate this problem.

A significant portion of the moderator system is constructed of stainless steel and therefore is not subject to serious corrosion by the oxygen produced by radiolysis. At PNGS-A, however, the HX tubes are copper alloy which is attacked by O_2 .

Heat Transport System (HTS)

A high pH in the HTS limits corrosion of carbon steel by maintaining a non-porous magnetite (Fe_3O_4) layer on the steel. However, O_2 formed by radiolysis presents a serious corrosion problem for carbon steel and its protective magnetite layer. O_2 is scavenged from the HTS by adding H_2 to react with it, producing H_2O . The H_2O produced downgrades the D_2O only slightly.

The high operating pressure (≈ 9 MPa) of the HTS keeps most of the D_2 and other gases in solution. Therefore, D_2 does not present an explosion hazard in the HTS. Hydrogen addition is valved out of service prior to a shutdown involving depressurizing the HTS to minimize the amount of hydrogen that will come out of solution.

Air

The concern with radiolysis of air is that oxides of nitrogen will ultimately be formed and will subsequently react with moisture (H_2O , D_2O) to form acids of nitrogen. In addition to causing corrosion, these acids also promote radiolysis of the D_2O which can lead to cover gas deuterium excursions. IX columns are used to remove acids from the moderator D_2O .

Radiolysis of air is of limited concern because it is uncommon for air to be in contact with the required high radiation fields. In the past, drained calandria maintenance outages permitted air to enter the calandria resulting in massive radiolysis-induced nitric acid problems when the reactor was put back into service. This problem is now minimized by keeping the calandria filled with helium during such outages. However, at BNGS-A it is still possible for small amounts of air to enter the calandria via the booster assemblies during operation.

Polymers and Oils

Polymers include IX resins and plastics (eg, tubing, wire insulation).

Plastics often become harder and more brittle due to radiolysis. These effects are due to cross-linking, or new bonds forming between long molecular chains. Cross-linking is bonding between long chains in a polymer. This occurs after bonds within chains are broken in the course of radiolysis. Oils tend to thicken when exposed to radiation.

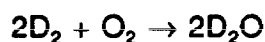
The use of polymers and oil must be restricted to accessible areas due to the danger and difficulty of replacing them in high radiation areas.

Summary

- Radiolysis is the chemical decomposition of molecules by radiation.
- Covalent molecules such as D₂O are especially prone to radiolysis.
- Explosion hazard due to O₂ and D₂ is the principle concern with respect to radiolysis in the moderator.
- Recombination units are used to minimize that explosion hazard.
- O₂ is potentially a serious corrosion problem in the HTS.
- O₂ is scavenged from the HTS by injecting H₂.
- Radiolysis of air leads to the production of acids which are corrosive and promote radiolysis in the moderator.
- Polymer and oil use is restricted to accessible areas to avoid radiolysis problems.

RECOMBINATION UNITS

As previously reviewed, moderator radiolysis can produce a potentially explosive mixture of deuterium (D₂) and oxygen (O₂) in the helium cover gas system. During normal plant operation, the recombination units are capable of maintaining safe levels of D₂ and O₂ in the cover gas by promoting the reforming of heavy water from its gaseous components. The following chemical equation depicts the recombination reaction:



The palladium catalyst in the recombination unit makes the reaction possible at low concentrations. Therefore:

- The D_2 and O_2 recombine at a lower temperature and below the lower explosive concentration limit.
- Low concentrations produce less heat because the amount of heat given off is proportional to the quantity of gases recombining.
- The reaction is described as proceeding "quietly", ie, without an explosion or combustion.

Without a catalyst, recombination will only occur by combustion.

If radiolysis proceeds more rapidly than recombination, the levels of D_2 and O_2 in the cover gas will increase. Deuterium in excess of 8% by volume in the helium is potentially explosive, and therefore running a unit at $\geq 4\%$ D_2 is not permitted.

Operational Concerns

Explosion

- The quiet reaction below the lower explosive concentration limits, due to the catalyst, helps to minimize the possibility of explosion.
- The flame arresters on the inlet and outlet of the units are added protection because the metal gauze dissipates heat from the reaction and reduces the probability of igniting the D_2 , O_2 mixture outside the recombination units.

