



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

Axial Offset Anomaly (AOA) was an unexpected problem of some PWRs. It has only been observed in high duty PWR cores with sub-cooled nucleate boiling when sufficient corrosion products are available for on-fuel deposition (Frattini *et al.*, 2001). Many PWR plants have experienced AOA that is either mild or severe for one or more fuel cycles. It is likely that differences in concentrations of coolant corrosion products, especially iron and nickel, may have contributed to variations in crud deposition on fuel rod surfaces and thus affected susceptibility to AOA (EPRI TR-107255, 1996). Therefore, many researchers have attempted to understand and mitigate this effect.

2.1 Pressurized Water Reactor (PWR)

PWR is a pressurized water reactor that uses ordinary water as its coolant and moderator and uses enriched uranium as its fuel. A schematic of PWR illustrating these features is shown in Figure 2.1. In the reactor, atoms of U-235 in enriched uranium dioxide pellets in zirconium alloy tubes are split through a process known as fission. When atoms are split, they produce a large amount of energy that is converted to heat. Heat from the fission reaction is removed by pressurized water (primary coolant) which is kept at high pressure so that the water heats but does not undergo bulk boiling. This heat is carried by pressurized water through the stainless steel pipes and headers to the steam generator where the heat is transferred to secondary coolant to produce steam. The steam is used to drive turbines, which spin the shaft of a generator to produce electricity.

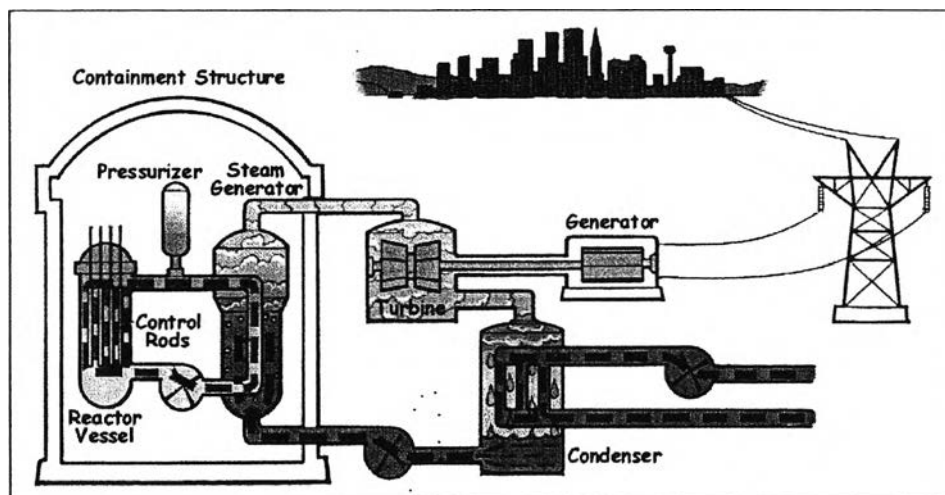


Figure 2.1 Schematic of Pressurized Water Reactor (PWR)

(<http://www.cleansafeenergy.org>).

2.1.1 Materials of PWR Primary Coolant Loop

The PWR primary coolant loop contains three major components: the reactor core, the steam generator tubing and the piping system as shown in Figure 2.1. A summary of the materials of construction of components in the PWR primary coolant loop is shown in Table 2.1 (Lister, 1988).

Table 2.1 Material construction of each component in primary coolant loop

Component	Material
Reactor core	Zirconium alloy
Steam generator tubing*	Nickel alloy - Inconel 600
	- Inconel 690
	- Incoloy 800
	Austenitic stainless steel
Piping	Austenitic stainless steel

*Depends on the PWR model

The zirconium alloy is used as the cladding metal in nuclear reactors because it has good mechanical and neutronic properties (such as a low cross-section for absorption of neutrons) and has high-temperature (330-350°C) aqueous corrosion resistance (Sastri *et al.*, 2006). However, under the higher primary coolant temperature at which sub-cooled boiling can occur in some assembly sub-channels, Zirconium alloys can develop deposits of corrosion products; that is the cause of AOA, which has been a problem in some PWRs.

In each steam generator there are several thousand tubes, which are the barrier between the primary and secondary side of the nuclear power plant. To efficiently generate electric power from PWRs, high-quality, small-diameter thin-walled tubing is required. The first steam generators used austenitic stainless-steel tubing. Later, it was substituted with Ni-base alloys because austenitic stainless steel is susceptible to chloride-induced stress corrosion cracking (SCC). Now, the steam generator tubing is commonly made from Alloy 600, Alloy 690 or Alloy 800 because of their corrosion resistance. A comparison of chemical composition of these alloys is shown in Table 2.2 (Special metals, 2004).

