
Material Properties and Corrosion

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1.0 OBJECTIVES

This course covers the following areas pertaining to Mechanical Properties:

- Mechanical and Thermal Stress
- Corrosion
- Pressure Tubes and Fuel Bundles

At the completion of training the participant will be able to:

Mechanical and Thermal Stress

- define terms as they relate to materials: mechanical stress and strain, hoop stress, thermal expansion, differential thermal expansion, thermal shock & residual stress
- describe factors which cause mechanical and thermal stress in a component
- explain the consequences of exceeding stress limits in materials
- explain why heating and cool down rates are limited
- define the following properties of materials: ductility, brittleness & nil-ductility transition
- explain the differences between ductile and brittle fracture
- explain why a material exhibiting a ductile/brittle transition temperature has operating limitations with respect to temperature
- define creep as it relates to materials
- explain why a large shaft becomes deformed when at rest
- explain why rolling a large shaft prior to operation reduces the deformation
- describe fatigue failure and work hardening

Corrosion

- describe the erosion of material
- describe wear or surface failure of materials
- given a plant system and associated chemical parameters with their normal operating ranges, explain the consequences of operating outside this range and the control methods used
- describe the following corrosion types: uniform, galvanic, pitting and crevice, stress corrosion cracking, erosion & microbiologically induced
- explain the importance of pH control in carbon steel based systems, including the significance of a magnetite layer, and describe the typical methods used to maintain proper control

- explain the importance of dissolved oxygen control in carbon steel based systems, and describe the typical methods used to maintain proper control
- explain the importance of conductivity control, and describe the typical methods used to maintain proper control
- define the term stress corrosion cracking (SCC), and state the conditions required to promote SCC
- explain the importance of pH control in stainless steel based systems, and describe the typical methods used to maintain proper control
- explain the importance of conductivity control, and describe the typical methods used to maintain proper control
- explain how scale can be formed on boiler tubes, state the adverse consequences of scale formation, and state the methods used to minimize scale formation

Pressure Tubes and Fuel Bundles

- state the effect of radiation on materials: oils and greases, plastics, metals & concrete
- describe the causes of creep in pressure tubes
- describe the process of hydrogen embrittlement and the occurrence of delayed hydride cracking and blistering of pressure tubes, including the factors affecting it
- explain how temperature cycling and reduced heat transport pressure can be used to minimize the potential for delayed hydride cracking in pressure tubes during start-up and cool-down

2.0 MATERIAL PROPERTIES

Notes:

2.1 INTRODUCTION

Materials of many types are important both in the design and operation of nuclear power plants. All materials may fail due to external or internal forces, such as mechanical and thermal stress, or to associated phenomena like creep, fatigue and erosion. In this module, we will discuss the main causes and consequences of mechanical failure for materials commonly encountered and over which an operator has some control.

2.2 MECHANICAL AND THERMAL STRESS

Stress is a familiar word today, but the technical definitions of stress and its resulting effect, strain, are quite precise. The following are definitions of these and associated terms.

2.2.1 Mechanical Stress and Strain

Whenever a load or force is applied to a material, that material is subject to a stress defined as the force applied over a unit area. (This concept allows us to ignore the size of the unit while exploring the effect of the force on the physical state of the part.) For example, external force due to gravity stresses all materials.

There are three types of stress:

- Tensile stress that tends to lengthen a material.
Example: a spring with a weight attached to one end.
- Compressive stress that tends to compress a material. Example: a car jack under load.
- Shear stress that results when a transverse load is applied. Example: to a shaft that is misaligned.

The three types are illustrated in Figure 1.

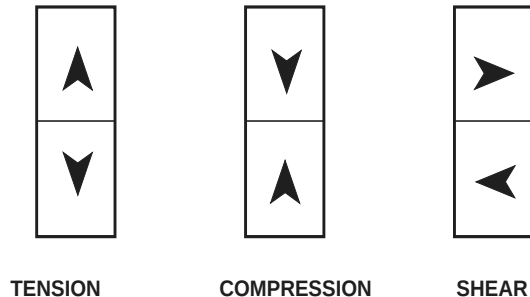


Figure 1
Types of Stress

Strain is the resulting effect of stress. For example, strain is often measured as the % of elongation or relative change in the length of a part to which a tensile force has been applied. In many materials, applied stress can have one or more of three effects, depending on the magnitude of the stress:

- At relatively low stress, material will deform elastically, that is, it will return to its original condition after the stress is removed.
- At moderate levels of stress, the material will reach its elastic limit or yield point and begin to deform plastically. It will not return to its original condition, but will remain permanently deformed.
- At relatively high levels of stress, the material will fail or fracture because its yield strength has been exceeded.

2.2.2 Thermal Stress and Strain

Materials are also subject to stresses because of temperature differences. These can cause changes in the dimensions of a part. Whenever a change in dimension is resisted, a thermal stress will result. Changes in the dimension of a unit can be resisted by external constraints or caused by internal temperature gradients, or both. For example, an external constraint could be a beam set in concrete at both ends. When the beam is heated or cooled significantly, compressive or tensile stresses will result.

Notes:

In cases where a temperature difference or gradient occurs within the material, the forces generated will be internal.

The hotter parts of the material will usually have expanded more than the colder parts, causing compression of the hotter areas and tension in the colder parts.

Sometimes, as opposed to the constrained case described above, this is considered to be a true heat stress. Some of the processes involved in discussing heat stress are described below:

- Thermal Expansion, (or the increase in length) for most materials, results from an increase in temperature. The extent of the expansion depends on the temperature change, the temperature itself, the length of the part, and the material(s) involved.
- Differential thermal expansion results whenever there is a temperature difference or gradient from point to point in metals. The differential occurs because most metals expand with increasing temperature. If the increase (or decrease) in temperature is different in different sections of a material, the sections will have expanded to a different extent. In this case, the compressive and tensile stresses can result in the bending of the part, as shown in Figure 2.

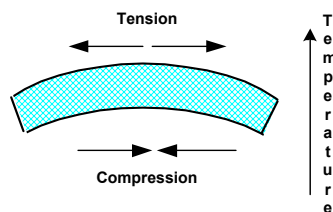


Figure 2
Bending Due to Differential Thermal Expansion

- Thermal shock is an internal stress that is the result of rapid heating or cooling of a part. In the case of heating, high compressive stresses near the surface can result in internal fracturing while in the case of cooling, the high tensile stresses on the surface of the part can result in external cracking.

Notes:

2.2.3 Hoop Stress

Hoop stress is stress in a pipe that resists the expansion of the pipe when the fluid inside the pipe is under pressure. In more technical terms it is the stress in a pipe wall acting circumferentially in a plane perpendicular to the longitudinal axis of the pipe and produced by the pressure of the fluid in the pipe.

2.2.4 Residual Stress

During manufacture, installation and maintenance material may be left in a state where there are permanent stresses inside the material. Residual stress is applied continually for the life of the equipment. Drilling holes, welding and bending pieces are among the many ways of applying residual stress onto material. The more formal definition follows. Residual stress is a tension or compression, which exists in the bulk of a material without application of an external load (applied force, displacement of thermal gradient).

2.2.5 Factors that Cause Mechanical or Thermal Stress in a Component

As mentioned, most materials being stressed have a tendency to deform reversibly (elastic deformation) at relatively low levels of stress while those that deform permanently (plastic deformation) do so at higher levels past the elastic limit. These concepts and others will be discussed later and are illustrated in Figure 3 below.

With increasing stress (force/area), the material deforms, and is subject to increasing strain, until the material reaches its elastic limit. Any further increase in applied stress will result in plastic or irreversible deformation. At some point, the material will begin to fracture and then the stress actually decreases.

Notes:

Figure 3 illustrates the effect of applying a mechanical tensile stress, but it should be noted that materials respond in similar ways to other modes of applied stress.

Notes:

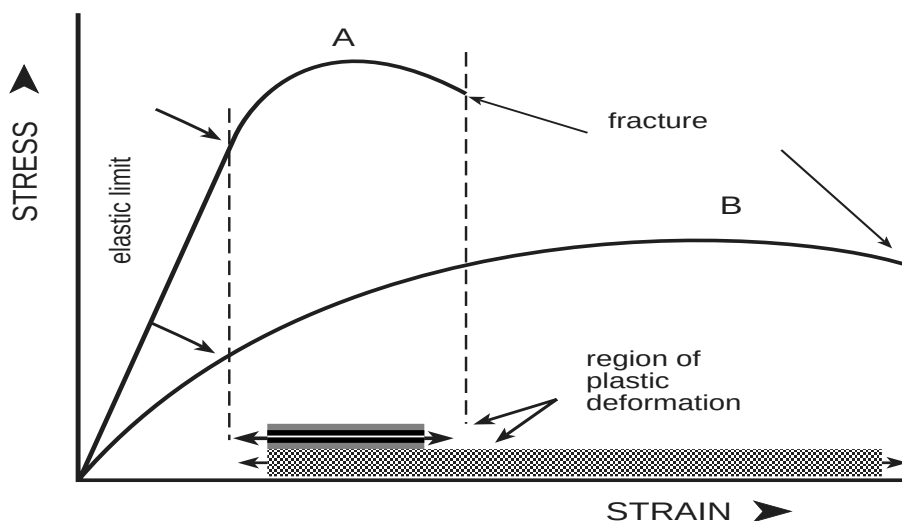


Figure 3
Plastic Deformation Regions

All materials on the earth's surface are subject to the mechanical stresses caused by the force of gravity. Gravity is also responsible for compressive loads on machine supports and for potential creep in large horizontal shafts (to be discussed below).

Other mechanical stresses occur in rotating machinery due to centrifugal forces and loads on thrust bearings.

Thermal stresses are caused by heating or cooling as temperature differentials are set up due to the flow of heat into or out of a part.

As discussed, the dimensions of a part depend on, and usually increase with, rising temperature. The consequence is that the surface of a part being heated expands more than the interior, causing compressive stresses near the surface and tensile and shear stresses inside the part. While heat exchanger tubes are also subject to thermal stresses, the effects are small because the temperature drop across a heat exchanger tube is usually very small.

Both thermal and mechanical stresses can result from sudden changes in pressure in a fluid (gas and/or liquid) system. Pressure is a measure of the force exerted by a fluid constrained by a solid surface (for example, boiler feed water or steam in a pipe).

Inside a pipe that is exposed to the atmosphere, the gauge pressure is a measure of the tensile forces exerted by the fluid on the pipe.

A sudden drop in pressure may indicate the possibility of a potentially catastrophic pipeline rupture. Should the flow of a fluid stop suddenly for any reason, there will be a nearly instantaneous increase in the system pressure and steam temperature, which can cause failure due to mechanical and thermal stresses.

2.2.6 Consequences of Exceeding Stress Limits of Materials

As materials are subject to increasing stress, the strain also increases through stages where the effect is reversible, irreversible and finally, total failure due to fracturing occurs. Clearly, the useful functioning of a part may end long before actual fracturing because the plastic deformation is irreversible and, therefore, the part will not return to its initial state.

