

**NUCLEAR OPERATIONS TRAINING**

**CHEMISTRY AND RADCON**

**CR-1**

**CORROSION OF NUCLEAR PLANT MATERIALS**

**REVISION 3**

**Recommended** Original Signed by Rusty Quick for JT **Date** 01/15/08

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## LIST OF ILLUSTRATIONS

<u>FIGURE</u>	<u>TITLE</u>
CR1.1	Corrosion Rate vs. pH in Iron
CR1.2	Galvanic Corrosion At A Zinc-Copper Junction
CR1.3	Crevice Corrosion of Two Iron Components
CR1.4	Reactor Coolant System Chemistry Tech Spec
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CR1.6	General Corrosion of Iron in Water

## OBJECTIVES

**TERMINAL OBJECTIVE:** The student successfully completing this lesson will be able to describe the mechanisms of corrosion of metals used in nuclear power plants and the purposes and means of controlling these processes.

**ENABLING OBJECTIVES:** Upon completion of this lesson, the student will be able to:

		<u>AO</u>	<u>RO</u>	<u>SRO</u>	<u>SE</u>
CR-1-01	<b>DEFINE</b> acid, base, and pH.	X			
CR-1-02	<b>EXPLAIN</b> the significance of pH to the process of general corrosion.	X	X	X	X
CR-1-03	<b>EXPLAIN</b> what is meant by an oxidation reaction.	X	X	X	X
CR-1-04	<b>GIVE</b> two reasons why the presence of loose corrosion products is undesirable for the Reactor Coolant System.	X	X	X	X
CR-1-05	<b>STATE</b> why the corrosion of iron is of significance for the power plant.	X	X	X	X
CR-1-06	<b>EXPLAIN</b> why the corrosion of Zirconium alloy is of importance to the power plant.	X	X	X	X
CR-1-07	<b>DESCRIBE</b> the consequences of a corrosion layer on the internal temperature of the fuel.	X	X	X	X
CR-1-08	<b>STATE</b> the general effect of temperature on corrosion rates.	X	X	X	X
CR-1-09	<b>STATE</b> the three principles which cause the rate of general corrosion to be minimized.	X	X	X	X
CR-1-10	<b>EXPLAIN</b> what is meant by CRUD.	X	X	X	X
CR-1-11	<b>GIVE</b> two reasons why CRUD adversely affects the plant.	X	X	X	X

		<u>AO</u>	<u>RO</u>	<u>SRO</u>	<u>SE</u>
CR-1-12	<b>STATE</b> the factors that combine to cause stress corrosion cracking.	X	X	X	X
CR-1-13	<b>STATE</b> the conditions that produce caustic corrosion.		X	X	X
CR-1-14	<b>EXPLAIN</b> the cause of galvanic corrosion.	X	X	X	X
CR-1-15	<b>EXPLAIN</b> two means used to limit galvanic corrosion.		X	X	X
CR-1-16	<b>EXPLAIN</b> the mechanism of crevice corrosion.	X	X	X	X
CR-1-17	<b>EXPLAIN</b> the mechanism of pitting corrosion.	X	X	X	X
CR-1-18	<b>LIST</b> the four limitations on plant chemistry that commonly limit all forms of localized corrosion given in this lesson.	X	X	X	X
CR-1-19	<b>STATE</b> the Technical Specification (Limits for RO, SRO, SE) associated with the Chemistry of the Reactor Coolant System (RCS).	X	X	X	X
CR-1-20	Briefly <b>EXPLAIN</b> the basis of the RCS Chemistry Technical Specification.		X	X	X
CR-1-21	Using selected operating experiences related to this course, <b>DESCRIBE</b> their applicability to your job (the cause), their significance to plant operations (the effect), and which of the seven Human Performance tools could have been used to prevent or mitigate the events.	X	X	X	X

## **LESSON TEXT**

### **OVERVIEW**

The use of water in the reactor has the benefits of cost effectiveness and predictable nuclear properties. However, water also corrodes virtually all the types of metal in the plant and undergoes certain reactions in radiation fields. Some knowledge of the basic causes and processes involved in corrosion is useful for an operator for at least three reasons:

- Corrosion products become activated when they pass through the core. They can also buildup in specific locations in a plant system. Therefore, certain system locations can be expected to have higher radiation levels than others, and corrosion buildup can have an undesirable effect on components with small clearances.
- The Reactor Coolant System (RCS) is the second fission product barrier, therefore, understanding the mechanisms used to control corrosion of RCS (and other) piping is important to the operator.
- Much valuable information from industry operating experience addresses incidents and failures of certain systems and devices that are related to plant chemistry and corrosion. In order to understand and apply such information, an operator must at least have a basic comprehension of the process involved.

## **CHEMISTRY FUNDAMENTALS**

The chemical reactions of concern in plant systems are metal reactions in solutions. A solution consists of two components: a solvent, and a solute. The solvent is the dissolving medium (water in the plant systems). The solute is the substance that is dissolved (plant metals). The solubility of a material is the maximum amount that can be dissolved in a solvent at a given temperature and pressure.

Corrosion is essentially the action of water as a solvent on the plant metal surfaces. General corrosion is the name applied to the case where a metal surface suffers chemical reactions all over its surface. Localized corrosion is the name given to a number of specific types of reactions that tend to occur only in small regions and under specific conditions.

General corrosion is primarily responsible for the products that tend to increase plant radiation levels. Small pieces of the corrosion layer break off from the surface and flow through the core where they become activated. This is one of the largest contributors to personnel radiation exposure. Localized corrosion has been responsible for the specific and sometimes very serious failures of individual components of nuclear plants. The most notable example of localized corrosion effects is ruptures of steam generator tubes.