Table 2.2 Chemical composition of Alloy 600, Alloy 690 and Alloy 800 (weight %)

	Alloy 600	Alloy 690	Alloy 800
Nickel	72 min.	58.0 min.	30.0-35.0
Chromium	14.0-17.0	27.0-31.0	19.0-23.0
Iron	6.0-10.0	7.0-11.0	39.5 min.
Carbon	0.15 max.	0.05 max.	0.10 max.
Silicon	0.50 max	0.50 max.	0.10 max.
Manganese	1.0 max.	0.50 max.	1.50 max.
Sulfur	0.015 max.	0.015 max.	0.015 max.
Copper	0.50 max.	0.50 max.	0.75 max.
Aluminum	-	-	0.15-0.60
Titanium	-	-	0.15-0.60

Alloy 600 is a nickel-chromium alloy which has a good oxidation resistance at high temperatures and is resistant to chloride stress-corrosion cracking (SCC), corrosion by high-purity water, and caustic corrosion. It can be used from cryogenic to elevated temperatures up to 2000°F (1093°C). From Table 2.2, the high nickel content of Alloy 600 provides a level of resistance to reducing environments, while the chromium content of the material provides resistance to sulfur compounds and oxidizing conditions in high temperature and high corrosive solutions. However, Alloy 600 has been the vulnerable tubing material in recirculating steam generators, where most failures occur in the hot leg (~305°C) rather than the cold leg (~285°C) (Lister, 1988). Thus, Alloy 600 is subjected to heat treatment processes to increase ductility and reduce corrosion cracking (Special metal, 2004). Alloy 600 was the SG tubing material in nuclear reactors until the introduction of Alloy 690 and Alloy 800.

Alloy 690 is a high-chromium nickel alloy having excellent resistance to many corrosive aqueous media and high temperature atmospheres. In addition to its corrosion resistance, Alloy 690 has high strength, good metallurgical stability, and favourable fabrication characteristics. From Table 2.2, it has higher chromium content and lower nickel content than Alloy 600. The higher chromium content provides higher resistance to stress-corrosion cracking while displaying low corrosion rates. Thus, Alloy 690 is widely used for steam generator tubes in nuclear power generating stations.

Alloy 800 is a nickel-iron-chromium alloy which was introduced to the industry in the 1950s to fill the need for a heat- and corrosion-resistant alloy in high-temperature services. It is a widely-used material for construction of equipment requiring corrosion resistance, heat resistance, strength, and stability for service up to 1500°F (816°C). At high temperatures it offers resistance to oxidation, carburization, and sulfidation along with rupture and creep strength. The chromium content in the alloy provides both aqueous and heat resistance, the iron content provides resistance to internal oxidation and the nickel content maintains a ductile, austenitic structure. The general corrosion resistance of Alloy 800 is between that of Type 304 and that of Type 316 stainless steels (Sastri *et al.*, 2006). Since Alloy 800 presents better mechanical characteristics than those of Alloy 600, Alloy 800 was designated to replace Alloy 600 until the introduction of Alloy 690.

Intasopa (2008) found that Alloy 800 has the lowest hardness value when compared with Alloy 600 and Alloy 690. It should be noted that the amount of nickel content significantly decreases from Alloy 600 to Alloy 800. This suggests that there is a relationship between the hardness value of the alloy and its nickel content. Thus, from Table 2.2, it can be seen that Alloy 600 has the highest amount of nickel; it is the most susceptible to stress corrosion cracking followed by Alloy 690 and Alloy 800.

Austenitic stainless steel is used as the primary coolant piping outside the core in PWRs; it is generally resistant to attack if the coolant chemistry is well controlled. However, intergranular stress corrosion cracking (IGSCC) can occur in the heat affected zones of welds if reduced sulphur species are present (Lister, 1988). Theus *et al.* (1983) found that levels of thiosulphate and tetrathionate at 1 mg.kg^{-1} have been shown to cause IGSCC at low temperatures.

2.1.2 PWR Primary Coolant Chemistry

In PWRs, the coolant chemistry in both the primary and secondary systems is controlled for good plant operation. PWR primary coolant chemistry comes from a balance between three main goals: (1) minimizing corrosion, (2) optimizing fuel performance and (3) reducing radiation fields. The coolant chemistry is intended to produce reducing conditions and alkalinity at high temperature above the value corresponding to the minimum in corrosion product solubility. The PWR primary coolant chemistry conditions are summarized in Table 2.3 (Rahn *et al.*, 1984; Millett and Wood, 1998).

Table 2.3 Coolant chemistry conditions

Condition	Value
Lithium-7 hydroxide	2.2-3.5 ppm ⁷ Li
Boric acid	0-4000 ppm (as B)
Hydrogen	2.2-4.5 ppm
Oxygen	0.1 ppm (max)
Chloride	0.15 ppm (max)
pH _{300°C}	6.9-7.4

Lithium-7 is used for the alkalization of the PWR primary coolant because of its favorable nuclear properties, while boron, in the form of boric acid, is used in conjunction with the absorber rods to control the chain reactions.