Cover Gas Deuterium Excursions

- Under steady state conditions of temperature, pressure and chemical purity in the moderator, an equilibrium between radiolysis and recombination is established. Cover gas deuterium excursions can occur, given sufficient moderator dissolved D_2 , when the steady state is disturbed. A significant rise in moderator temperature or deterioration in moderator chemical purity are examples of such disturbances. The movement of D_2 into the cover gas is generally fast; an excursion occurs if the dissolved D_2 concentration is high.

Palladium Catalyst Concerns

- Water can "poison" (reduce it's effectiveness) the palladium catalyst. Heaters on the units ensure the catalyst is dry and ready for operation in advance of start-up. The heaters are not required during reactor operation because the heat of reaction protects the catalyst by removing the water formed as vapour.

Summary

- Moderator radiolysis can produce a potentially explosive D_2/O_2 mixture in the cover gas system.
- The recombination units recombine the D_2 and O_2 "quietly", owing to the action of the palladium catalyst.
- Because of the catalyst, the D_2 and O_2 will recombine below the lower explosive concentration limits.
- A cover gas deuterium excursion can occur when the equilibrium between radiolysis and recombination is disturbed.
- Water can poison the palladium catalyst.

ACTIVATION

Materials that are bombarded with neutrons will become radioactive by a process known as neutron activation. Any ingress of air to the moderator system is therefore a concern because Argon will be activated to Ar^{41} , with a resulting increase in cover gas area radiation fields. Note that alpha, beta and gamma radiation do not cause activation.

IX COLUMN OPERATION

Ion exchange is a chemical adsorption process which entails an interchange of ions in solution to produce a different chemical compound, through the use of an ion exchange resin. The focus of the process is not on the compound formed, but rather upon the effect on the solution resulting from this interchange of ions; an undesirable ion is removed from solution and replaced by a desirable one.

Resins are manufactured as tiny plastic beads of organic polymers. The surfaces of CATION exchange resins (Catexers) have positive hydrogen ions attached to them and the surfaces of ANION exchange resins (Anexers) have negative hydroxyl ions attached to them. A CATION (+) resin is used to make cation exchanges. An ANION (-) resin is used to make anion exchanges. A MIXED BED IX column contains both cation and anion resins and removes both cations and anions. It is sometimes called an ionexer.

Resins may also be classed as STRONG or WEAK. A WEAK resin is effective for removing strongly ionized substances such as gadolinium nitrate. A STRONG resin is effective for removing both strongly ionized and slightly ionized substances. An example of a slightly ionized substance is boric acid.

The exchange mechanism is affected by three major factors:

- (a) **Ion Size** - Large ions readily displace smaller ions.
- (b) **Ion Concentration** - High concentrations of a **SMALL** ion will displace **LARGE** ions. This makes regeneration possible.
- (c) **Ion Charge** - The greater the charge on an ion, the more readily it displaces ion(s) having a lesser charge. The charges must balance, eg, M^{+3} displaces $3X^{+1}$.

Resin Regeneration

IX resins possess a fixed number of exchange sites. As saturation approaches, "impurity" ions begin to pass through the resin bed, effluent conductivity changes, and the IX column is removed from service. Regeneration is the process of removing the impurity ions from the resin by replacing them with desirable ions via ion exchange. Cation resins are regenerated using dilute (2-6%) sulphuric acid. Anion resins are regenerated using dilute (4%) sodium hydroxide. The service/regeneration cycle can be repeated many times but some bead attrition does occur. This is usually the loss of fractured beads as resin fines.

Resins from **radiologically active** sources are not regenerated. In Ontario Hydro, these resins are transported to the BNPD waste management site.

Deuteration and Dedeuteration

Resins are shipped damp with light water because wetting dry resin would crack many beads. The resin may appear dry but there is bulk water present on the surface of the beads as well as $[H^+]$ and $[OH^-]$ in the exchange sites. Since the resins are received with ordinary hydrogen in the exchange sites, any ion exchange would release light water in place of soluble impurities. Any light water would downgrade the D_2O in the moderator or HTS. Therefore, the resin is deuterated before use in these systems. Deuteration is ion exchange of $[D^+]$ for $[H^+]$ and $[OD^-]$ for $[OH^-]$ by slowly flowing D_2O up through the resin bed to displace H_2O . An IX column is ready for service when effluent and influent isotopic are the same.

Dedeuteration of saturated resin is the reverse of the above. H_2O is passed slowly down through the resin and displaces D_2O by exchanging $[H^+]$ for $[D^+]$ and $[OH^-]$ for $[OD^-]$. The saturated resin is dedeuterated, before transporting it to the waste management facility, in order to minimize D_2O losses and unnecessary tritium handling.