### **Acid-Base Chemistry and pH**

An acid is a substance that dissociates to form hydrogen ions ( $H^+$ ) in solution. A base dissociates to form hydroxide ions ( $OH^-$ ). The commonly accepted parameter used to describe the hydrogen ion concentration in a solution is pH. The pH is defined as the negative logarithm to the base ten of the hydrogen ion concentration.

$$pH = -\log [H^+]$$

A solution with a pH less than 7 is acidic, greater than 7 basic. A solution with a pH of 7 is a neutral solution. Another word for a basic solution is "alkaline" or caustic. (An extreme example of an alkaline solution is lye. Extremes in either direction of pH are not desirable.)

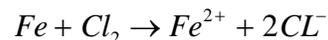
The pH of the primary and secondary water systems in the plant is an important parameter. The corrosion of metals varies significantly with solution pH. Consequently, the pH of a chemistry-controlled system is one of the basic parameters used by the plant chemists.

### **Oxidation-Reduction Reactions**

Oxidation is a chemical change in which valence electrons are lost from an atom. Reduction is the gain of electrons by an atom. Oxidation and reduction reactions always occur simultaneously. The total number of electrons lost from an atom always equals the number gained by another atom. An example of oxidation-reduction is the iron-chlorine reaction.



The total reaction can be written by summing the two equations:

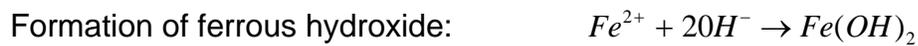
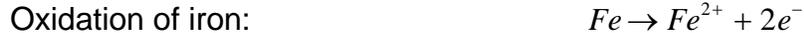


Oxidation-reduction reactions are an important consideration in the power plant. The oxidation of metals is the common term used in describing the types of corrosion that occur in the plant.

## GENERAL CORROSION

As stated earlier, general corrosion is a process which results in a uniform removal of material from all metal surfaces in contact with water. The general corrosion of a metal varies with the type of metal, the composition of the water solution, and various environmental conditions in the plant. The best illustration of general corrosion is the corrosion of iron, which is the most prevalent metal in the plant. The general corrosion of other metals is similar to that of iron.

Iron atoms are unstable in water and tend to oxidize to form ferrous ions ( $Fe^{2+}$ ) and electrons. These ferrous ions in turn form ferrous hydroxide ( $Fe(OH)_2$ ) when the metal surface is in contact with high temperature water. The electrons from the oxidation reaction combine with hydrogen ions to form neutral hydrogen. The ferrous hydroxide continues to react to form magnetite ( $Fe_3O_4$ ) (sometimes called gamma-hematite), a black rust. The following equations depict these chemical reactions:



Magnetite builds up as a film on the surface of the metal. The ferrous ions must pass through this film to react further with water. As the thickness of the magnetite layer increases, the process slows down until the corrosion rate decreases to some acceptable value. This phenomenon of film buildup slowing down the corrosion rate is typical of most metals. Consequently, since general corrosion will occur anyway, a thin corrosion layer is not necessarily bad since it tends to slow further degradation of the metal surface.

This process explains why it is common for a new system to be deliberately run for a period of "conditioning," where a thin stable corrosion layer is deliberately made to form.

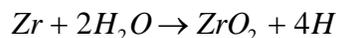
An undesirable effect occurs if pieces of a system's corrosion layer are caused to break off from metal surfaces and flow through the system itself. These particles can reduce flow in small channels. However, as these particles pass through the core, they become radioactive and increase overall radiation levels or local radiation levels in system low flow points where they collect.

### **Stainless Steel**

Stainless steel is the most widely used alloy in the plant. Iron is the predominant metal in stainless steel. In addition to the formation of magnetite, the chromium and nickel in stainless steel will oxidize as well. The corrosion product of stainless steel appears as a black adherent film. The film contains chromium and nickel oxides ( $\text{Cr}_2\text{O}_3$  and  $\text{NiO}$ ). Chrome oxide slows down the diffusion of ferrous ions and makes the film adhere strongly to the surface of the metal.

### **Zircalloy**

The alloys of zirconium were developed specifically for nuclear reactor applications. Zirconium has many desirable properties such as a low neutron absorption cross-section, high melting point, and adequate mechanical strength up to 800°F. In the presence of high temperature water, zirconium is oxidized similar to iron:



The oxide of zirconium forms a smooth, continuous adherent corrosion film. As with stainless steel, this thin oxide film acts as a protection mechanism, reducing the general corrosion rate.

A more serious problem in the corrosion of zirconium alloys is the production of zirconium hydride. The monatomic hydrogen formed in the oxidation of zirconium can either combine to form elementary hydrogen gas ( $H_2$ ), or it can diffuse into the very crystal structure of zircalloy itself. If the hydrogen diffuses into the crystal structure, the zirconium reacts to form zirconium hydride. This process of zirc-hydridding produces a very brittle compound, causing the metal to weaken, which may result in structural failure. Since zirc-hydridding has a direct impact on the properties of one of the barriers to the release of fission products (namely the cladding), this is one reaction with which the operator should be thoroughly familiar. The generation of  $H_2$  is of concern in post-accident analysis as a combustible hazard.

### **Inconel**

The predominant metal in inconel is nickel (about 76 percent). Inconel also contains a significant amount of chromium. The oxide film that forms on inconel is mostly  $NiO$  and  $Cr_2O_3$ . As with stainless steel and zircalloy, the adherent inconel corrosion film resists further general corrosion. The corrosion rate of inconel is generally slower than that of stainless steels. Therefore, inconel is used to line certain critical components such as the reactor vessel.

### **ENVIRONMENTAL EFFECTS ON CORROSION**

Many environmental conditions affect the corrosion rate of metals in the plant. These environmental conditions include temperature, solution velocity (flow rate), chemicals in solution, and radiation.

Generally, as the temperature of a metal surface increases, corrosion rate increases. This phenomenon is particularly significant on heat transfer surfaces. During steady state operations, the heat transfer rate across the fuel rods or SG tubes remains constant. As a corrosion film builds up, the temperature of the metal must increase in order to transfer the same heat since the corrosion layer has a lower thermal conductivity. The increase in metal temperature then increases the corrosion rate. Any loose products that form in the corrosion process also tend to collect on high temperature surfaces.