2.2 Corrosion of Materials

2.2.1 Definition of Corrosion

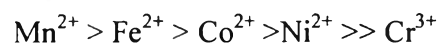
Corrosion is defined as the destruction or deterioration of a material because of a reaction with its environment. Higher temperatures and pressures usually involve more severe corrosion conditions leading to costly outages and repairs and can affect plant reliability and safety. However, corrosion is beneficial or desirable in some cases. For example, in chemical machining or chemical milling, unmarked areas are exposed to acid and excess metal is dissolved. Anodizing of aluminum is another beneficial corrosion process used to obtain better and more uniform appearance in addition to a protective corrosion product on the surface (Mars G. Fontana, 1987).

Corrosion is of primary concern in engineering and design; every metal is subject to it. Even though this corrosion cannot be eliminated, it can be controlled.

2.2.2 Oxide Film Formation

The corrosion of metals is a natural process. Most metals are not thermodynamically stable in the metallic forms when they are in corrosive media so they are susceptible to corrosion and revert to more stable forms, such as oxides. In the power generation industry that operates at high temperature, for example, the materials of construction will form corrosion product films or oxide films which protect the materials from excessive additional corrosion.

In general, the materials of construction in high-temperature water-cooled circuits, such as PWR primary coolant loop, are steel and nickel alloys. The natural oxide films which form on the metal surface are generally duplex-layered with a crystal structure based on that of the spinels (Lister, 2003). The duplex-layered oxide is composed of the inner layer formed with an access of oxygen in some form, such as water, through oxide micropores to the metal at the metal-oxide interface and the outer layer growing by precipitation of metal ions diffusing from the solution at the outer oxide surface. Dieckmann (1984) mentioned that the diffusion rates of metal ions in the oxides have been measured and are found in order as follows:



The metal ions that have faster diffusion rate will pass through to the outer layer, while the metal ions that have lower diffusion rates, such as Cr, will be oxidized without movement and remain in the inner layer. Moreover, the morphology of the oxide film depends on the chemical composition of the alloy, exposure conditions and surface finishing (Lister *et al.*, 1994).

Carbon steel, with no alloying components, is corroded in high temperature water and forms a double layer of magnetite (Fe_3O_4) in supersaturated conditions, known as the Potter-Mann layers. Potter and Mann (1962) found that the inner magnetite layer, growing at the metal-oxide interface, is very fine-grained and grows by taking up the volume of metal corroded. The outer layer is relatively coarse-grained growing by precipitation from solution at the oxide-coolant interface of the roughly 50% of the corroded ion that has diffused through the film from the

metal-oxide interface. The typical magnetite film formed on carbon steel is shown in Figure 2.2.

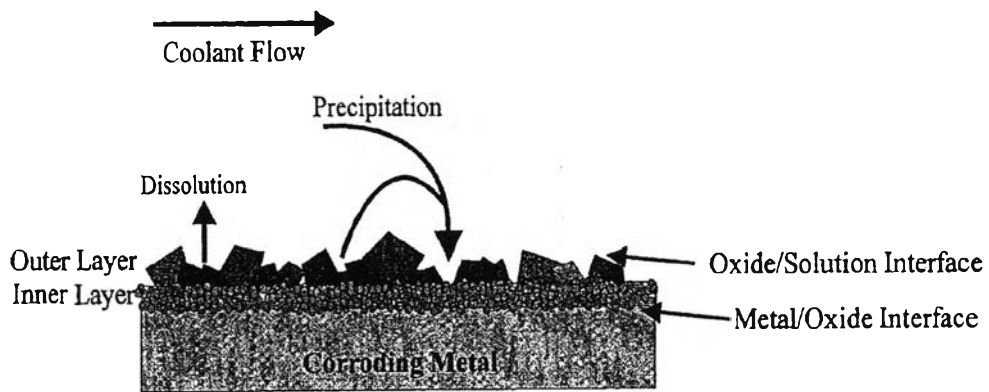


Figure 2.2 Schematic cross-section through magnetite film on carbon steel (Lister *et al.*, 2001).

A schematic of the magnetite film formed on a steel surface in a high temperature water solution illustrating the formation mechanism of the magnetite film is shown in Figure 2.3.