With experience, designers have learned the relationships among stress, strain, temperature and operating conditions. With these data, stress limits have been set that can permit operation and use of a component for an acceptable time. Exceeding the stress limit however, can cause premature component failure, with all the associated consequences.

2.2.7 Why Heating and Cool Down Rates are Limited

Thermal stresses are generated whenever temperature gradients exist in a material and temperature gradients are created whenever a component is heated or cooled.

As noted, due to differential rates of thermal expansion, very large gradients can result whenever a large component is heated or cooled rapidly. To avoid the possibility of internal or external failure of the component, heating and cooling down rates are designed to limit temperature differences and the consequent strains due to thermal stresses to acceptable levels.

Notes:

2.2.8 Why valves should be cracked open during warm-up of a system

During warm-up of a system, large temperature differences may develop on either side of a closed valve. The thermal stresses that develop across the valve can cause valve-failure by the mechanisms previously discussed.

If valves are not cracked open during a system warm-up, the expanded volume of the confined water in the pipes, tanks and other vessels, which comprise the solid containment, will cause an increase in pressure and temperature. The resulting additional mechanical stress or opening of pressure relief valves, are undesirable consequences.

2.3 BRITTLE/DUCTILE TRANSITION

2.3.1 Ductility

Ductility is a measure of the property of a material that allows it to deform or change shape plastically under shear or tensile stresses without fracturing. Plastic deformation is irreversible. This means that some fundamental structural changes have occurred during the deformation. For most materials, ductility increases with temperature.

Hardness, or the resistance of a material to penetration by a sharp object, is a property closely associated with ductility. Ductile materials are usually relatively soft, and hard materials are often quite brittle (lacking in ductility). Diamonds and alundum are examples of very hard materials, and talc of a very soft material.

Copper for instance is a relatively ductile, hence soft material. It can be bent many times without fracturing but, as we know from experience, if it is bent too many times, it becomes work-hardened, then brittle and fractures easily.

Toughness is a related property that combines ductility and strength. Leather is an excellent example of a tough material. Generally, ductile metals will also tend to be tough.

2.3.2 Brittleness

Brittle metals have relatively little capacity for plastic deformation before they fracture. This means that a brittle part under excess stress loading can fail suddenly and potentially catastrophically without any initial elongation or deformation. The less ductile a metal, the more brittle it will be.

Notes:

2.3.3 Nil-Ductility Transition Temperature

Certain metals, such as carbon steel, and some plastics experience a fairly sharp change from a ductile to a brittle behaviour as the temperature falls.

One way of characterizing this property involves measuring the energy absorbed by the material to the point of fracture as a function of temperature.

The nil ductility transition temperature is: the temperature at which the energy needed to cause fracture is half the difference between those energies required for ductile and for brittle fracture. This concept is illustrated in Figure 4, below.

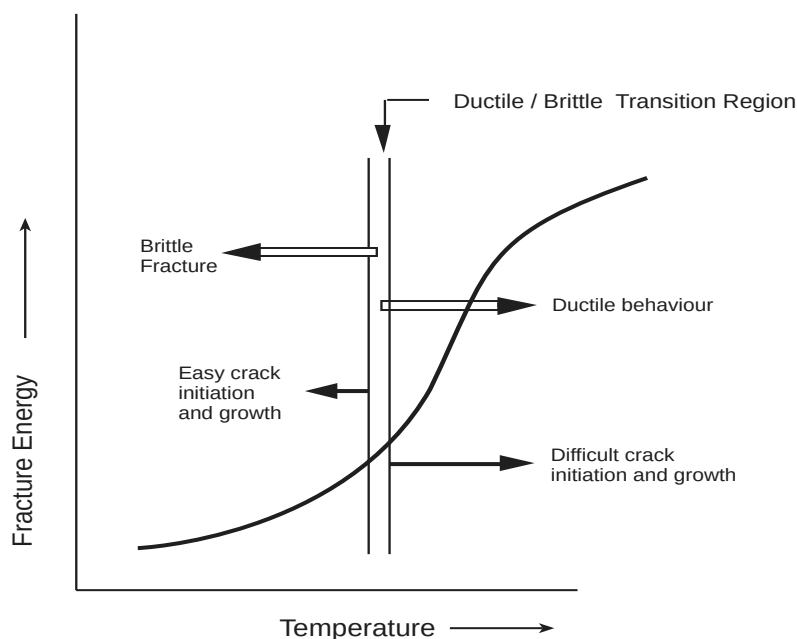


Figure 4
Nil Ductility Transition Temperature

Metals that display this property are known as notch sensitive as failure is particularly likely to occur at zones of high stress, such as those caused by a notch.

At temperatures below the transition temperature, fracture is brittle, with easy crack initiation and growth.

At temperatures above the transition temperature, fracture is ductile and crack initiation and growth are difficult. At temperatures close to the transition temperature, cracks may grow rapidly.

Notes:

2.3.4 Differences between Ductile and Brittle Fracture

The following Table 1 summarizes the differences between brittle and ductile fracture:

Generally, ductile fracture is the preferred failure mode because appreciable plastic deformation occurs before fracture, giving early warning, if noted, of impending trouble.

Characteristics of a Ductile Fracture	Characteristics of a Brittle Fracture
Primarily a flow process (i.e., deformation) where the material is slowly torn apart with a large expenditure of energy.	Involves little or no flow (deformation) of material.
Crack growth is a slow process. Significant plastic deformation before and during crack growth.	The crack growth is rapid (about 2000 m/s). (Brittle fracture is possible only when cracks can propagate at high velocities.)
The crack grows through the grains (transgranular) and the fracture appearance is grey and fibrous.	The crack grows along the grain boundaries (intergranular) and gives the fracture surface a bright crystalline or granular appearance.

Table 1
Characteristics of Ductile and Brittle Fracture

2.3.5 Operating Limitations for Materials Exhibiting a Ductile/Brittle Transition Temperature

Clearly, the safety and integrity of the facility depend on operating with all materials well above the nil ductility transition temperature.

When this is impossible, as during the use of isolation ice plugs, the temperature of the piping in the area of the plug will be well below the transition temperature of carbon steel.

Every precaution possible must then be taken to avoid mechanical and thermal shocks in the area of the plug. The same precautions must apply whenever work, for any reason, is done on materials below the transition temperature.

Notes:

The turbine and generator shaft have transition temperatures in the range 90-100 °C. To avoid brittle fracture due to thermal stresses, turbine and generator shafts are pre-warmed initially with the shaft rotating slowly, which evens out the stresses.

2.4 CREEP

Creep is the permanent or irreversible, time-dependent deformation of a material under a continuing loads. If the deformation is not managed properly, cracking and permanent failure can result. Examples of conditions under which metals must sustain a continuing load include:

- A stationary turbine shaft supporting its own weight (gravitational force)
- Walls of vessels or piping e.g., pressure tubes in a CANDU station, operated under pressure (pressure force)
- The blades on a turbine rotor (centrifugal force)
- Cables in pre-stressed concrete beams (imposed tensile force)
- Overhead power lines (gravitational force)

For a given material, the creep rate will increase under the following conditions:

- An increase in applied stress
- An increase in temperature
- An increase in neutron fluxes (where applicable) combined with elevated operating temperatures.

Normally, neutron irradiation damage tends to harden a material but, at elevated temperatures, the increase in ductility with temperature actually more than offsets the normal hardening process in a neutron field.

2.4.1 Why a large shaft becomes deformed when at rest

The force of gravity applies a constant load to turbine shafts, whether at rest or rotating. This stress always applies downward towards the centre of the earth. When the rotor is stationary, the metal is stressed in one direction only and tends to sag. Initially, the turbine shaft experiences time dependent-anelastic stress.

Ultimately, the sag may become irreversible, and the resulting creep can lead to extra stress on bearings, vibration, and potential failure of the turbine.

Notes:

Notes:

2.4.2 Why rolling a large shaft prior to operation reduces the deformation

Rolling the shaft evens out the effect of the gravitational stress on the shaft metal and reduces or eliminates the effects of anelastic stress and sag. If the turbine is left stationary for a long time, the undistributed stress may result in creep, which is irreversible. For this reason, turbines must be rolled regularly.

2.5 FATIGUE

2.5.1 Failure mechanisms due to fatigue caused by work hardening

Fatigue is a failure phenomenon associated with work-hardening of materials caused by fluctuating or repeated loads that result in increased brittleness and reduced service life. Fatigue is characteristic of ductile materials but the final failure is rapid and characteristic of brittle fracture.

The time leading up to fatigue failure cannot be predicted exactly but the following conditions are known to result in work- hardening, leading to fatigue:

- a relatively large, fluctuating applied stress
- a sufficiently large number of stress cycles

Fracture failure due to fatigue often occurs at relatively low applied stress and well within specified design loads. The stress can be mechanical, thermal or both and can alternate between compression and tension, or simply alternate between high and low values.

The best ways to ensure a reasonable service life for parts subject to the above conditions is; to ensure that scratches and other surface imperfections are removed by polishing and, if possible, by heat treatment, which relieves internal strains.

The only reasonably reliable methods of checking the progress of fatigue are by visual, x-ray or ultra-sound examination for surface and other cracks of the parts likely to be subject to work- hardening.

2.6 EROSION

2.6.1 Surface failure due to wear and erosion of materials

Surface failure is the loss of material from components due to corrosion or wear. The main causes and mechanically based mechanisms of wear are discussed in this section.

Notes:

The main causes of wear failure are abrasion, adhesion and fretting. Wear failure would be much less of a concern if solid surfaces were completely smooth. Unfortunately, even highly polished surfaces have microscopic imperfections, with high spots, or hills and low spots (valleys). The load on a part is not uniformly distributed but tends to be concentrated on the hills. This means that stress levels on the hills can be severe and beyond design limits

The three mechanisms of abrasion, adhesion and fretting are illustrated in Figure 5 below. All three mechanisms depend on the motion of surfaces relative to each other.

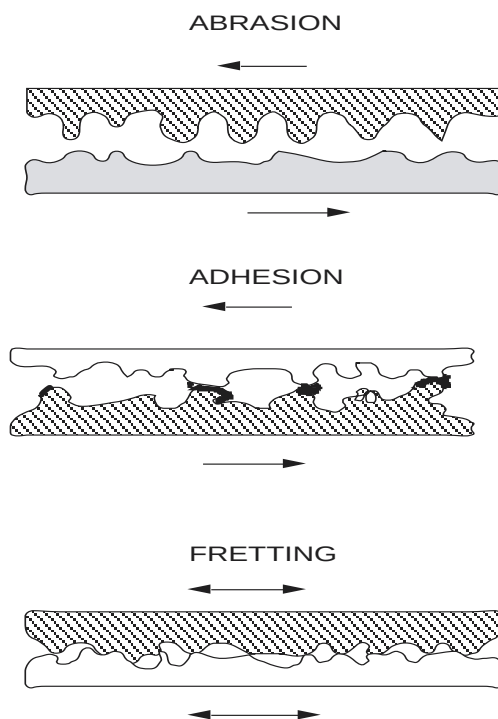


Figure 5
Types of Surface Wear

2.6.2 Abrasion

Abrasion is the microscopic gouging of a softer surface by the hills of a harder moving surface, or by hard particles trapped between the moving surfaces. The particles may be brought into the system from outside or may be the broken bits of hills from another surface.