The velocity of the water through the system has an effect on corrosion. In areas of high fluid velocity, the corrosion layer will remain relatively thin due to the mechanical action of the fluid flow. Any extra thickness of film will be mechanically "scrubbed" from the metal. In areas of low flow, the corrosion products will have a tendency to build to thicker layers and also any products dispersed in the water will have a tendency to settle out. This later occurrence can lead to many problems with maintenance and/or repair efforts, especially if the products that settle out are highly radioactive. For example, a low point drain line in a reactor system may be a point of high radiation levels. In order to do work near such "hot spots", extra planning and shielding are required, increasing the cost and difficulty of outages.

Certain chemicals produce harmful effects on metal surfaces. For example, chloride ions attack stainless steel, fluoride attacks zirconium, and zinc cause damage to inconel. Heavy metals such as mercury and lead cause damage to metals containing nickel such as Inconel and Stainless Steel. To minimize corrosion, the concentration of these and other chemicals must be controlled. The prevention of any impurities entering a plant system is therefore a serious operating concern.

The final environmental consideration that is important and unique to the nuclear power industry is effects related to radiation. High-energy radiation can change the crystalline structure of an oxide layer. If a metal surface is radioactive, loose products resulting from corrosion could also be radioactive and transported throughout the system. Corrosion products produced outside the core could become activated upon passing through a radiation flux. Loose corrosion products tend to precipitate on radioactive surfaces just like high temperature surfaces.

Ultimately the problems that stem from loose corrosion products in the plant can be averted by avoiding any sort of shock to the plant that could cause an otherwise relatively stable corrosion layer to break up. Such shocks can result from thermal shocks (rapid temperature changes), chemical shocks (bad chemistry), or mechanical shocks (possible from pump starts).

### **CONTROL OF GENERAL CORROSION**

With so many variables to consider, corrosion control becomes a very complex matter. Experimental data on various metals show that the general rate of corrosion can be controlled through three mechanisms:

- Reduce oxygen content
- Maintain neutral to basic pH
- Utilize corrosion inhibitors

The oxygen content in water affects the corrosion of most metals. Oxygen content can be reduced by using deaerated makeup water, maintaining an excess of hydrogen in the water (in a  $\gamma$  radiation field), or adding an oxygen scavenger such as hydrazine ( $N_2H_4$ ) (at low temperatures).

The corrosion rate of most metals in water is a function of pH. Metals usually corrode at a slower rate in a neutral to high pH (basic). An example of corrosion rate as a function of pH is shown in Figure CR-1-1. In addition, the corrosion film tends to be more adherent at higher pH. Chemicals that dissociate into hydroxide ions in solution can be added to the water to achieve a desirable high pH.

The final means of controlling general corrosion is through the use of corrosion inhibitors. Corrosion inhibitors cannot be used in all applications. They are not used in the Reactor Coolant System because they generally decompose under conditions of high temperature and high radiation flux. An example of a corrosion inhibitor is potassium chromate ( $K_2CrO_2$ ) (not used in RCS) which reduces the rate of corrosion by producing an insoluble chromate film on the surface of iron.

The effects of temperature and radiation on corrosion are uncontrollable factors in an operating power plant. These parameters are considered in the design of systems and when deciding what other means of controlling general corrosion are to be used.

## **CRUD**

The description of general corrosion of iron, zirconium, chromium, and nickel has focused on the production of an adherent layer on the surface of the metal. The general corrosion of metals is of little importance with respect to the service life of the components because the rate is very slow. For most stainless steels, the general corrosion rate is something less than a milligram per decimeter per year. However, any corrosion of metal produces suspended products in the form of finely divided material. The general name for these materials as well as the loose corrosion products mentioned earlier is CRUD. Crud can result from the erosion of an oxide film or the production of corrosion products after metal ions leave the surface of the metal and combine with impurities in the water. The general corrosion rate is very important with respect to crud formation.

The purity of the coolant and the cleanliness of the system must always be maintained to minimize CRUD formation and transport.

If the loose corrosion products become suspended in the water, a hazard results when crud is deposited at various locations in the system. The deposition of crud must be minimized for three reasons: crud deposits can cause fouling of heat transfer surfaces; the buildup can block or bind close fitting mechanical joints (which may result in failure or reduced operation of some equipment); and crud deposits can become activated and can cause significant radiological problems during maintenance and waste disposal.

Although all of the factors in deposition rates are not clearly defined, experimental evidence indicates deposition of crud is affected by these factors:

- Crud tends to collect on hotter (heat transfer) surfaces.
- Crud deposits increase in an area of radiation flux.
- Crud deposition is increased in areas of low fluid velocity.
- Crud will more readily deposit in a low pH environment.

The primary heat transfer surface in the plant is the fuel cladding. Crud has been observed to deposit more readily on zircalloy surfaces than on stainless steel surfaces. Since a crud layer buildup causes the fuel temperature to increase, fouling of the zircalloy clad must be minimized to avoid damage to the fuel.

The steam generator tubes are another critical heat transfer surface. Crud deposits cause steam generators to become highly radioactive, making maintenance and repair dangerous. Crud buildup also reduces steam generator heat transfer, thus reducing steam output. This, together with certain localized corrosions associated with steam generators to be mentioned later, makes the steam generator chemistry control particularly important.

For safe and effective plant operation, the production and deposition of crud must be minimized. Reducing oxygen content, maintaining neutral to basic pH, and utilizing corrosion inhibitors, all help to do so.

## **LOCALIZED CORROSION**

One of the fundamental requirements of the plant is to maintain the structural integrity of each system and component. General corrosion of metals is a very slow process, attacking metals uniformly over the whole plant. With the exception of the binding of mechanical components, many years may elapse before general corrosion causes structural failure. Localized corrosion is a very rapid, destructive attack on a metal at a select location. In an extreme case, failure of a component may take only days. Only certain metals in specific environments are susceptible to local corrosion. The five types of localized corrosion of concern in the plant are stress cracking, caustic, galvanic, crevice, and pitting corrosion.