Applications of IX Columns

1. Water Treatment Plant (WTP)

Anion, cation and mixed beds are used. The "deionized" water conductivity must be low enough to be an effective electrical insulator in the generator stator cooling system. Deionized water is also required as boiler feedwater to minimize corrosion and the buildup of sludge in the boiler.

Although volatile carryover of silica is a problem in thermal stations, because of higher operating temperatures and pressures, it has not been a significant problem to date in the NGD boilers. However, to minimize the possibility of carryover of solids in the steam, the anion resin in the mixed bed must be strong enough to remove silica, which is only slightly ionized.

2. Heat Transport System IX Columns

As impurities are adsorbed, LiOD is displaced from the resins. (The cation resin used is in the Lithium form.) LiOD is a strong base which dissociates readily, contributing alkalinity for pH control and hence protection from corrosion. **These resins are not regenerated.**

3. Moderator System

IX columns are used to remove acids that may form as a result of radiolysis of air. Any other ions, eg, added neutron absorbing poisons are also removed from the moderator by the IX columns. **These resins are not regenerated.**

4. Auxillary Systems

Various other systems utilize IX columns for on-going purification. These include End Shield Cooling, Liquid Zone Control, Recirculated Cooling Water, Irradiated Fuel Bay Cooling and Stator Cooling Water.

Summary

- Ion exchange is a chemical adsorption process entailing an interchange of ions between process water and ion exchange resins.
- Resins are either cation exchange resins or anion exchange resins, in separate or mixed-bed columns.
- Resins are classed as weak or strong resins.
- The ion exchange mechanism is affected by ion size, ion charge and ion concentration.

- IX resins can be regenerated when they become saturated.
- Regeneration is the procedure of replacing impurity ions in an IX column with desirable ions by flushing with a suitable acid or base.
- Radiologically active resins are not regenerated.
- Resins for use with D_2O must be deuterated before use and dedeuterated after use.
- Deuteration is ION exchange of $[D^+]$ for $[H^+]$ and $[OD^-]$ for $[OH^-]$.
- Dedeuteration is ION exchange of $[H^+]$ for $[D^+]$ and $[OH^-]$ for $[OD^-]$.

FILTRATION

Filtration is the process of passing a fluid containing suspended matter through a suitable porous material in such a manner as to effectively remove the suspended matter from the fluid. The filtering process may be via mechanical blockage of particles larger than the pores of the filter, or by adsorption.

Filtration is an important step in the operation of the Water Treatment Plant (WTP), where high purity water is prepared for a number of nuclear plant applications. Sand and activated charcoal filters are used in this application.

In heavy water applications, insoluble corrosion products are removed by cartridge filters in the purification circuits. Here the primary objective of the filtration process is to remove activated and potentially active particles from the heavy water, thus reducing the radiation hazard from their deposition on system surfaces. This type of filter is not backwashed. When clogged, the filter medium is removed and stored at the Radioactive Waste Management Facility.

Filters which utilize the **adsorption** principle include activated charcoal and molecular sieves. Activated charcoal is used in respirators to remove radioactive iodine from air, and in the WTP to remove organic materials responsible for colour and odour from water. Molecular sieves are used to remove moisture from station air, including D_2O and tritiated D_2O , for both safety and economic reasons. These filters remove molecules from a fluid by adsorption.

Colloids/Colloidal Suspensions

Colloids consist of extremely fine, insoluble, solid particles held in suspension in a liquid, eg, the turbidity or haziness in raw water. Their significance is that the solid particles will pass through all common filter mediums, making it virtually impossible to remove them by filtration.

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An example of a potentially troublesome colloid is the formation of $Gd(OH)_3$ in the moderator if the pH is too high. (See 224.03, Non-Standard Operation)

Summary

- Filters remove solids from fluids by mechanical blockage of particles larger than their pore size, or by adsorption.
- Mechanical filters include sand, cartridge filters; adsorbent filters include activated charcoal and molecular sieves.
- Colloids are extremely difficult to remove from solution because they pass through all common filter mediums.

CORROSION

Corrosion Principles

Corrosion is the process of metal wastage produced by chemical action (oxidation). Corrosion of metals is caused by oxidizing agents, acids, bases or galvanic action.