Filtering out the hard particles from a re-circulating lubricant reduces the effects of abrasion on seals and glands.

Notes:

Moving parts in slurry and gas/liquid transport are also subject to abrasion. Specially designed seals and regular maintenance are important to minimize abrasion in these systems.

Cavitation also results in the erosion of valves and pumps. Very high stresses are caused as vapour bubbles collapse, initially causing embrittlement that will finally lead to the development of pits and cavities.

2.6.3 Adhesion

Adhesion is a process of surface failure in which the hills of metal parts are fused or welded together on a microscopic level, followed by the ripping off of the welds as the parts move relative to each other.

Relatively rough and soft surfaces are particularly prone to this type of failure.

To avoid this type of failure, run-in periods are specified for new machines and parts - high loads are then avoided and adequate lubrication is provided to ensure the controlled reduction of surface roughness.

2.6.4 Fretting

Fretting is usually associated with corrosion and occurs when corrosion products, such as oxides, accumulate between two surfaces in small displacement, periodic motion relative to each other. The oxides are quite hard and exacerbate the wear process.

This type of surface erosion occurs frequently in piping and heat exchangers, where even a small vibration can start the fretting process.

REVIEW QUESTIONS

Notes:

MECHANICAL & THERMAL STRESS

1. Define the following terms as they relate to materials.
 - Stress
 - Strain
 - Thermal expansion
 - Differential thermal expansion
 - Hoop stress
 - Residual stress
2. Give four examples of mechanical forces that put stress on equipment in a power plant.
3. A tank containing a gas undergoes a sudden rapid pressure drop. This pressure drop causes thermal stress in the walls of the tank. Briefly explain this phenomenon.
4. There are operating limits as to how faster equipment can be heated or cooled during plant start-ups and shutdowns. Explain the potential consequences of exceeding these limits.
5. Define the following terms.
 - Ductility
 - Brittleness
 - Nil-ductility transition
6. Fractures of materials can be divided into two major types: ductile and brittle. Describe the difference between these two types of fracture.
7. A material exhibiting a ductile/brittle transition temperature will have operating limitations. State 2 typical limitations and explain how they protect the material.
8. Define the term creep as it relates to materials.
9. Explain why the rotor of a turbine generator is occasionally rotated even during a shutdown.

10. Before start-up of a large turbine generator after a shutdown it is placed on turning gear for a number of hours. Explain why this is a standard operating practice.
11. Describe how metal components fail by the mechanism referred to as fatigue.
12. There are three major mechanisms that cause surface failure. Name the three methods and briefly describe each.

Notes:

3.0 CORROSION

Notes:

3.1 INTRODUCTION

Almost all metals except noble metals like gold, silver and, rarely, copper are found in nature in chemical combination with non-metals, that is, they have transferred to or shared electrons with other elements. The minerals so formed through chemical combination are often different from each other, but under the geological conditions in which they are found, they are in a stable and preferred state.

Corrosion is the undesirable combination of processes by which metals tend to chemically bind with other materials by losing or sharing electrons to or with other elements.

The chemical tendency for metals to form compounds by chemical reaction is not always undesirable. For example, as will be discussed below, carbon (mild) steel can react with oxygen to form the mineral magnetite, which protects the steel from corrosion.

3.2 TYPES OF CORROSION

The common types of corrosion are reviewed below.

3.2.1 Uniform Corrosion

Uniform corrosion is characterized by a relatively even rate of corrosion over an entire exposed surface. This type of corrosion is usually anticipated for parts like structural elements that can be sacrificed over time, but affects all common metals. In the case of carbon steel, the iron reacts with oxygen to form the mineral magnetite, an iron oxide, with the formula Fe_3O_4 .

Magnetite forms a protective layer that decreases the rate of corrosion. The magnetite layer consists of tiny, tightly packed black crystals that are dense and impermeable.

The formation of this protective layer depends on pH. At low pH (high acidity), no protective layer forms, and the steel will dissolve rapidly. At high pH, > 12 , the magnetite layer is no longer stable, and relatively porous rust permits rapid corrosion. Rust is another hydrated form of iron oxide that is porous and tends to be non-crystalline (amorphous) and has the approximate formula $\text{Fe}(\text{OH})_3 \cdot x\text{H}_2\text{O}$.

Notes:

The effect of pH on uniform and other types of corrosion on some common materials is discussed below:

- As noted above, the corrosion rate of carbon steel is a minimum in the pH range of 10 – 12.
- Many common metals, like steel, aluminium and magnesium are subject to acid attack at low pH.
- Zirconium alloys have high corrosion resistance to acidic solutions and alkaline solutions up to pH 12.
- A near neutral pH is best for stainless steel and copper alloys, and is absolutely essential for aluminium.
- Nickel alloys such as monel and inconel demand a high pH environment.

The addition of chemicals and the use of surface coatings (paint) usually control the rate of uniform corrosion.

3.2.2 Galvanic Corrosion

Reactions

At the Anode:



At the Cathode:



In the Electrolyte:

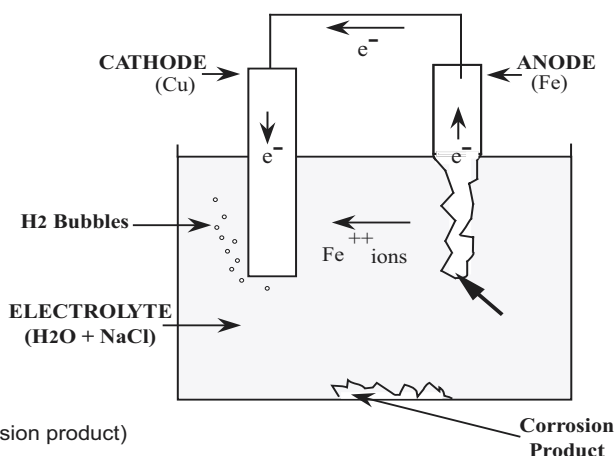
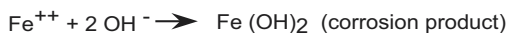


Figure 1A
Typical Galvanic Cell

Each metal or alloy has a different tendency or potential for donating or sharing electrons. If two dissimilar metals say copper and carbon steel are connected in an electric circuit (galvanic cell), as shown in Figure 1, the steel will tend to donate electrons to the hydrogen ions in the aqueous solution, producing hydrogen gas (H₂). The aqueous salt solution (electrolyte) acts both as a conductor of electricity, and as a reagent.

The galvanic cell shown has two electrodes; the steel anode, which donates electrons, and the copper cathode, which receives them and transfers them to hydrogen ions.

The galvanic cell can also be used to help prevent corrosion. For example, if the copper electrode in the scheme above is replaced with magnesium metal, the steel electrode will become the cathode as the magnesium electrode (anode) dissolves (corrodes) preferentially to produce positive magnesium ions. The magnesium metal dissolves preferentially because it has a much greater tendency than steel to donate electrons. This procedure is called cathodic protection. Whenever two different metal electrodes are connected as shown in Figure 1, the metal with the greater tendency to donate electrons will always form the anode, and the metal with the lower tendency will always form the cathode. Other factors, which affect the rate of galvanic corrosion, include:

- The oxygen concentration of the electrolyte (process water). Oxygen can pick up some of the electrons from the cathode, and react with hydrogen ions to produce water.
- Increases in temperature, generally, increase the rate of chemical reactions. Corrosion is a chemical reaction.
- The conductivity of the water (electrolyte). Clearly, the water concentration should be as low as reasonably achievable (ALARA) to increase the resistance of the circuit to the transfer of electrons and thereby reduce the corrosion rate.
- The ratio of the surface area of the cathode to that of the anode (cathode/anode surface area ratio). The corrosion rate increases as the relative cathode area increases because the resistance to electron transfer decreases (current flow increases).

Galvanic corrosion occurs whenever two dissimilar metals are in electrical contact with each other in water that can transfer electrons, that is, has non-zero conductivity.

Galvanic corrosion, then, can be minimized by selecting metal couples that have relatively close potentials to donate electrons, by isolating dissimilar metals from each other, and also by isolating the anodic metal from the process water. An example of how to isolate dissimilar metals from each other is the use of a plastic isolating bushing in pipe couplings connecting steel and copper. The protective magnetite layer formed on steel in the right pH range tends to isolate the anodic metal from the electrolyte (process water).

Notes:

3.2.3 Pitting and Crevice Corrosion

Pitting and crevice corrosion are special cases of galvanic corrosion by which metal loss is localized over a relatively small region of a metal. In these cases, corrosion occurs because of localized concentration differences of oxygen or of a hostile ion, for example, the chloride ion, or of differences in pH. This situation can develop wherever conditions in the flow result in regions of low flow or stagnation, for example, in small cracks, gaps, or crevices, such as those associated with bolts, gaskets, and metal contact points.

Pitting corrosion is associated with scale and crud deposits which form a barrier between the main flow and the stagnant water trapped under the scale or crud deposit. Under these conditions, oxygen dissolved in the process water cannot penetrate the scale. In the relative absence of oxygen, the metal under the deposit becomes anodic, that is, it will tend to dissolve and form a deep pit. This situation is illustrated in Figure 2.

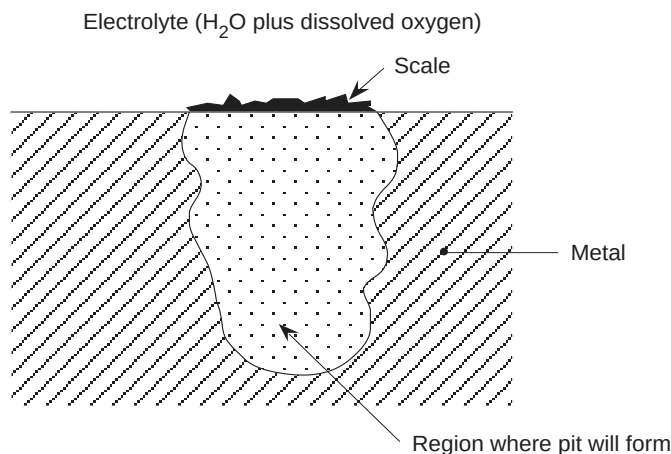


Figure 2
Pitting Corrosion

Pitting and crevice corrosion are minimized by chemical control, proper drainage of vessels during shutdown, removal of suspended solids by filtration, removal of corrosion products by ion exchange, and removal of scale, crud and bacterial deposits.

Oxygen control and removal is important, because this tends to reduce the chemical potential for the formation of oxygen depleted, anodic zones.