### **Stress Corrosion Cracking**

Stress corrosion cracking has been observed in virtually all alloyed metals. With few exceptions, pure metals are not susceptible. The following conditions must exist in order for stress corrosion to occur:

- Susceptible metal alloy and a corroding substance
- Tensile stress
- Oxygen in water
- Temperature greater than 140°F

A metal surface does not undergo stress corrosion cracking unless subjected to a high tensile stress. The stress must be greater than some threshold value for a given alloy. The stress could result from service loads, residual stress from manufacturing processes, mismatch of components during construction, or wedging action due to accumulation of corrosion products. Once a stress is applied to a material, the other factors must be present to initiate stress corrosion. If the factors are not present, stress corrosion does not occur.

Through experimentation and examination of previous failures, methods of preventing stress corrosion have been devised. Avoiding all stress is impractical in plant applications. However, careful fabrication can reduce residual stresses. Since most alloys are susceptible, avoiding use of susceptible materials is impossible. The most effective and practical means of minimizing stress cracking is maintaining fluoride, chloride, and oxygen contents in water well below specified limits. High concentration of fluoride or chloride can be tolerated if oxygen concentration is very low. The reverse is also true. A specific plant Technical Specification imposes very restrictive limits on each of the above substances.

### **Caustic Corrosion**

Although stress corrosion cracking and caustic corrosion are the most important types of localized corrosion, they are also the least understood. Caustic corrosion can occur in zircalloy and all ferrous metals. The conditions necessary for caustic corrosion to occur are as follows:

- Susceptible metal
- Concentrated caustic
- Tensile stress

The difference between caustic and stress corrosion cracking is the chemicals necessary to initiate the corrosion mechanism.

To minimize general corrosion of most metals, a neutral to high pH is required. However, too high a concentration of hydroxide is even more destructive. At a pH near 14, ferrous metals and inconel undergo caustic corrosion if a stress is also present. At a pH greater than 11.3, the oxide film on zircalloy will dissolve, leaving the metal surface susceptible to caustic corrosion. This high pH and exposure of zircalloy surface also increases zirc-hydrating.

The principle means of concentrating caustic material in a localized area is through boiling. As boiling occurs, caustic material plates out of solution. When the surface rewets, the caustic dissolves forming a short-lived localized region of high pH. This specific area is then susceptible to local caustic corrosion.

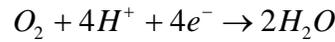
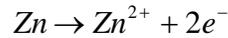
Avoiding tensile stress and using nonsusceptible materials are not viable solutions for preventing caustic corrosion. The most effective means is to avoid high caustic concentrations. Since boiling cannot be avoided in some components, strict pH control is required.

### **Galvanic Corrosion**

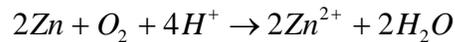
When any two dissimilar metals come in contact in water which can conduct electricity, one of the metals may suffer accelerated corrosion. This is essentially the principle by which a wet-cell battery works. The difference in electrical potential between the two metals produces a small current. The metal with the lower electric potential more rapidly oxidizes in water. These conditions are required to produce galvanic corrosion:

- Two dissimilar metals in contact
- Oxygen concentration in water

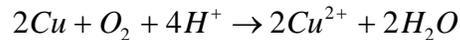
Figure CR-1-2 is an illustration of galvanic corrosion occurring at a zinc-copper junction in water. Both copper and zinc are oxidized in the presence of oxygen in the water:



Zinc reaction:



Copper reaction:



The electric potential of copper is 1.90 and that of zinc is 1.65. As a result, electrons flow from the zinc to the copper, which inhibits the corrosion of copper. The zinc corrodes at a faster rate than the copper surface.

Galvanic corrosion can be minimized in several ways. Metals which are corrosion resistant can be used. If this is impractical, the metals selected should be similar in electronegativity. For example, copper and nickel are similar in electronegativity: 1.90 and 1.91 respectively.

Two other design considerations used to prevent galvanic corrosion are the use of sacrificial anodes and transition pieces. A sacrificial anode uses the principle of galvanic corrosion to an advantage. It is placed next to a component to corrode intentionally, thus maintaining the integrity of the important component. A transition piece minimizes the contact area of two dissimilar metals. It is placed between them to reduce the potential difference from one metal to another. The transition piece must be close to the electronegativity of both metals.

The above mechanisms are all used in the design of systems and components. In the primary plant, minimizing the oxygen content of water is the main means of preventing galvanic corrosion. Sacrificial anodes are used in various heat exchangers of the secondary plant.

### **Crevice Corrosion**

A specialized case of galvanic corrosion is crevice corrosion, which involves the function of two pieces of the same metal. These conditions are required for crevice corrosion:

- Two closely fitted parts
- Soluble salts or oxygen in water

All closely fitted parts have crevices which tend to corrode at an accelerated rate. For the corrosion to occur, a difference in soluble salt or oxygen concentration must exist between the water in the crevice and in the main body of water. The increased concentration causes an increase in the reaction of the metal at that specific area. Figure CR1.3 illustrates crevice corrosion of iron where the two components are closely fit.

As with other types of corrosion, the most effective means of minimizing crevice corrosion is by keeping the water pure. The soluble salt and oxygen content of the water must be minimized. Since many close-fitting parts may be moving parts, crevice corrosion can seriously affect the mechanism's ability to function. In the design of these components, larger crevice clearances minimize localized high concentrations of damaging chemicals. During operations, frequent movement of closely fitted components will minimize crevice corrosion.

## **Pitting Corrosion**

The following conditions are required for pitting corrosion to occur:

- Inconsistencies in material composition of metal
- Oxygen and fluoride or chloride concentration in water

Slight differences in material composition on the surface of the metal result in an area of greater chemical activity. The electric potential at one part of the metal may be different from another part just a short distance away. Pitting corrosion begins at these points of high activity. Chlorides foster the formation of these active areas. When dissolved oxygen is present, the areas are attacked first by oxygen. Accelerated corrosion occurs, producing a pit in the metal surface. If the attack continues, the component could completely fail.