The effect of solution pH on the rate of corrosion depends on the metals involved. For example:

- A pH range of 10 - 12 minimizes the corrosion of iron; the corrosion rate rises outside this range.
- Metals with oxidation potentials > 0 are vulnerable to simple acid (low pH) attack.
- Zirconium alloys have high corrosion resistance to **both** acidic solutions, and alkaline solutions up to pH 13.
- A neutral pH is best for stainless steel and copper alloys and is absolutely essential for aluminum.
- Nickel alloys such as monel and inconel demand a high pH environment.

The following is a brief review of the major types of corrosion.

Uniform Corrosion

This common form of corrosion is characterized by uniform attack over the entire exposed surface. Corrosion products may form a protective layer on the metal that decreases the rate of corrosion, for example, magnetite on the carbon steel in the HTS. The original design criteria normally account for the extent of material wastage.

Chemical control and the use of protective coatings are the most commonly used protection against uniform corrosion.

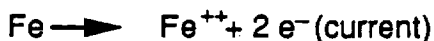
Galvanic Corrosion

A galvanic cell consists of two dissimilar metals in an electrolyte and also having external electrical contact with each other. At least one of the metals must have a positive oxidation potential.¹ A potential difference due to the different oxidation potentials of the metals causes electrons to flow in the circuit. Oxidation (corrosion) occurs at the anode where metal is removed. Reduction (of electrolyte) occurs at the cathode as shown in Figure 3.

The determination of anode and cathode in a galvanic cell depends upon the oxidation potentials of the two metals. The anode always has a higher oxidation potential than the cathode.

REACTIONS

At the Anode:



At the Cathode:



In The Electrolyte:

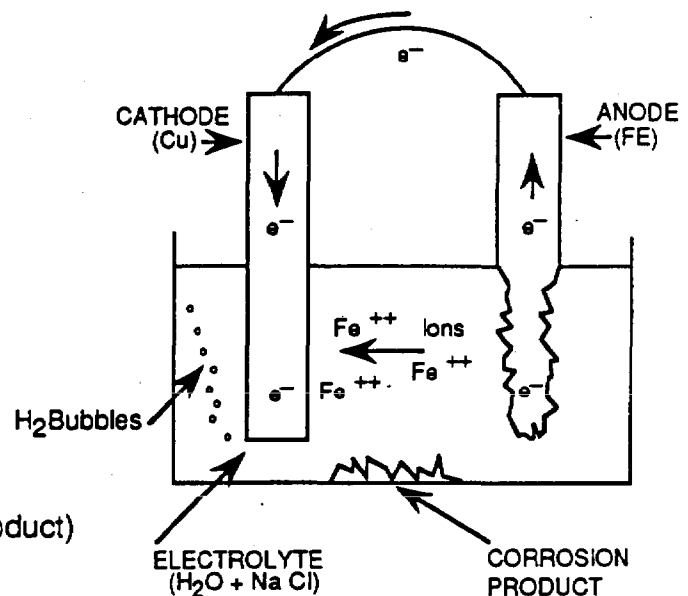
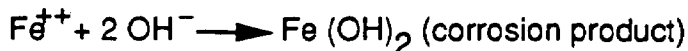
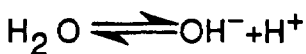


Figure 3: A Typical Galvanic Cell

¹Oxidation potential, measured in volts, represents the ease with which metals lose their outer electrons. The greater the oxidation potential, the more reactive is the metal.

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Many factors increase the rate of corrosion and the extent of metal damage. These include an **Increase** in the following:

- oxidation potential of the anodic metal (see Footnote 1)
- O₂ concentration: more oxygen produces more corrosion, and its reduction to water increases cell voltage
- temperature: increasing temperature increases the rate of chemical reactions
- electrolyte conductivity: as the concentration of the electrolyte rises, ions can move more readily from electrode to electrode, ie, more current flow
- cathode/anode surface area ratio: corrosion per unit area of the anode increases as the cathode area increases in order to accommodate the increased current flow resulting from increased cathode area

Galvanic corrosion occurs when two dissimilar metals are in electrical contact in an electrolytic solution. Recall that the anode, ie the metal having the highest oxidation potential, always corrodes. Also, if the cathode metal surface area is large compared to the anode the rate of corrosion of the anode increases in order to accommodate the increased current flow resulting from increased cathode area.