Notes:

3.2.4 Stress Corrosion Cracking (SCC)

Stress corrosion cracking can occur whenever steady tensile stresses combine with corrosion to cause the formation of localized cracks. Typically, SCC is found in stainless steel systems and is promoted aggressively by chloride ions. SCC can cause sudden failure without warning.

The tensile stresses are caused during part manufacture, from faulty installation, or from in-service conditions.

Methods of controlling SCC are discussed in section 3.4.

3.2.5 Erosion Corrosion

Erosion corrosion occurs when the flow of water combines with corrosion to effect significant increases in the rate of metal removal over that experienced at lower flow rates. The effect of the flow is due to the removal of metal ions and protective layers as they form, which increases the chemical driving force for corrosion and may tend to prevent the formation of a protective layer. This latter effect is a major cause of loss of metal in copper alloy steam condenser tubes. Corrosion product fines and other particulates like sand and silt in the cooling water can also increase corrosion rates.

Erosion corrosion has also been observed to cause thinning of carbon steel outlet feeder piping in the primary heat transfer system (PHTS). The control of this phenomenon is discussed in the sections below.

Grooves, waves and valleys in the metal surface, and short time periods to unexpected failures characterize erosion corrosion. Erosion corrosion is promoted by high water velocity, turbulence, the presence of particulates and the impingement of water at high velocity on metal surfaces. These effects are minimized by good design.

3.2.6 Microbiologically Induced Corrosion (MIC)

Bacteria, commonly in stagnant water promote microbiologically induced corrosion (MIC). The process can take place with or without the presence of oxygen, because specific bacteria have evolved to take advantage of either condition. For example, thiobacillus ferrooxidans can oxidize sulphur to sulphuric acid in water-cooling systems.

Nodules of oxygen loving bacteria can deposit on metal surfaces, creating conditions similar to those described in the section on Pitting Corrosion. Chlorination and replacement of exchanger tubes are used to control corrosion in heat exchangers using service water.

Notes:

The elimination of stagnant conditions is a major factor in the minimization of MIC in systems such as irradiated fuel bays, or demineralized water storage tanks. In systems where water is being circulated, e.g., through heat exchangers, a pH > 10.5, and the exclusion of air help minimize bacteria growth. Bactericides, chemical treatment and filtration are also used for control.

3.3 CARBON STEEL BASED SYSTEMS

The PHT, steam and feedwater, endshield cooling and condensate systems are generally considered to be the carbon steel systems.

3.3.1 pH Control in Carbon Steel Systems

As noted in the section above, pH is generally maintained greater than 10 and less than 12 to minimize the corrosion rate of carbon steel. The range in the PHT is 10.1 to 10.4. The pH on the Secondary side is generally 9 to 9.8 at condensate feedwater conditions (Pickering is lower). The pH may approach 12 at boiler temperatures.

The relatively narrow range of pH is necessary to minimize the rate of the dissolution of the protective magnetite layer, to prevent the acid attack of the steel at low pH, and to reduce the rate of conversion of magnetite to porous rust by dissolved oxygen at high pH.

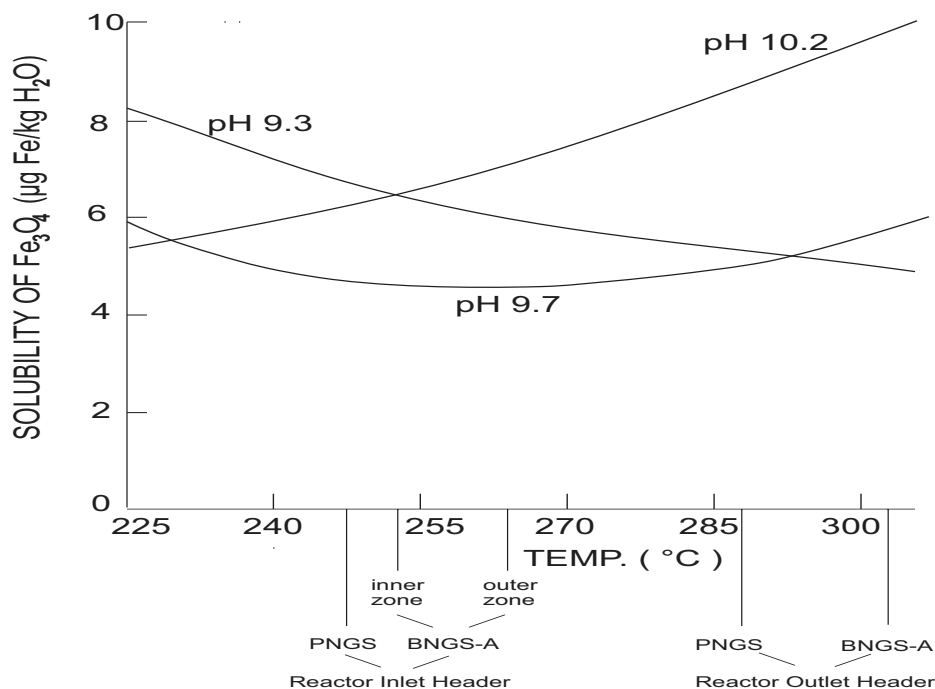


Figure 3
Solubility of Magnetite as a Function of Temperature at Different pH

Notes:

The Primary Heat Transfer System (PHTS)

At a high pH, say 10.2, as illustrated in Figure 3 above, the solubility of magnetite is quite high and decreases with temperature. The consequence of this is that magnetite will tend to dissolve near the reactor outlet header where the temperature is highest, and deposit on cooler parts of the PHTS, endangering the protective zirconia layer. Corrosion of the pressure tubes beneath the fuel bearing pads will also be promoted. Damage to the zirconia layer can result in increased hydriding of the pressure tubes. Lithium deuterioxide can concentrate at the fuel bearing pads, and attack the zirconium alloy by the mechanism of crevice corrosion. Thinning of the outlet feeder pipes due to erosion corrosion is also a concern when the pH is off spec on the high side.

High pH on start-up is common in units where lithium deuterioxide hide out has occurred. When cooling down or lowering reactor power, the HTS shrinks, drawing heavy water and concentrated lithium deuterioxide from the pressurizer into the HTS, causing a high pH excursion in the HTS. Valving in a deuterated IX column to replace excess lithium with deuterium ions controls high pH.

At a low pH, say 9.3 as shown in Figure 3, magnetite is less soluble at higher temperatures, and will deposit on the hotter in-core surfaces, leading to reduced heat transfer, fuel sheath hot spots, and fuel failure. (Increased corrosion of carbon steel will also cause increased activated corrosion products in the core, and higher fields out-of-core.)

One or more of the following causes low pH:

- Spent IX columns.
- Presence of lithium as carbonate rather than deuterioxide. Carbonate is a much weaker base than deuterioxide. Carbonate can come in the resin as purchased, by the radiolysis of organic matter, or from air if the HTS is open during shut down.
- Lithium deuterioxide hide out in stations with passing pressurizer valves. Steam escapes from the pressurizer to the bleed condenser and is replaced by HTS water, containing lithium deuterioxide. As the steam escapes, the concentration of the non-volatile deuterioxide increases in the pressurizer. A corresponding drop in system pH will occur requiring the addition of lithium deuterioxide. (There are no pressurizers at Pickering.)

Low pH is controlled by addition of lithium hydroxide and/or by valving in fresh IX columns, as required.

Notes:

The Condensate, Feedwater and Boiler System (C, FW, B System)

CANDU stations in Ontario use volatile bases (morpholine and/or ammonia, usually by hydrazine addition) for their pH control to minimize corrosion in ferrous systems. For the all-volatile treatment (AVT), volatility is important because all water cycling through the boiler is vaporized. If the added chemicals did not boil off with the water, they would tend to concentrate in sludge deposits in the boiler, creating corrosive conditions.

The chemicals used to control pH and minimize corrosion are added downstream from the condensate extraction pump (CEP).

The condenser and feedheater tubes of C, FW, B systems in all newer CANDU stations are stainless steel, the piping and most other components are carbon steel. Thus, the C, FW, B systems are essentially all-ferrous.

In all-ferrous stations, on-line pH measurements are made ahead of the LP feed heaters, to ensure control of condensate pH in the range 9.8 to 10.0. Ammonia maintains control of pH in most stations with all-ferrous trains. The ammonia forms as a result of the decomposition of excess hydrazine, or may be added directly. Morpholine is also specified in all-ferrous stations because its use reduces corrosion product transport in the feedwater, and also reduces erosion/corrosion in two-phase (wet steam) regions. When the desired condensate pH is maintained, the boiler water pH will follow at the desired value of > 9.5 .

Notes:

Notes:

Auxiliary Systems

Auxiliary systems, although not covered in the Objectives or K-Statements of the Module, also require pH control. Auxiliary systems include End Shield Cooling, Liquid Zone Control, Recirculating Cooling Water, and Irradiated Fuel Bays. Control is affected by ion exchange, as noted in Table 1 below:

System	Resins in Mixed Bed	Purpose
End Shield Cooling	Li^+ , OH^-	To remove unwanted impurities (ions) and to maintain system pH (typically pH 10.0 – 10.5)
Liquid Zone Control	H^+ , OH^-	To remove unwanted impurities (ions) and to maintain system pH (typically conductivity < 0.1 mS/m, pH 6.0 – 8.0)
Recirculating Cooling Water	Li^+ , OH^-	To remove unwanted impurities (ions) and to maintain system pH (typically pH 9.0 – 10.8)
Irradiated Fuel Bay	H^+ , OH^-	To remove unwanted impurities (ions) and to maintain system pH (typically pH 6.5 – 7.5, conductivity < 0.2 mS/m)
Stator Cooling Water	H^+ , OH^- and Deoxygenating Column	To remove dissolved oxygen by deoxygenating column and other unwanted impurities (ions) in a mixed bed column, and to maintain system pH (typically pH 6-8, conductivity < 0.1 mS/m, dissolved oxygen < 20 ppb)

Table 1
pH Control in Auxiliary Systems by Ion Exchange

3.3.2 The importance of dissolved oxygen control, and typical methods for proper control

The Primary Heat Transfer System (HTS)

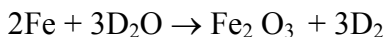
Elemental oxygen gas is produced in the primary heat transfer system (HTS) by radiolysis of heavy water (D_2O). Maintaining low dissolved oxygen minimizes the corrosion of carbon steel and zirconium.

Low oxygen gas concentration is also important because:

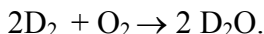
- Oxygen can cause stress corrosion cracking of Inconel boiler tubes and corrosion of Monel-400.
- Oxygen gas increases the aggressiveness of the chloride ion.

These concerns are discussed in the section below.