Pitting corrosion can be minimized by the use of more homogeneous metals. Since no metal can be totally flawless, oxygen and chloride concentration are minimized to make pitting corrosion reactions less likely to occur.

## **CONTROL OF LOCALIZED CORROSION**

High temperatures and load stresses are part of plant design. Operationally, neither of these can be controlled. The metals used are selected for their nuclear properties, strength, cost, compatibility with other materials, and corrosion resistance. Effectively, the only variable that can be controlled in an operating plant to reduce corrosion is the chemical environment where susceptible metals exist. The following conditions are necessary to minimize all types of localized corrosion:

- Low chloride concentration
- Low fluoride concentration

- Low oxygen concentration
- Neutral to moderately high pH

These conditions reflect the common chemistry rules. There may be numerous other limitations imposed with regard to very special reactions. Figure CR1.5 states the RCS chemistry limits and surveillance requirements.

For example, an additional chemistry requirement is the exclusion of mercury and lead in the water systems. Mercury and lead cause accelerated corrosion on metals containing nickel such as stainless steel and Inconel.

The Technical Specifications given in Figures CR1.4 and CR1.5 give very specific limits for the content of fluorine, oxygen, and chlorine in the primary coolant. Notice that by limiting each of these, most forms of localized corrosion in the RCS are automatically limited.

In the written Basis for this Technical Specification, it will be found that these limits are based primarily upon the control of stress corrosions over the entire life of the plant.

## **SUMMARY**

The structural integrity and operational status of the plant and all its systems must always be maintained. Through chemical reactions in water, all metal surfaces in the plant are subjected to corrosion. Corrosion is an undesirable situation, yet cannot be completely avoided. In the design of the plant, corrosion prevention and control is a high priority design criterion, and materials are chosen for their resistance to corrosion. After the plant is built, maintaining a satisfactory chemistry environment to minimize corrosion is a responsibility of those operating the plant. Technical Specifications address the chemistry-related limits for the Reactor Coolant System and the bases for these limits.

The mechanisms of corrosion are divided into two basic categories: general and localized. General corrosion is a gradual process, the wearing away of all metal surfaces in contact with water. This process produces an adherent film on the surfaces of the most prevalent metals in the plant: stainless steel, zircalloy, and inconel. Through other chemical reactions and the erosion of the adherent film, loose corrosion products, or crud, may become suspended in the water and transported throughout the system. If crud is deposited in the system, heat transfer surfaces can be fouled or close fitting mechanical joints can block or bind. Irradiated crud deposits can cause potential danger to maintenance and repair personnel. General corrosion can be reduced by reducing the oxygen content of water, maintaining a neutral to high pH, and, in some cases, using corrosion inhibitors.

Localized corrosion is usually more rapid and more destructive than general corrosion. Localized corrosion occurs at specific, susceptible locations in the plant. Stress cracking, caustic, galvanic, crevice, and pitting corrosion are the most important types of local corrosion. Stress corrosion cracking occurs when a component under tensile stress and high temperature is exposed to certain chemicals and oxygen. Caustic corrosion is similar, except the component is exposed to caustic material, or a concentrated high pH. Galvanic and crevice corrosion occurs at a junction of two metal

parts. In galvanic corrosion, the corroding of a metal is accelerated due to the potential difference between two metals. In the process of crevice corrosion, corrosion is accelerated in a crevice when soluble salts or oxygen is highly concentrated. In pitting corrosion, increased corrosion at a select location occurs where an inconsistency in material composition exists.

As with general corrosion, an operating plant's most effective safeguard against uncontrollable localized corrosion is strict and continuous control of the chemistry of the water systems. In addition to maintaining low oxygen concentration and neutral to high pH, the concentration of chloride and fluoride must be kept below a defined limit.

The Reactor Coolant System has specific limits for oxygen, chlorides, and fluorides:

<b><u>Steady State Operations</u></b>	<b><u>Transient Limit</u></b>
$O_2 \leq .10 \text{ ppm}$	$\leq 1.0 \text{ ppm}$
$CL \leq .15 \text{ ppm}$	$\leq 1.50 \text{ ppm}$
$FL \leq .15 \text{ ppm}$	$\leq 1.50 \text{ ppm}$

These limits are based upon the control of the stress corrosion over the entire life of the plant.

## **EROSION OF PLANT COMPONENTS**

In materials science, **erosion** is the recession of surfaces by repeated localized mechanical trauma as, for example, by suspended abrasive particles within a moving fluid.

Erosion can also occur from non-abrasive fluid mixtures as, for example, continuous and repeated feedwater flow through an Orifice or Throttle Valve can eventually recess the surfaces and change the desired flow characteristics provided by the component.

Cavitation is another example of how erosion can be induced in plant components.

## **Cavitation**

As a pump impeller moves through a fluid, low pressure areas are formed as the fluid accelerates around and moves past the impeller blades. The faster the blades move, the lower the pressure around it can become. As it reaches vapor pressure, the fluid vaporizes and forms small bubbles of gas. This is Cavitation. When the bubbles collapse later, they typically cause very strong local shockwaves in the fluid, which may be audible and may even damage the blades (**erosion**).

Cavitation in pumps may occur in two different forms:

### **Suction Cavitation**

Suction Cavitation occurs when the pump suction is under a low pressure/high vacuum condition where the liquid turns into a vapor at the eye of the pump impeller. This vapor is carried over to the discharge side of the pump where it no longer sees vacuum and is compressed back into a liquid by the discharge pressure. This imploding action occurs violently and attacks the face of the impeller. An impeller that has been operating under a suction Cavitation condition has large chunks of material removed (**erosion**) from its face causing premature failure of the pump.