Galvanic corrosion is therefore minimized by selecting metal couples having similar oxidation potentials, by isolating dissimilar metals from each other, and also by isolating the anodic metal from the electrolyte. An example of isolating dissimilar metals from each other is the use of a plastic isolating bushing in a fitting which joins two types of metal pipe, eg, copper and steel. An example of isolating the anodic metal from the electrolyte is the formation of an impervious magnetite layer on the surface of carbon steel pipe in the HTS. Also, if all moisture is removed there is no electrolyte and a galvanic cell cannot exist.

Pitting and Crevice Corrosion

Pitting and crevice corrosion are similar electrochemical corrosive actions with metal loss or destruction occurring at localized anodic areas. The electrochemical action does not depend upon contact between dissimilar metals, but on localized differences in electrolyte concentration, ie, the electrolyte contains a "hostile" ion/element at two distinct concentrations. This situation may be prompted by low-velocity, stagnant type conditions.

Pitting corrosion is commonly associated with deposits or scale creating a barrier between differing concentrations of the hostile substance in the electrolyte. Pitting is minimized by chemical control, proper drainage of vessels during shutdown, removal of suspended solids from the system and frequent inspection and removal of deposits.

Crevice corrosion describes the location, eg, bolts, gaskets, metal contact points, where this type of metal attack occurs. It is of particular concern in boilers. Because the electrolyte has limited access to the crevice or crack, differences in hostile ion concentration develop and the anodic area is set up. A crevice must allow liquid entry, but must also maintain a stagnant zone.

Crevice corrosion is minimized by avoiding designs that facilitate crevices, and by applying the same controls as for pitting corrosion.

Stress Corrosion Cracking (SCC)

Stress corrosion cracking is the formation of cracks where localized corrosion has combined with steady tensile stresses in the metal to cause the damage. This effect has been seen in low pressure turbine disks and blade roots and also in boiler tubes. The hostile electrolytic environment can attack particular metals or alloys, for example, chloride and stainless steels. Excessive SCC can cause failure, typically sudden and without warning.

Two general theories are used to explain the SCC mechanism. The electrochemical theory centres around galvanic cell action in the grains and between grain boundaries. The stress sorption theory suggests that SCC proceeds by weakening the cohesive bonds between surface metal atoms.

The source of tensile stresses may originate during manufacture or from in-service conditions. Lowering tensile stress by decreasing applied load, stress relieving or introducing residual compressive stress through procedures such as shot peening will minimize SCC.

SCC is also minimized through chemical control of the water in the system, or applying coatings to reduce or eliminate contact between the metal and the hostile ion.

Corrosion Fatigue

Corrosion fatigue is characterized by a wedge-shaped crack in an area subjected to cycling stresses in a corrosive environment. The crack usually begins at a pit or surface irregularity and propagates transgranularly. Metal failure occurs at a lower stress level and after fewer cycles than for non-corrosive conditions. The combined effect of corrosion and fatigue is greater than the sum of their individual damages.

Erosion Corrosion

Erosion corrosion is the acceleration of corrosion owing to relative movement of the corrosive fluid and the metal surface.

It is characterized by grooves, waves and valleys in the metal surface, and short time periods to unexpected failures. Erosion corrosion is promoted by high fluid velocity,

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turbulent flow and the impingement of these high-velocity fluids on metal surfaces, for example, at elbows in pipelines.

Erosion corrosion is obviously minimized by reducing fluid velocities, promoting less turbulent flow and by the avoidance of sharp changes in flow direction.

Microbiologically Induced Corrosion (MIC)

MIC is corrosion involving the action of bacteria on metal surfaces, most commonly in stagnant water. Slime-forming bacteria are aerobic and thrive in most cooling-water systems. As they metabolize dissolved oxygen from the water, they create an anaerobic environment at the metal surface. Anaerobic bacteria can then attack the metal surface.

Some bacteria can oxidize or reduce metal species directly, for example Fe^{II} to Fe^{III} . The ferric compounds precipitate in pipes. Concentration gradients form under these deposits, resulting in corrosion. Other bacteria can reduce ferric iron to the more soluble ferrous form. This strips off the ferric compounds which normally stabilize the surface of mild steel, leaving it reactive. Corrosion is thus accelerated. Other bacteria can metabolize chromium, thereby corroding stainless steels.

A major factor in minimizing MIC is the elimination of stagnant water. A clean metal surface with sufficiently high fluid velocities will also prevent bacteria from establishing a foothold.