Oxygen corrodes zirconium and carbon steel, and can convert protective oxide (zirconia and magnetite) into porous hydrated oxide layers. This porosity permits water to attack the underlying metals, producing oxides and deuterium:



Maintaining dissolved deuterium within specification (3-10 cc/kg D₂O) controls dissolved oxygen in the HTS. The slight excess of dissolved deuterium (or hydrogen) consumes dissolved oxygen by the following reaction



The Condensate, Feedwater, and Boiler Systems

For convenience, the term Condensate, Feedwater and Boiler (C, FW, B) System refers to the complete secondary (light water) side. The overall working unit includes the boiler, turbine, condenser, condensate extraction pump, LP feedheater, de-aerator, boiler feed pumps and HP feedheaters. The governing Objective of chemical control is the minimization of corrosion and its consequences, particularly sludge and scale formation.

Dissolved oxygen gas is the most harmful impurity in the condenser, feed water and boiler system because, as discussed above, it converts protective magnetite on carbon steel to porous rust, and promotes corrosion throughout the system. Corrosion products lead to tube sheet sludge and crud deposits. These adverse effects increase with increasing oxygen gas concentration.

Dissolved oxygen increases the aggressiveness of the chloride ion, particularly under localized anodic conditions that encourage pitting.

Because of its aggressive chemistry, dissolved oxygen has action levels in the feedwater system to minimize corrosion product formation and transport in the boilers, and to minimize corrosion, particularly pitting corrosion of the boiler tubes in the presence of chloride.

Notes:

To maintain the dissolved oxygen As Low as Reasonably Achievable (ALARA), dissolved oxygen control is achieved in three stages:

Notes:

The first stage is the condenser air extraction system. Most dissolved oxygen or air removal occurs above the condenser water line. Sources below the water line are the main contributors to the dissolved oxygen content in the condensate.

In the second stage, dissolved oxygen is removed from the condensate by the deaerator, which contains sprays, steam spargers, and cascade trays over which the hot water tumbles. The combination of heat and large surface area provides very efficient stripping of dissolved gases. Oxygen is reduced to < 5 ppb (wt/wt) and non-condensable gases are also removed. This efficient stripping reduces chemical consumption in the final stage.

In the final stage of oxygen removal, hydrazine is added to chemically react with the remaining dissolved oxygen to produce nitrogen gas and water.

An excess of hydrazine is required to control the dissolved oxygen below 5 ppb. The excess will cause the pH to rise, as hydrazine slowly converts to ammonia, a weak base. This compound too must be controlled to protect against corrosion of ferrous brass systems containing copper, which is dissolved in ammonia. (In all-ferrous systems, the concern is an environmental release in the blowdown water)

3.4 THE IMPORTANCE OF CONDUCTIVITY CONTROL, AND TYPICAL METHODS FOR PROPER CONTROL

The Primary Heat Transport System (HTS)

Conductivity and lithium are not specifically controlled in the HTS but are important diagnostic parameters. They are used in trouble-shooting at all action levels, if the HTS pH goes out of specification. If the amount of lithium present is substantially greater than the system pH would indicate, conductivity measurements of grab samples are used to help explain this discrepancy. The presence of other ions (such of carbonate) would usually show from the conductivity. Correlations between conductivity and the concentrations of ionic species are possible because the specific conductivities of individual ions are known.

The Condensate, Feedwater and Boiler Systems

As noted above, the term Condensate, Feedwater and Boiler (C, FW, B) System refers to the complete secondary (light water) side. The overall working unit includes the boiler, turbine, condenser, condensate extraction pump, LP feedheater, de-aerator, boiler feed pumps and HP feedheaters.

The governing objective of chemical control is the minimization of corrosion and its consequences, particularly sludge and scale formation. The latter problem area is discussed in the section below.

Boiler water cation conductivity is an operating parameter with a shutdown limit. The impurities are both aggressive inorganic anions such as sulphate and chloride, as well as more benign organic anions from the additives or the water treatment plant. Since the organic anions are less corrosive, the inorganic contribution must be determined before shutdown. Maintaining the inorganic contribution to cation conductivity ALARA, protects against boiler tube corrosion.

Boiler water has a high background conductivity from pH additives (morpholine, hydrazine and ammonia), traces of raw cooling water salts and dissolved corrosion products. Because of the masking conductivity effect, ordinary (specific) conductivity is not sensitive enough to be used as a control parameter. Cation conductivity is used because it is more sensitive to the presence of harmful anions, like chloride, sulphate, and silica.

Possible causes of high cation conductivity include a water treatment plant acid excursion, which allows sulphate ion to enter the makeup water. Alternatively, a leak in one or more of the condenser tubes will admit raw water into the C, FW, and B System.

Cation conductivity is reduced and/or controlled by boiler blow-down, and by the repair of leaks, if necessary. If the conductivity is not controlled, the consequences include:

- Boiler tube scale formation;
- Boiler tube corrosion and failure;
- Loss of the protective magnetite layer on carbon steel surfaces permits general corrosion (acid excursion only).

To determine the cation conductivity, a sample of boiler water is passed through a cation exchange column. The column replaces all cations (including those of morpholine, ammonia and hydrazine) with hydrogen ions.

The water exiting the cation exchange column will contain hydrogen ions and various anions. By doing this, the conductivity signal is heightened because the anions are more likely to be fully ionized, that is, to have their maximum negative charge. The conductivity of water treated in this way is called the Cation Conductivity. The desired cation conductivity for boiler water is ALARA. The specification is $< 0.25 \text{ mS/m}$ for most stations.

Notes:

The use of very low conductivity makeup water from the water treatment plant is a major factor in maintaining the conductivity of the boiler water ALARA. Continuous blowdown controls the boiler water conductivity by constantly removing impurities from the system. Cation conductivity of the boiler water is monitored by continuous analysis, with grab sample verification.

3.5 STAINLESS STEEL BASED SYSTEMS

Systems covered as Stainless Steel based are the Moderator, Endshield Cooling and the Liquid Zone Control System (LZCS)

The phenomenon of stress corrosion cracking is defined in previous section 3.2.3

3.5.1 SCC in the Moderator

Stress corrosion promoted by chlorides can occur in the calandria and other stainless steel parts of the moderator system. Although high chlorides are not a common problem, the most likely chloride source is spent resin in the ion exchange column. Chlorides are removed by proper ion exchange control.

3.5.2 SCC in the End-shield Cooling and the Liquid Zone Control Systems

End Shield Cooling system materials are as follows:

Pumps-stainless steel;

- Expansion tank-carbon steel;
- Filter-stainless steel;
- Ion exchange column-stainless steel;
- Strainer-carbon steel;
- Valves-majority carbon steel with stainless steel relief valves;
- Piping-carbon steel;
- Heat exchanger-admiralty brass, Darlington-titanium plates.

This system has a pH specification of 10 to 10.5 with a desired value at 10.2. The pH is maintained by circulation through lithiated ion exchange resins at all stations. The other control parameter for this system is 0.2 mg/kg. Hydrazine cannot be used in this system to control dissolved oxygen because it may promote hydrogen production and result in a cover gas excursion.

The chemistry of the end shield cooling system, and of the Liquid Zone System is essentially the same as that of the Moderator, except that light water is used to control the neutron flux and reactivity.

Notes:

High chloride ion concentrations can promote stress corrosion cracking. As noted, the source of chloride is a spent IX column eluting into the water. Replacing the spent column controls it. Oxygen is also associated with SCC, promoting the effect of chloride ion.

Notes:

3.5.3 pH Control in Stainless Steel Based Systems, and Typical Methods to Maintain Proper Control

pH Control in the Moderator

Moderator pH is controlled only in conjunction with conductivity using ion exchange columns to remove impurity ions, and replace them with deuterioxy and deuterium ions, that is, with heavy water. When moderator conductivity is held at its practical lower limit, the heavy water is nearly pure, and ionized very slightly. As the pH of the moderator moves from neutral in either direction, the conductivity increases. The pH is analyzed on power only to troubleshoot high conductivity.

An exception occurs whenever gadolinium nitrate is present in relatively large amounts in the moderator heavy water. In this circumstance, because gadolinium deuterioxide may precipitate out if the pH is too high, the pH specification is 4-6. (The pH becomes a control parameter during over-poisoned guaranteed shutdown).

Under special circumstances, (during unit start up), when gadolinium nitrate is present, the pH of the moderator may drift to 7 and higher. This can occur when the cationic resin in the mixed bed IX column is spent before the anionic resin, releasing excess deuterioxy ions. The result is an increase in pH above 6.

Localized high pH can also occur within an ion exchange column where, after the resin has been slurried, stratification of resin beads occurs, resulting in a high proportion of anion resin in a localized zone above the cation resin. Elution of deuterioxy ions from the anion resins will increase the pH of the solution and cause the precipitation of gadolinium deuterioxide within the column. To ensure sufficient cation resin is present to remove gadolinium, and to prevent the precipitation of the gadolinium deuterioxide in the column, stations add extra cation resin to the mixed bed to minimize the possibility of separation and to ensure the bed does not spend on cation (Gadolinium is present as a cation).

High moderator pH is caused by:

- Inadvertent use of the heat transport system resin (lithium based) in an IX column.
- Too much anion resin relative to cation resin the IX columns, removing gadolinium ions but not nitrate ions.
- Contamination of the moderator by alkaline sources such as heat transport system heavy water or lithium hydroxide.

High moderator pH is controlled by the proper use of the ion exchange system.

Low moderator pH is most likely due to air leakage into the cover gas. The nitrogen in air is converted by radiolysis to nitric acid, which lowers the pH of the moderator.

Low pH will accelerate corrosion of the heat exchangers and increase the concentrations of deuterium gas and oxygen in the cover gas.

Low pH is controlled by:

- Minimizing air in-leakage;
- Purging cover gas when the nitrogen concentration is too high, for example, after the system has been opened for maintenance;
- Ensuring the IX columns are operating properly.

pH Control in the End-shield Cooling and Liquid Zone Control Systems

The chemistry of the LZCS, including its cover gas, and of the end shield cooling system, is the same as that of the moderator system, except that gadolinium is not used. However, conductivity is the only parameter used for the control of water purity in the end shield cooling and LZC systems.

Impurities, especially chloride ion, promote the release of radiolytic hydrogen and oxygen gases, which, together with nitrogen and argon, are monitored in the cover gas. As discussed above, nitrogen is converted radiolytically to nitric acid, and argon can be activated to Ar-41, increasing fields in the piping areas. The above contaminants in the cover gas are kept ALARA.

Notes:

3.5.4 Conductivity Control in Stainless Steel Based Systems, and Typical Methods to Maintain Proper Control

Notes:

Conductivity Control in the Moderator

Corrosion can affect the calandria body, calandria tubes, reactivity mechanisms, liquid zone tubes, cleanup circuits, heat exchangers and any other metal surfaces exposed to the moderator.

Moderator conductivity is maintained ALARA to ensure that the moderator water is as pure as possible. As noted above, moderator conductivity is the only control parameter for the moderator. High conductivity in the moderator increases the rate of radiolysis, the break down of water into its component parts O_2 and D_2 by gamma radiation. A high concentration of D_2 in the cover gas gives the danger of explosive mixtures in the cover gas. When boron is present as a reactivity poison, it has little effect on conductivity or on radiolysis products.

Gadolinium nitrate, on the other hand, increases the formation of radiolytic deuterium gas and affects the conductivity.