## **Discharge Cavitation**

Discharge Cavitation occurs when the pump discharge pressure is extremely high. It normally occurs in a pump that is running at less than 10% of its best efficiency point. The high discharge pressure causes the majority of the fluid to circulate inside the pump instead of being allowed to flow out the discharge. As the liquid flows around the impeller it must pass through the small clearance between the impeller and the pump cutwater at extremely high velocity. This velocity causes a vacuum to develop at the cutwater (similar to what occurs in a Venturi) which turns the liquid into a vapor. A pump that has been operating under these conditions shows premature wear of the impeller vane tips (**erosion**) and the pump cutwater.

## VOCABULARY

Acid: A substance that dissociates to form hydrogen ions ( $H^+$ ) in solution.

Base: A substance that dissociates to form hydroxide ions ( $OH^-$ ) in solution.

Caustic Corrosion: A type of corrosion that occurs in zircalloy and all ferrous metals. Although very little is known about it, it is one of the most important types of localized corrosion.

Corrosion: The act or process of wearing away, especially of metals.

Crevice Corrosion: A specialized case of galvanic corrosion that occurs when two pieces of the same metal are in contact.

Crud: A finely divided material, produced from the corrosion of metals, suspended in water.

Electronegativity: The ability of an atom to attract electrons, similar to electric potential.

Erosion: The recession of surfaces by repeated localized mechanical trauma.

Galvanic Corrosion: A type of corrosion that occurs when two metals with dissimilar electronegativities are in contact in water. The metal with the lower electronegativity oxidizes faster in water.

General Corrosion: A gradual process which results in a uniform removal of material from all metal surfaces in contact with water.

Localized Corrosion: A rapid destructive attack on a metal at a select location.

Oxidation: A chemical change in which electrons are lost to an atom.

pH: The negative logarithm to the base ten of the hydrogen ion concentration.  
 $\text{pH} = -\log [\text{H}^+]$

Pitting Corrosion: A type of corrosion that begins at points of high activity on the surface of a metal. For example, where nucleate boiling occurs or where flaws in a plate surface exist.

Radiolysis: The processes of dissociation of water into elementary  $\text{H}_2$  and  $\text{O}_2$  in the radiation field of the core and the activation of corrosion products.

Reduction: The gain of electrons in an atom.

Solubility: The maximum amount of a solute that can be dissolved in a solvent at a given temperature and pressure.

Solute: Substance that is homogeneously dispersed in the solvent.

Solvent: Dissolving medium in a solution.

Stress Corrosion Cracking: A type of corrosion that attacks almost all alloyed metals. It attacks very few pure metals.

Zirc-hydriding: A process in which hydrogen diffuses into the crystal structure of zirconium which then reacts to form zirconium hydride.

## **SELF-ASSESSMENT QUESTIONS**

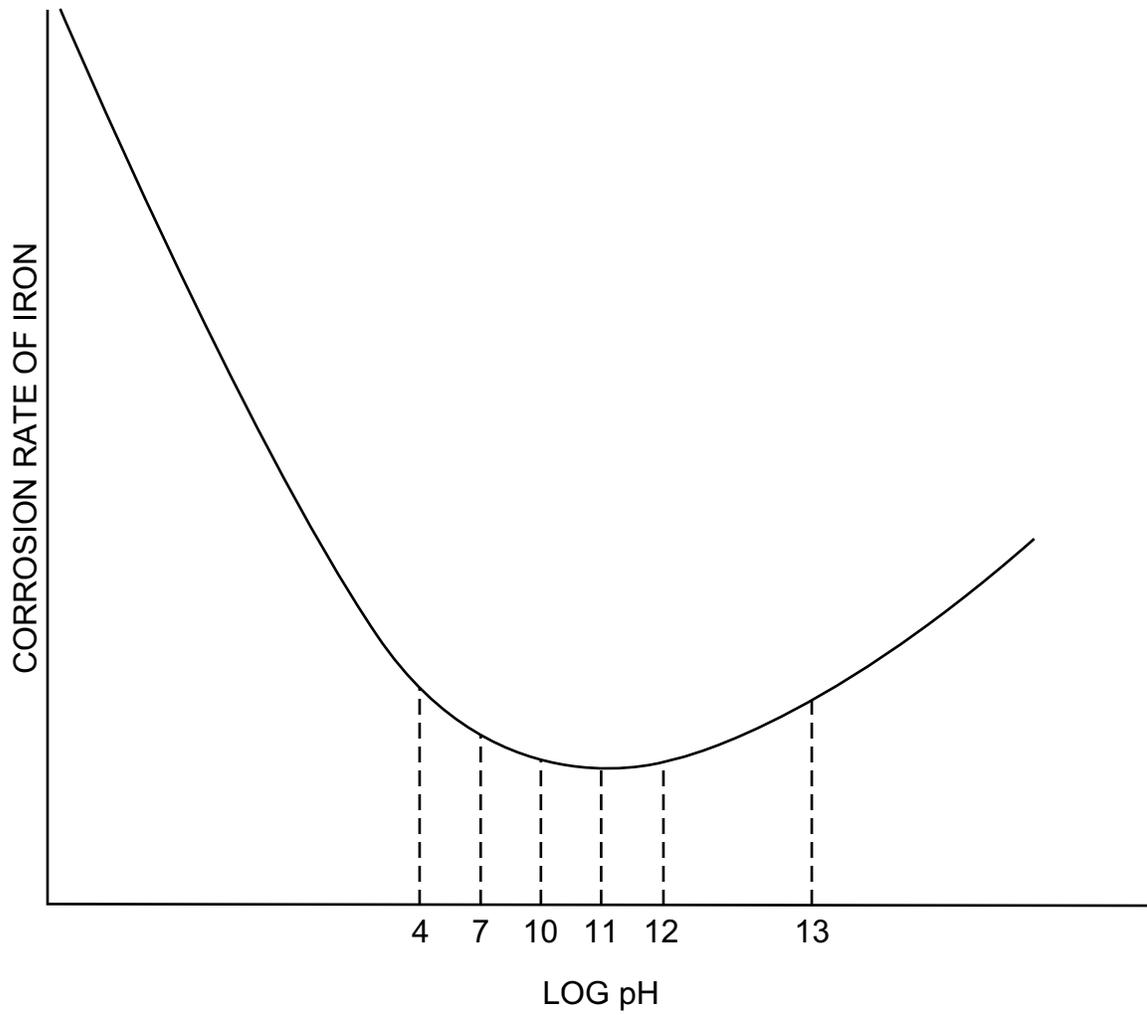
1. Describe the process of zirc-hydriding. What are the consequences of this process?
2. What environmental conditions affect the corrosion rate of metals in a plant?
3. List three mechanisms by which the general rate of corrosion can be controlled.
4. Define crud, and explain how crud deposits can affect the operation of the plant.
5. What sort of events can cause shocks that free corrosion products from their oxide layers?
6. What are the five types of localized corrosion? Briefly describe the conditions which contribute to or are necessary for each type.