Corrosion Control

Three corrosion control methods used in nuclear generating stations are:

- (a) Coatings
- (b) Chemical Control
- (c) Control of MIC

Methods (a) and (b) remove one or more of the essential requirements for a simple electrochemical corrosion cell, or prevent the direct attack of a corrosive chemical. The control of MIC involves bacteria control.

(a) Coatings

Coatings are widely used for corrosion control, with the general approach being to isolate the metal from the electrolyte.

Paint and a wide variety of synthetic coatings (epoxy, resins, plastics) are applied directly.

Protective oxide films are formed by inducing a chemical reaction between the metal surface and the electrolyte, eg, chemical conditioning of the HTS.

(b) **Chemical Control**

The objective of chemical control is to promote and maintain a desirable environment which minimizes corrosion. This involves:

(i) **Removing corrosives before they enter the system**

The water treatment plant removes a major proportion of ions such as chloride, sulphate, silica, calcium and magnesium which are hostile to the feedwater circuit.

Nitrogen blanketing is used to minimize oxidation by excluding air/oxygen from systems such as the ECI when poised, or the HTS when drained.

(ii) **Eliminating corrosives which gain access to the system or are generated within it**

Oxygen which enters the feedwater circuit through air inleakage or dissolved in fresh makeup is removed using both physical techniques such as deaerators and chemical techniques such as scavenging with hydrazine. Boiler blowdown is used to remove both dissolved and suspended solids from the boiler. Removal of the former lowers the concentration of undesirable ions in the boiler. Unfortunately, however, removal of suspended solids is very inefficient. This leads to the major objective on the secondary side of minimizing corrosion, and transport of corrosion products to the boiler.

Acids of nitrogen generated via radiolysis within the moderator cover gas system are removed from the moderator D_2O by ion exchange, to prevent corrosion and especially to prevent enhanced radiolysis.

(iii) **Inhibiting corrosion by adding chemicals which react with the corrosive agent**

Neutralizing amines (morpholine or ammonia) are added to the condensate return to neutralize the acidity produced by any ingress of carbon dioxide, in addition to providing an alkaline medium which minimizes corrosion of the system metals.

A further example of a desirable chemical environment is the alkalinity level maintained in the heat transport system. Its careful control minimizes dissolution of the magnetite layer on carbon steel surfaces, as well as corrosion of system metals.

(c) Control of Microbiologically Induced Corrosion

A major factor in controlling MIC is to prevent it by eliminating the conditions which encourage the growth of bacteria. Raw water in populated areas is a particularly good medium for bacteria growth. Raw water must therefore be chemically treated to kill existing bacteria. It must also be filtered to reduce available nutrients. Metal surfaces must be kept clean.

Where water is being recirculated, eg, through heat exchangers, a pH of > 10.5 , and the exclusion of air help minimize bacteria growth. High velocity flows also prevent bacteria from settling out and forming colonies.

Large tanks of stagnant water, eg, the irradiated fuel bays or the demineralized water tanks, are very prone to bacteria growth. Control is by chemical treatment and filtration.

If bacteria colonies become established in a system, either mechanical cleaning or very strong chemical treatment is required to remove them.

Summary

- Corrosion is a process of metal wastage by chemical action.
- Corrosion usually is an electrochemical process.
- In a galvanic cell, the metal having the more positive oxidation potential is always the anode.
- Oxidation (corrosion) always occurs at the anode in a galvanic cell.
- Corrosion is enhanced by **increases** in temperature, O_2 concentration, solution conductivity, cathode surface area and anode oxidation potential.
- Effects of pH on corrosion depend on the metal involved.
- Metal wastage by uniform corrosion is commonly reduced by chemical control and protective coatings.
- Galvanic corrosion is reduced by minimizing oxidation potential differences between component metals, and electrically isolating metals from each other or from the electrolyte.
- Pitting and crevice corrosion depend on localized differences in electrolyte concentration due to deposits, eg, scale, or crevices in the substrate metal.

- SCC is the formation of cracks where localized corrosion has combined with steady tensile stresses to cause the damage. SCC may lead to premature, sudden metal failure.
- Corrosion fatigue can cause metal failure when cycling stresses occur under corrosive conditions.
- Erosion corrosion is the acceleration of corrosion by the rapid flow of the corrosive agent.
- Corrosion is controlled via coatings and chemical control.
- MIC is corrosion involving bacteria colonies on metal surfaces.
- MIC is minimized by discouraging bacteria growth via chemical treatment high velocity flows, pH > 10.5, and the exclusion of air.

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