High moderator conductivity is caused by:

- Air leakage, producing nitric acid by radiolysis;
- Spent IX columns, allowing impurity ions to pass into the column effluent;
- Addition of gadolinium nitrate for reactivity control;
- Other impurities from dissolved corrosion products.

High moderator conductivity is controlled by:

- Preventing air in-leakage and ingress of contaminants;
- Purging cover gas nitrogen, when high, for example, after opening the system;
- Ensuring the IX columns are not spent.

Although controlling conductivity ALARA helps reduce corrosion rates, its most important objective is reducing the probability of a cover gas deuterium excursion, which can occur very quickly, in minutes.

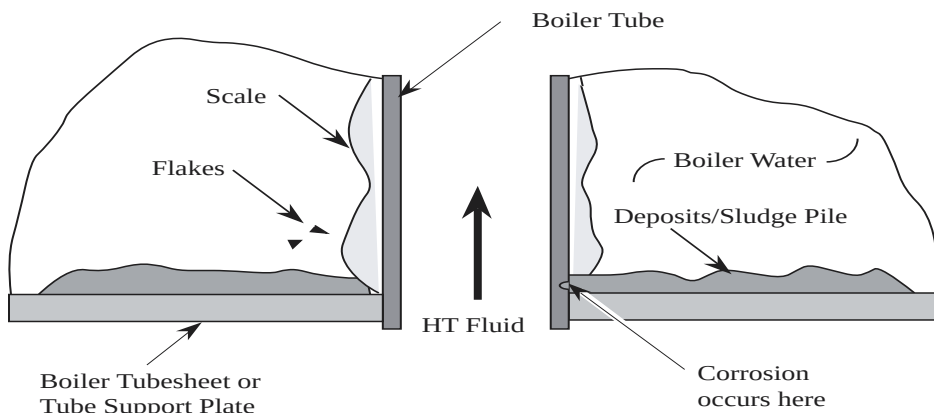


Figure 4
Boiler Tube Scale and Tube Sheet Deposits

3.6 SCALE FORMATION

3.6.1 Mechanisms for Formation and Adverse Consequences of Scale Formation on Boiler Tubes-Methods Used to Minimize Scale

Over time, unless controlled, the concentration of impurities, except some of the water treatment chemicals, will tend to build up in the boiler water. Even with IX control, where the flow is low or restricted, localized impurities, for example, in crevices, can reach very high levels. The result is the formation of sludge and sites for scale formation. These trapped impurities are called are called hideout impurities because they are not measured during sampling.

Figure 4 shows boiler scale, which is a layer of foreign material built up on the surface of the boiler tubes. Suspended particulate matter is formed from corrosion products, and tends to settle out in regions of low flow, forming sludge deposits. Scale can also flake off the tubes, contributing to the formation of sludge.

To summarize, sludge and scale forming substances are:

- Suspended Inorganic Solids (Particulates);
- Dissolved Inorganic Matter;
- Dissolved and Suspended Organic Matter.

If the water treatment plant malfunctions, it too can contribute to high concentrations of ionic impurities such as chloride, sulphate, calcium and magnesium, in the boiler.

Notes:

Notes:

Corrosion products, typically iron and copper oxides, formed throughout the boiler steam and feed-water circuit are the main source of suspended inorganic particulates. Smaller amounts enter the circuit in the freshwater make-up, although this water is usually very pure. The other source is raw water entering through perforated condenser tubes, which contributes mainly silicates of calcium and magnesium.

Some organic material can result from the breakdown of water treatment chemicals, leakage of lubricating oil, raw water entering through failed condenser tubes, bacterial growth in the demineralized water system, and resin fines from the IX systems.

To summarize, boiler tube scale and sludge deposits are caused by the presence of inorganic salts, small amounts of organic material and of corrosion products in the boiler water.

3.6.2 Adverse Effects of Sludge and Scale Formation

If sludge and scale deposits form in sensitive parts of the boiler system, serious corrosion problems can develop under the deposit. The concentration of impurities in low flow regions of the boiler can increase by 10,000 to 100,000 times that in the bulk flow due to the concentrating effect of boiling in sensitive parts of the boiler.

Pitting corrosion under sludge deposits can result in part from high concentrations of chloride and/or sulphate at the base of the boiler tubes. Caustic soda (sodium hydroxide) can cause a similar caustic attack on the boiler tubes.

Particles entrained in the flowing water can contribute to erosion corrosion and may settle out and form deposits of sludge that are extremely hard to remove.

Any corrosion process can shorten boiler tube life, contributing to the possibility of heavy water and tritium leakage into the boiler system.

Scale deposits on boiler tubes can also contribute to corrosion, and, in addition, reduce heat transfer efficiency, forcing up the temperature of the heat transport heavy water system and/or reducing heat transfer rates.

Large deposits on the tube support plates may also cause level control problems by restricting water/steam flow up through the boiler.

In Summary, the adverse effects of impurities on boiler performance and materials include:

- the accumulation of solid impurities in the form of sludge creates a very hostile corrosive environment.
- pitting corrosion and or caustic attack occurs under sludge deposits.
- erosion corrosion can be caused by suspended particles in the flow.
- scale and sludge deposits on tube support plates may lead to level control problems by restricting water and steam flow.
- over time, sludge becomes extremely difficult to remove.
- reduced tube life and increased down time will result if perforations develop due to corrosion of the tubes.
- lost production time and outages will occur due to boiler tube leaks and time taken for deposit removal.
- scale will cause increased resistance to heat transfer, leading to increased heat transport system temperatures and/or reduced heat transfer.

Notes:

Notes:

REVIEW QUESTIONS

CORROSION

1. Describe each of the following types of corrosion.
 - Uniform
 - Galvanic
 - Pitting
 - Stress corrosion cracking
 - Erosion
 - Microbiologically induced
2. State the typical pH range that is considered optimum for carbon based steel piping systems. Explain the consequences of operating with a pH outside of this range.
3. Describe how the pH is controlled in the heat transport system.
4. Explain the consequences of high O₂ levels in water systems.
5. State the method used to control the O₂ levels in the heat transport system.
6. State three methods used to control the O₂ level in the condensate and feedwater systems.
7. Describe the negative consequences of high conductivity in the moderator system.
8. Describe four potential sources of high conductivity in the moderator system.
9. Describe three methods of maintaining a low conductivity in the moderator system.
10. Define the terms sludge and scale and state three substances that contribute to their formation.
11. State and explain four adverse consequences of excessive sludge and scale formation in a boiler

4.0 PRESSURE TUBES AND FUEL BUNDLES

Notes:

4.1 INTRODUCTION

Materials in nuclear reactors are exposed to ionizing radiation, for example, gamma, beta, and alpha, as well as to fast and thermal neutrons. These forms of radiation are highly energetic, and cause damage by interaction with the nuclei and/or orbital electrons of atoms that constitute materials of all kinds

The changes in the atomic structure of the elements can and do cause fundamental changes in the mechanical properties of materials. In particular, ionizing gamma radiation, unlike alpha and beta radiation, has a very high potential for permanently damaging materials.

Fast neutrons cause structural damage by displacing atoms, creating vacancies and interstitial atoms in the crystal structure of materials. This phenomenon accounts for increased creep rates in pressure tubes. Thermal neutrons may be captured by nuclei, changing the material's identity. For example, cobalt-59 becomes activated to radioactive cobalt-60. This phenomenon is one of the main reasons that the concentration of dissolved metal ions is kept as low as possible.

Thermal neutrons also form gases, such as krypton, xenon and iodine, which may migrate to form gas bubbles that may cause embrittlement and blisters in the fuel sheath, increasing the potential for rupture.

4.2 EFFECTS OF RADIATION ON COMMON MATERIALS

4.2.1 Oils and Greases

Oils and greases are affected both by ionizing radiation and neutrons. Oils become more viscous (stiffer, more resistant to flow). Some oils actually solidify, forming tar-like polymers. These phenomena reduce or stop fluid flow to some degree.

Soap-oil based greases, on the other hand, become less viscous, and more fluid because radiation breaks down the soap-base binder. Radiation increases the rate of oxidation by air, which also reduces the amount of radiation required to cause significant damage.

Radiation-promoted oxidation and other damage can be limited by using grease manufactured with special additives.

Both lubricants used in the fuelling machines are changed more frequently than those used in other equipment not exposed to radiation.

Notes:

4.2.2 Plastics

Plastics are formulated from long chains of molecules (polymers) and other chemicals that control some of their properties. The chemical bonds of plastics are very sensitive to radiation, which can dramatically change their properties. The types of chemical and structural changes that are caused by radiation include:

- Embrittlement and increased rigidity due to cross-linking of atoms between chains;
- Loss of strength softening due to fragmentation into shorter-chain polymers. Teflon and Plexiglas are very susceptible to this process;
- Embrittlement and rigidity from the formation of new long-chain polymers;
- Embrittlement and increased rigidity due to oxidative cross-linking;
- Gas evolution.

Problems that have been caused by radiation damage to plastics in nuclear stations include:

- Damage to the insulation on power and control cables, especially those within the reactor vaults;
- Damage to the outer jacket on some ion chamber instrument cables, which has been so severely affected that it has become brittle, cracked and fallen off. Insulators in the associated connectors have also become brittle and failed;
- Decomposed terminal blocks inside junction boxes exposed to high radiation fields;
- Damage to ion exchange resins, which are polymers, based on polystyrene. The radio nuclides removed from active water systems deposit much of their energy within the resin bed, leading to its degradation.

Programs are in place to manage the effects of these problems.

4.2.3 Metals

Fast neutrons affect the mechanical properties of metals (and other materials) as follows:

- Ultimate tensile strength increases;
- Yield strength increases sharply;
- Hardness increases;
- Ductility decreases.

Notes:

Fast neutrons cause vacancies and displacement of atoms in the damaged metal.

These disrupt the crystal structure and cause internal stresses, which increase the energy, required to deform the metal

If the radiation-damaged metal is annealed at about 850-1000 °C, the mechanical properties will return almost to their original values. This occurs because the defects become mobile at high temperature, moving to preferred locations and eliminating some of the defects. This phenomenon is not entirely a good thing, because the process promotes creep.

4.2.4 Carbon Steel

Carbon steel materials may benefit from the increase in strength from fast neutron irradiation, but at the cost of increased risk of brittle fracture. Two sorts of components in CANDU operation show an increase in the ductile/brittle transition temperature when irradiated:

- The impact resistance of many pressure vessels operating at ambient temperatures is reduced. Radiation induced brittleness of pressure vessels operating at 260 °C is not corrected by annealing because the temperature is too low.
- The ductile/brittle transition temperature of carbon steel piping in the Heat Transport System gradually increases over their long service life.

4.2.5 Zirconium Alloys

Although irradiation causes the same effects on mechanical properties of zirconium alloys as those of carbon steel, cold working the material before installation reduces the changes.

The creep rate is increased, greatly reducing the service life of pressure tubes made of zirconium alloys.