7. What are the common limitations on the chemical environment that address all five types of localized corrosion?
  
8. How is the formation and deposition of CRUD associated with radiation levels?
  
9. What is the Technical Specification for the Reactor Coolant System for O<sub>2</sub>, FI, CI? List at least four specific types of corrosion that this Technical Specification limits.

## REFERENCES

1. Cohen, Paul, *Water Coolant Technology of Power Reactors* (Illinois: American Nuclear Society, 1980).
2. Drago, Russell S., *Principles of Chemistry with Practical Perspectives* (Boston: Allyn and Bacon, Inc., 1977).
3. Roberts, J. T. Adrian., *Structural Materials in Nuclear Power Systems* (New York: Plenum Press, 1981).
4. LER-90-05, Steam Generator Tube Eddy Current Results - Category C-3 Applied.
5. IN-91-67, Problem with Detection of Intergranular Attack.

# CORRECTIVE RATE vs. pH IN IRON



**Figure CR1.1**

# GALVANIC CORROSION AT A ZINC - COPPER JUNCTION

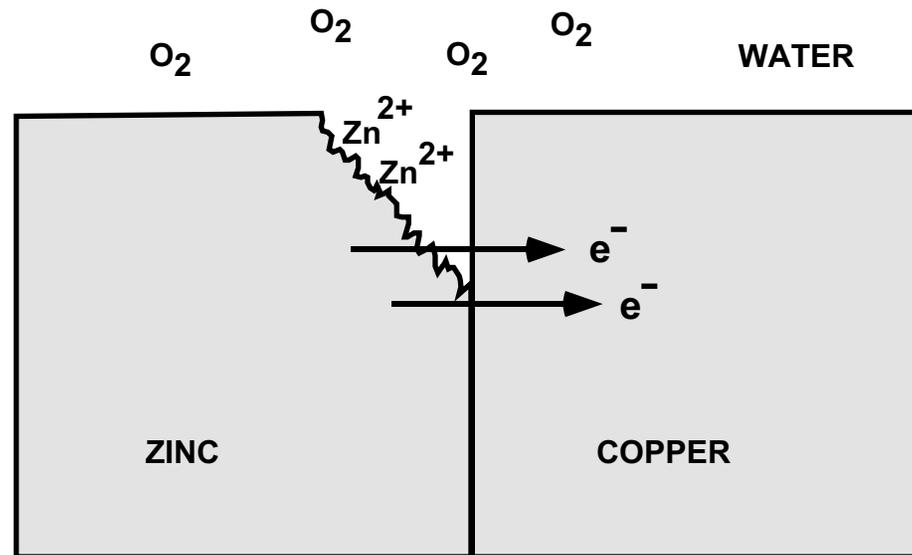


Figure CR1.2

# CREVICE CORROSION OF TWO IRON COMPONENTS

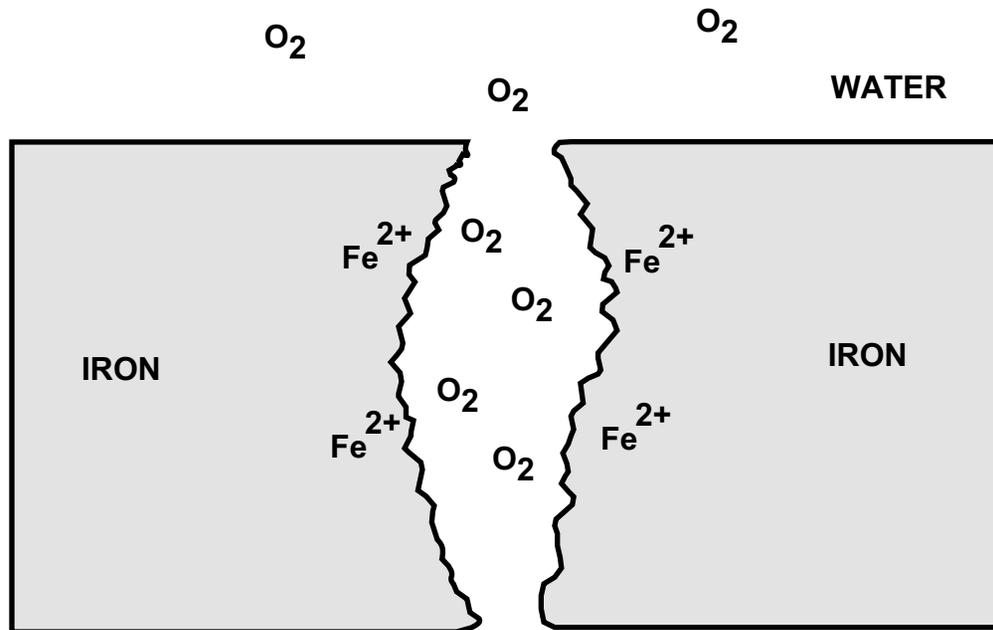


Figure CR1.3

# REACTOR COOLANT SYSTEM CHEMISTRY TECH SPEC

## REACTOR COOLANT SYSTEM

3/4 4 4.7 Chemistry

## LIMITING CONDITION FOR OPERATION

3.4.7 The Reactor Coolant System chemistry shall be maintained within the limits specified in Table 3.4-2.

APPLICABILITY: \_\_\_At all times

ACTION:

MODES 1, 2, 3, and 4:

- a. With any one or more chemistry parameter in excess of its Steady State Limit but within its Transient Limit, restore the parameter to within its Steady State Limit within 24 hours or be in at least HOT STANDBY within the next 6 hours and in COLD SHUTDOWN within the following 30 hours.
- b. With any one or more chemistry parameter in excess of its Transient Limit, be in at least HOT STANDBY within 6 hours and in COLD SHUTDOWN within the following 30 hours.