Fuel sheathing made of zirconium alloy becomes harder and embrittled by radiation. This does not significantly reduce the life expectancy of fuel sheathing, but reduces the number of positions to which fuel can be shifted to avoid handling problems after the fuel bundles are removed from the reactor

4.2.6 Concrete

Like all materials, concrete, used extensively in nuclear stations for structural and radiation shielding applications, is susceptible to radiation

damage. Gamma radiation is absorbed and converted into heat. Neutrons also give up their energy in the form of heat and activate cobalt and other metals in the rebar.

Gamma radiation and neutron bombardment affect the structural integrity and shielding properties in two ways:

- Heat drives water out of the concrete, resulting in internal stresses, cracking and spalling of pieces of concrete from the surface.
- Water in the concrete slows down neutrons, thermalizing them and providing an effective radiation shield. The loss of water due to the heat generated by radiation reduces the neutron shielding efficiency of the concrete. This is a serious matter since the concrete serves as a biological shield that protects station workers from radiation.

Two methods are used in CANDU stations to reduce the effects of radiation on concrete and maintain its effectiveness as a shield:

- In early stations, thick concrete walls provided the biological shield. A system of pipes was built into the concrete and cool water circulated to remove the heat generated by radiation.
- In other stations, a water filled thermal and biological shield with its own cooling system is employed. The concrete walls beyond this shielding are not heated enough to warrant cooling pipes.

4.2.7 Factors Affecting Creep in Pressure Tubes

Creep is discussed in some detail previously. You may recall that creep is a process in which metals under constant stress at high temperature gradually and permanently deform.

At low, ambient temperatures, ionizing and neutron radiation hardens and decreases the ductility and creep rate of materials. At high temperatures, on the other hand, in the presence of radiation, the formation and movement of defects actually cause an increase in creep rates.

Pressure tube elongation due to thermal expansion and creep is a major concern in CANDU reactors. This is in spite of the fact that designers allowed for elongation and selected zirconium alloys in preference to pure zirconium because of their higher strength and creep resistance.

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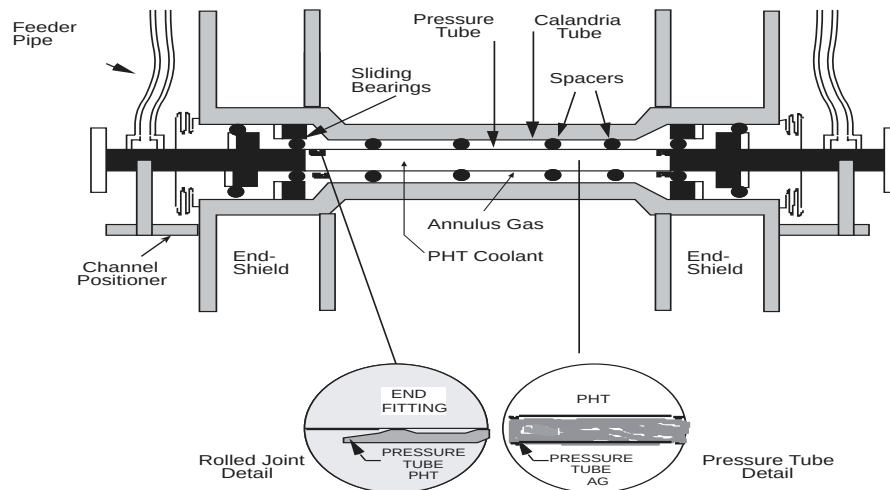


Figure 1
Fuel Channel Schematic

The support mechanism for pressure tubes in fuel channels is shown in Figure 1 above. Longitudinal creep (creep along the axis of the tubes) is affected by the following factors:

- Applied stress; creep rate increases with increasing load;
- Neutron flux at elevated temperatures; as explained above increased neutron flux at high temperature increases the creep rate;
- Previous cold work; cold work increases strength and resistance to deformation, but cold working during fabrication increases the creep rate;
- Radiation growth; some materials, like the zirconium alloys used in pressure tubes, have different properties in different directions (they are said to be anisotropic for this reason). Under radiation, the effect of the difference in crystal properties results in elongation along the length of the tubes, further compounding creep problems.

Possible problems due to excessive elongation of pressure tube include:

- The journal can hang up on the sleeve end, which is fixed within the reactor face. This prevents the sleeve from moving as the tube contracts during cooling, causing high stresses on the reactor face;
- Skewing of the end fitting while off-bearing makes alignment of the fuelling machine difficult;
- Possible contact between feeder pipes. This kind of contact causes fretting and supplementary loads on the feeder connection assemblies. In the extreme case, fretting could compromise the HTS pressure boundary.

Note that since the creep rate depends on the neutron flux, significant variations in tube elongation between adjacent channels could occur, reducing initial feeder spacings and increasing the possibility of feeders touching.

Actual creep rates in some units range from 3.2 to 4.6 mm per year. Early units with a single floating end had a total allowance of about 40-mm. Clearly, this allowance is not enough to provide for a 30-year service life. Newer designs, with both ends of the tube fixed or floating, allow for axial growth of up to 160 mm, providing for a service life of at least 30 years.

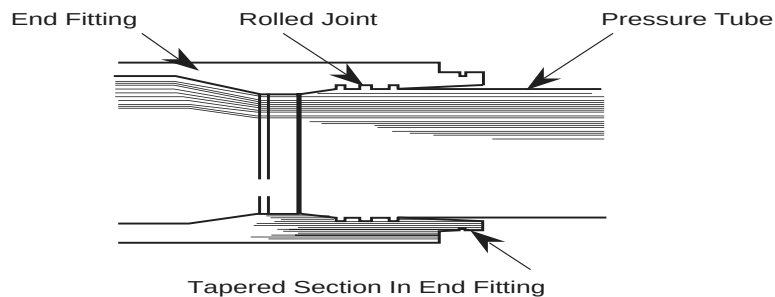
Alternative procedures for dealing with pressure tube elongation have been developed under the pressure tube rehabilitation program. The large scale fuel channel replacement deals with tube elongation, but was developed primarily to solve the problem of delayed hydride cracking (DHC)

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4.3 HYDROGEN EMBRITTLEMENT, DELAYED HYDRIDE CRACKING, BLISTERING OF PRESSURE TUBES AND CONTRIBUTING FACTORS

Pressure tubes contain about 10-ppm residual hydrogen from the manufacturing process.



Rolling

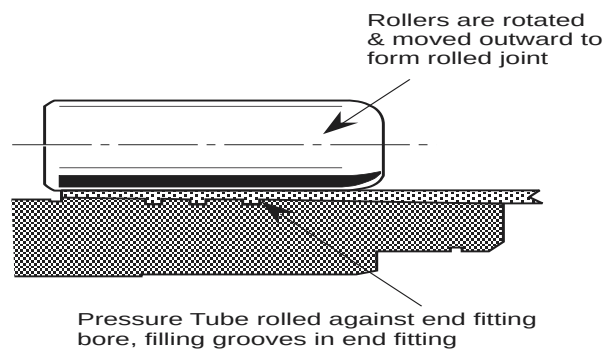


Figure 2
Rolled Joint Between Pressure Tube and End Fitting

Hydrogen (deuterium gas) is also produced in the HTS by the radiolysis of water, by the chemical reaction of water with zirconium, and hydrogen gas is added to control oxygen that would otherwise cause corrosion problems. The hydrogen/deuterium gases tend to be absorbed by the pressure tube material, particularly in the rolled joint area. Hydrogen tends to accumulate in regions of highest stress, i.e., in the rolled joints. The rolled joint is illustrated in Figure 2 above.

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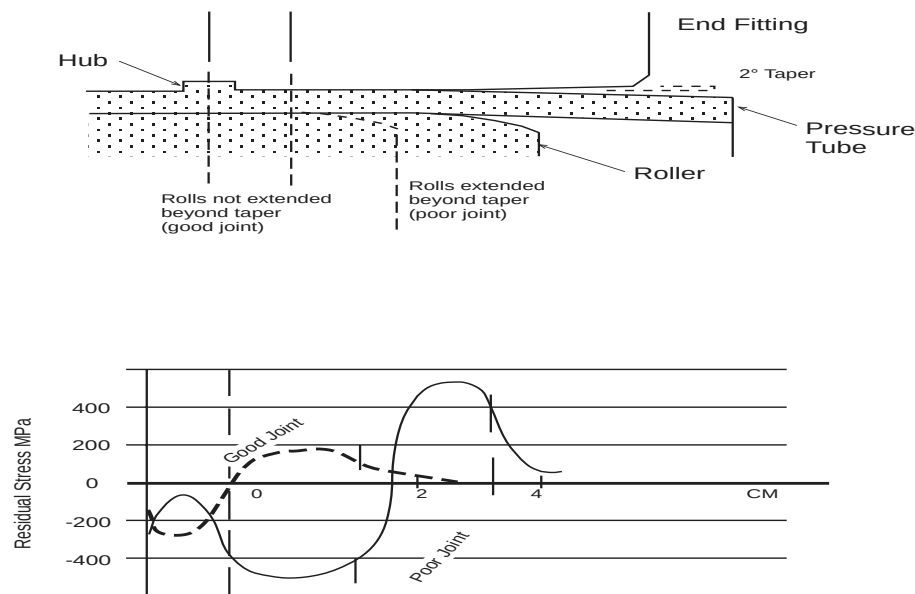


Figure 3
Relative Position of Rolling Tool During Installation Causing Residual Stresses in Joint

To form a joint, the pressure tube wall is squeezed into grooves on the end fitting by rollers. During the rolling operation, the rolling tool was pushed too far (about 13mm) into the end fitting. As a result, the pressure tube wall was expanded out at the tapered section of the end fitting. This created an extra region of deformation in the tube wall thickness where high residual tensile stresses were built up (see Figure 3).

Laboratory examination of failed pressure tubes revealed that cracks occurred in a region close to the rolled joint.

After these problems, improved rolling procedures and a modified style of joint (lower clearance between the pressure tube and the end of the fitting) were implemented in all reactors. Low levels of residual stresses in the rolled joint were ensured by these improvements.