At All Other Times:

With the concentration of either chloride or fluoride in the Reactor Coolant System in excess of its Steady State Limit for more than 24 hours or in excess of its Transient Limit, reduce the pressurizer pressure to less than or equal to 500 psig, if applicable, and perform an engineering evaluation to determine the effects of the out-of-limit condition on the structural integrity of the Reactor Coolant System; determine that the Reactor Coolant System remains acceptable for continue operation prior to increasing the pressurizer pressure above 500 psig or prior to proceeding to MODE 4.

**Figure CR1.4**

# REACTOR COOLANT SYSTEM CHEMISTRY LIMITS

## CHEMISTRY LIMITS

	<u>STEADY STATE</u>	<u>TRANSIENT</u>
<u>PARAMETER</u>	<u>LIMIT</u>	<u>LIMIT</u>
DISSOLVED OXYGEN*	0.10 ppm	1.00 ppm
CHLORIDE	0.15 ppm	1.50 ppm
FLUORIDE	0.15 ppm	1.50 ppm

## CHEMISTRY LIMITS SURVEILLANCE REQUIREMENTS

<u>PARAMETER</u>	<u>SAMPLE AND ANALYSIS FREQUENCY</u>
DISSOLVED OXYGEN*	At least once per 72 hours
CHLORIDE	At least once per 72 hours
FLUORIDE	At least once per 72 hours

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\*Limit not applicable with  $T_{avg} \geq 250^{\circ}\text{F}$

**Figure CR1.5**

# GENERAL CORROSION OF IRON IN WATER

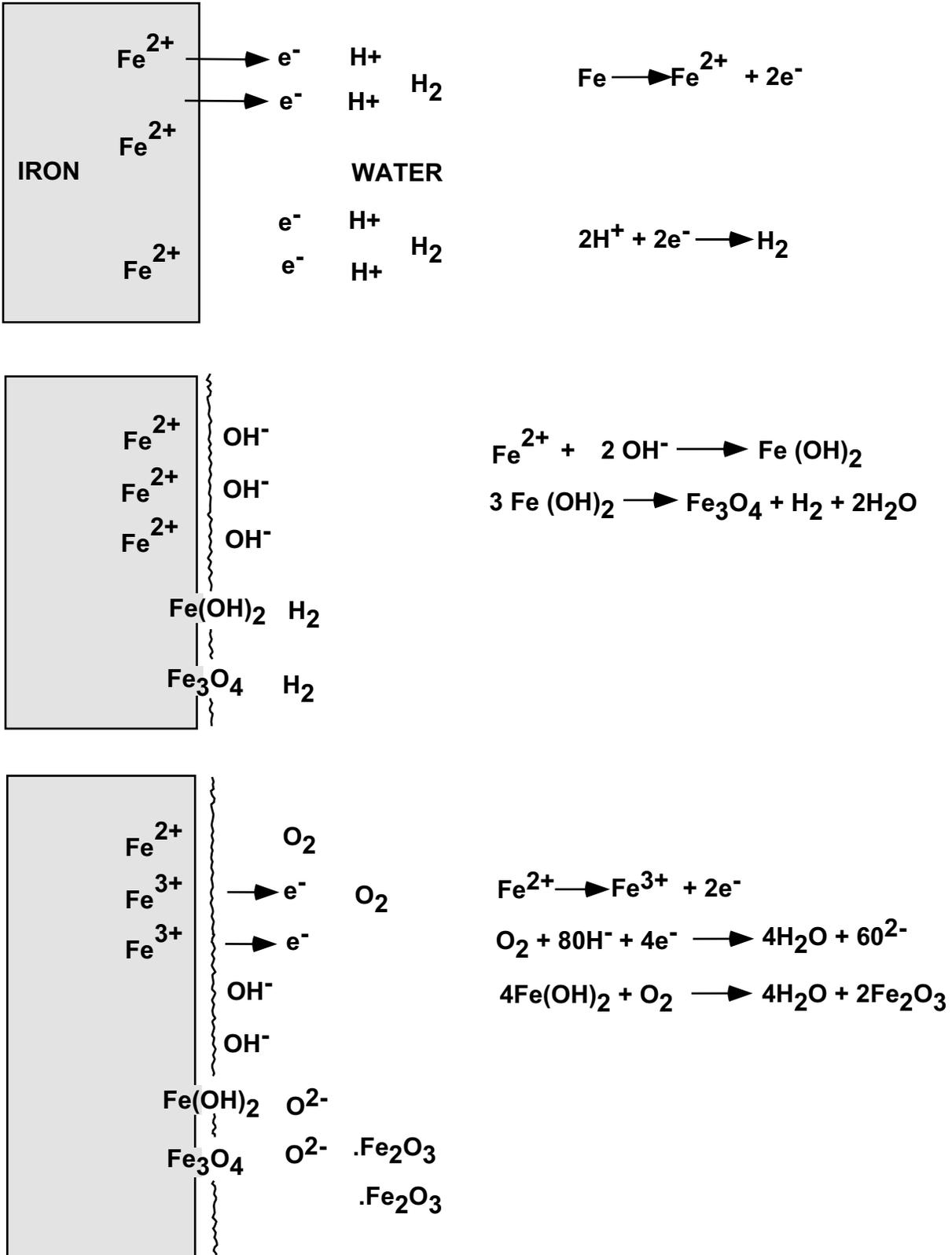


Figure CR1.6