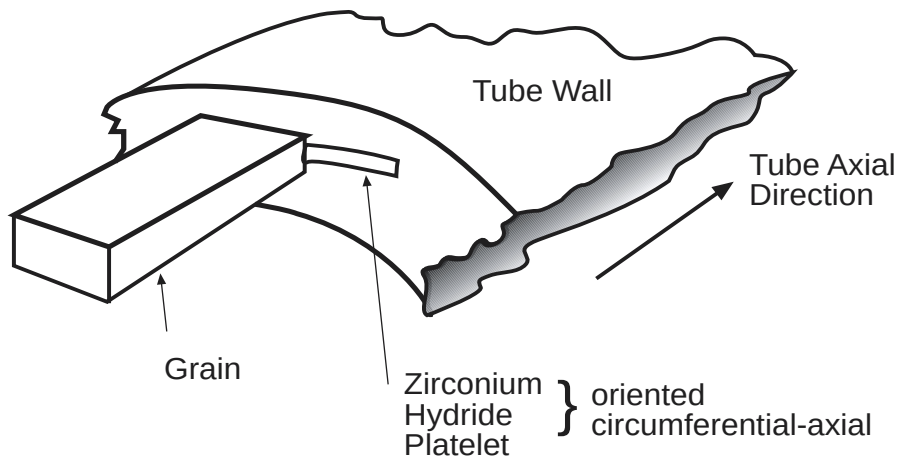


Figure 4a
Usual Microstructure of Pressure Tubes and Orientation
of Zirconium Hydride Platelets

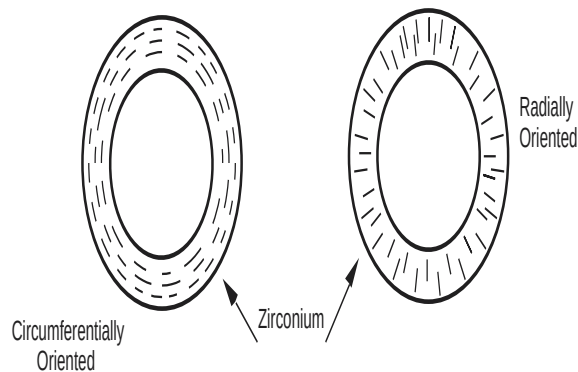


Figure 4b
Representation of Orientation of Precipitated Zirconium
Hydride Platelets in Pressure Tubes

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The three routes by which the gases can enter the tube metal are:

- Diffusion of deuterium through and along the stainless steel end fittings and across the rolled joint (stainless Steel is quite permeable to hydrogen/deuterium gas);
- Migration through the protective oxide layer on the inside wall of the pressure tube; and
- Absorption through the surface oxide on the annulus gas side of the pressure tube-this absorption process can be very rapid if surface oxide integrity is not maintained. That is, by oxygen control. The deuterium gas will have migrated to the annulus through the end fitting.

Hydrogen embrittlement in the pressure tubes is caused by the formation of zirconium hydride, a compound that has a greater volume than the corresponding zirconium metal. The hydride precipitates in the metal matrix in the form of platelets (like minute corn flakes) that stress and cause strains in the component. Figure 4.4a) illustrates the usual microstructure of pressure tubes and the orientation of zirconium hydride platelets.

During fabrication, the tubes are cold-worked, (that is, stretched axially, thinning the walls and reducing the diameter). Strains from the fabrication tend to orient any precipitated hydride in the circumferential orientation. This is the preferred orientation of hydrides under the normal stress distribution in the tube wall.

Over-rolling puts high tensile residual stresses on the inside surfaces of the tubes, just inboard of the rolled joints. This tends to orient any precipitated hydride platelets in the radial direction, leading to tube cracking from the inside outwards. Figure 4b) shows the circumferential and radial orientations of the zirconium hydride platelets. Hence, the components strained by over-rolling have then become susceptible to crack development and propagation. This is because the principle pressure stress is perpendicular to the orientation of the hydride platelets.

Hydrogen/deuterium gas that has reached the pressure tube material is dissolved in the metal at temperatures above 150°C. Below 150°C, the hydrogen forms minute gas bubbles because the solubility of the gas decreases with temperature. The operational restriction caused by this phenomenon will be reviewed below. The mechanism by which

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Delayed Hydrogen Cracking is believed to occur is:

- Hydrogen molecules diffuse to regions of high stress like rolled joints, or to localized flaws such as notches or cracks, which concentrate stress. Hydrogen may then combine chemically with zirconium to form zirconium hydride platelets.
- Zirconium hydride platelets re-dissolve when the temperature is raised above 150°C.
- Zirconium hydrides are very brittle, and fail readily under tensile loading.
- Pressurizing fuel channels with naturally oriented platelets add sufficient stress to cause the hydride to crack. Evidence from cold-worked zirconium alloys suggests that the process then occurs in the following stages:

Precipitation and re-orientation of hydride platelets at the crack tip, due to the increased stress there;

Brittle fracture through the hydride precipitate when the platelets reach a critical size;

Crack growth continues as hydride forming at the new crack tip fails, causing a further increment of the fracture. Figure 5 illustrates this process.

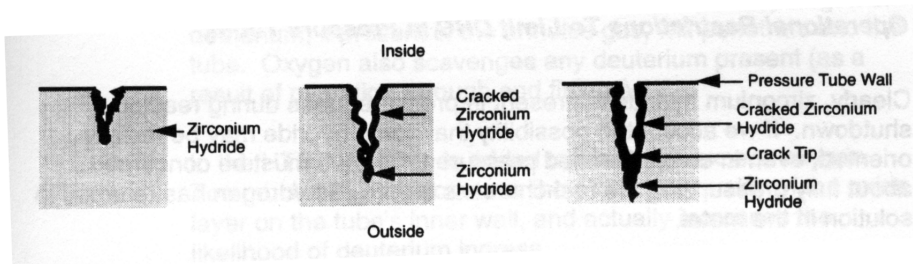


Figure 5
Schematic Representation of the Growth of a Crack Through
Failure of Zirconium Hydride Precipitating at Crack Tips

Some of the zirconium hydride which must be present in pressure tubing during shut-down (temperature below 150°C) may be oriented in such a way that there is a risk of tube cracking if the tubes are pressurized improperly before all the hydride is re-dissolved in the metal.

Experience has shown that the risk is highest when the temperature in the HTS is in the range 100°C to 200°C. Procedures restrict operation in this temperature range, and require that passage through the range must be as rapid as possible during both heat up and cool down of the unit.

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To further limit stress levels, this transition should take place at pressures lower than those of normal operation. The hydrides will then experience less stress for a minimum time, reducing the probability of through wall cracks due to DHC.

Hydride blister formation is believed to be due to sagging of hot pressure tubes into contact with the colder calandria tube. Two conditions are associated with this phenomenon:

- Creepsag, which is defined as the deflection of the pressure tubes from their vertical axis due to changes in curvature caused by neutron flux, stress, gravity and temperature. The tubes droop.
- Missing, displaced or mislocated spacers (garter springs).

The steep temperature gradient in the pressure tube at the point of contact (cold spot) then leads to the formation of hydride blisters and cracking, as shown in Figure 6.

Hydrogen present in the tube diffuses down the temperature gradient, collecting and forming hydride deposits at the outside wall of the tube. Because the hydride has a 17% greater volume than the tube metal it displaces, blisters form on the outer surface of the tube.

Cracks may initiate and form in the blistered area. Since the zone of contact between the pressure and calandria tubes tends to be long, a string of blisters may form on the bottom of the pressure tube. The blisters are extremely brittle, and may crack.

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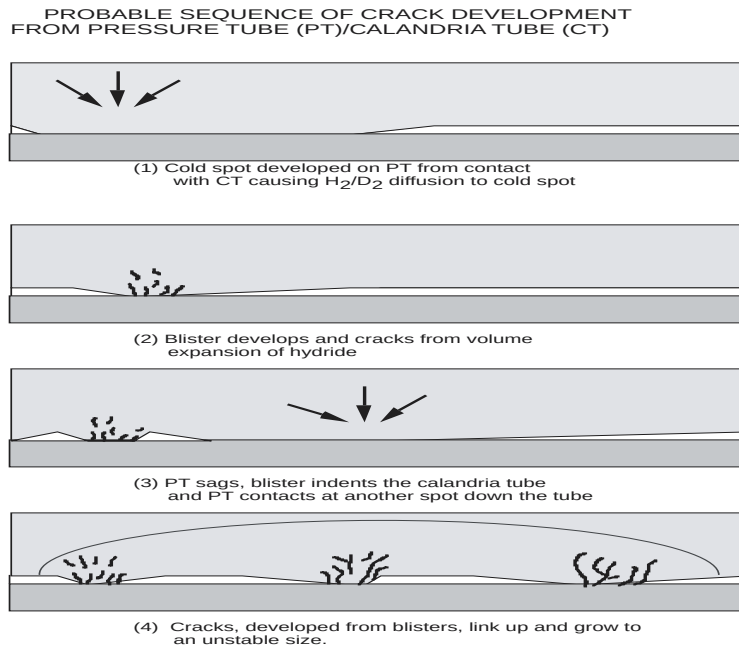


Figure 6
The Development of Hydride Blisters and Cracking

An engineering solution (Spacer Location and Reposition or SLAR) to the blistering and associated cracking problems has been developed.

4.4 MINIMIZING DELAYED HYDRIDE CRACKING DURING UNIT STARTUP AND COOL-DOWN

As discussed above, the risk of delayed hydride cracking due to the formation of zirconium hydride platelets is greatest in the relatively narrow temperature range from 150°C to 200°C .

At temperatures below 150°C , hydrogen is virtually insoluble in the zirconium alloy, and at temperatures above 150°C to 200°C , the hydride is completely soluble. For these reasons, risk of delayed hydride cracking is minimized by passing through the critical temperature zone as quickly as possible.

The presence of deuterium/hydrogen can be minimized by the addition of oxygen, and by careful control of the HTS hydrogen addition system. Limiting Factors Affecting the Duration of a Fuel Bundle in the Core

During exposure of the UO_2 fuel pellet to neutron irradiation, it experiences a change in linear and radial dimensions. This size change is related to the density of the neutron flux and the time of exposure to it. This phenomenon is called radiation growth.

The fuel pellets Zircalloy sheathing experiences embrittlement when exposed to a neutron flux. The density of the neutron flux and the time of exposure dictate the degree of embrittlement experienced. This phenomenon is called neutron embrittlement. Neutron embrittlement causes the Zircalloy sheathing to lose its durability and toughness, such that as the embrittlement progresses, any increased stress on the sheathing is more likely to cause cracking to occur than the normal deformation experienced by a tough and durable material.

While the Zircalloy sheathing is becoming more brittle, the UO_2 pellet inside is continuing to grow. After a period of time and neutron irradiation, the enlarging pellet starts to exert high stresses on the embrittled sheathing and beyond a certain time the sheathing will crack, releasing fission product gases into the PHT system.

On this basis, fuel bundles are removed from the core while still reasonably ductile and before an increased incidence of fission product release occurs.

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REVIEW QUESTIONS

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PRESSURE TUBES AND FUEL BUNDLES

1. State how fast neutron damage affects each of the following properties of metals.
 - Ultimate tensile strength
 - Yield Strength
 - Hardness
 - Ductility
2. State the effect of neutrons and ionizing radiations on oil and soap based greases.
3. The loss of water from concrete reduces the effectiveness of the concrete as a biological shield. Briefly explain the process that causes this to happen.
4. State four factors that affect the creep of the pressure tubes.
5. State three sources of hydrogen in pressure tubes.
6. Describe the process of hydrogen embrittlement of a pressure tube.
7. Explain how the orientation of the zirconium hydride platelets affects the tensile strength of the pressure tube.
8. Describe the mechanism by which delayed hydride cracking takes place.
9. Describe how hydrogen blisters form on the outside of pressure tubes.