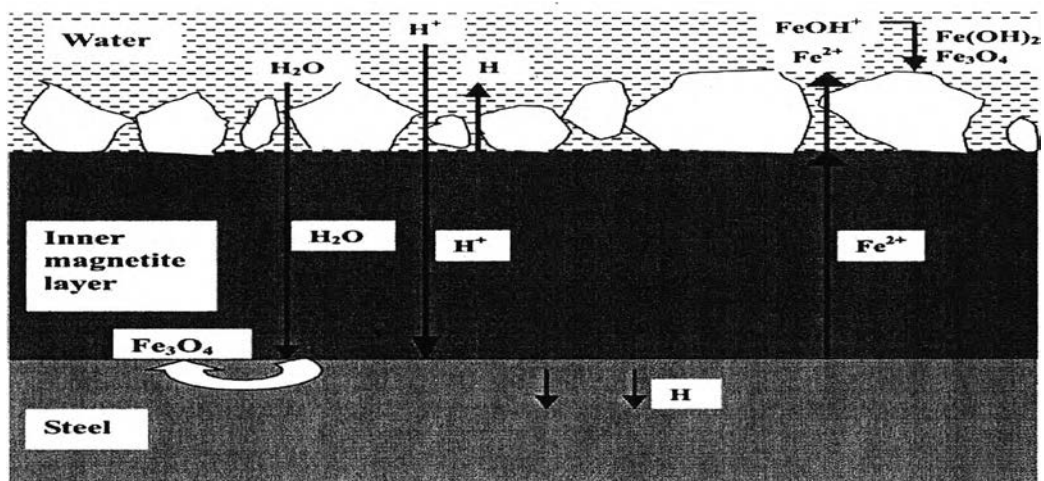
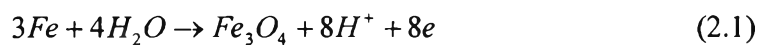
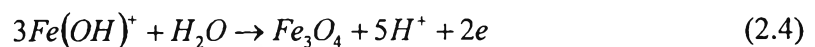


Figure 2.3 Schematic of the formation mechanism of the magnetite film on the steel surface in high temperature water (Cheng and Steward, 2004).

The mechanism starts when water molecules diffuse through the inner oxide layer and react directly with steel at the steel/oxide interface. Iron dissolution occurs where no oxide layer exists. Protons at the oxide/water interface diffuse through the oxide layer to consume the electrons produced by anodic reactions and discharge as hydrogen atoms at the steel/oxide interface. The relevant reactions occurring at the steel/oxide interface are:



The ferrous ions diffusing out of the oxide layer exist as $Fe(OH)^+$ and as $Fe(OH)_2$ in high-pH water. In high-temperature water, $Fe(OH)^+$ species must stabilize themselves by decreasing their charge/radius ratios through hydrolysis to form hydrous iron ions (Macdonald, 1976). The hydrous iron ions will deposit as loose $Fe(OH)_2$ once the saturation of the iron ion is achieved. The outer deposition of the magnetite layer is then formed in high temperature water, accompanying the discharge of hydrogen ions. Therefore, the electrochemical reactions occurring at the oxide/water interface are:



From the reactions, there are two molecules of Fe_3O_4 formed, one at the steel-oxide interface, and the other at the oxide-water interface. The formation of Fe_3O_4 film on a steel surface reduces the dissolution rate of steel substantially. However, the protectiveness of the Fe_3O_4 film over the steel is affected by environmental factors and the operational parameters, including the velocity, wall shear stress, solution pH, temperature, concentration of dissolved iron, quality of solution, etc (Cheng and Steward, 2004).

The corrosion on stainless steel is similar to that on carbon steel. The alloying elements, such as chromium, form spinel oxides with iron that are more protective than magnetite (Fe_3O_4). The inner layer, growing at the metal-oxide interface, is a thin, coherent and protective oxide based on iron chromite (FeCr_2O_4). Since chromium species are virtually insoluble in reducing coolant, all the 12-20% chromium (depending on the alloy) in the corroded metal is assumed to remain as chromite in the inner layer. This causes the amount of chromite to be insufficient to fill the space occupied by the corroded metal, so the inner layer overall must be a so-called “non-stoichiometric” spinel of the type $\text{M}_x\text{Cr}_y\text{O}_4$, where M is Fe or Ni (or both), $x+y=3$ and $x<1$. It is possible that the inner layer is inhomogeneous because the crystallites range in composition from FeCr_2O_4 to Fe_3O_4 perhaps with some nickel content, or that individual crystallites themselves are inhomogeneous. The elements in stainless steel that are not incorporated in the inner layer precipitate from solution as magnetite or non-stoichiometric nickel ferrite ($\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$) in the outer layer (Lister, 2003). In addition, Robertson (1991) mentioned that since Cr and Ni dissolving in reducing coolant move more slowly than the majority constituent, Fe, so the outer layer is expected to contain the Fe as magnetite and the inner layer to contain the balance of the Fe plus the Cr and the Ni as a Fe, Cr, Ni spinel. The typical oxide film formed on stainless steel is shown in Figure 2.4.

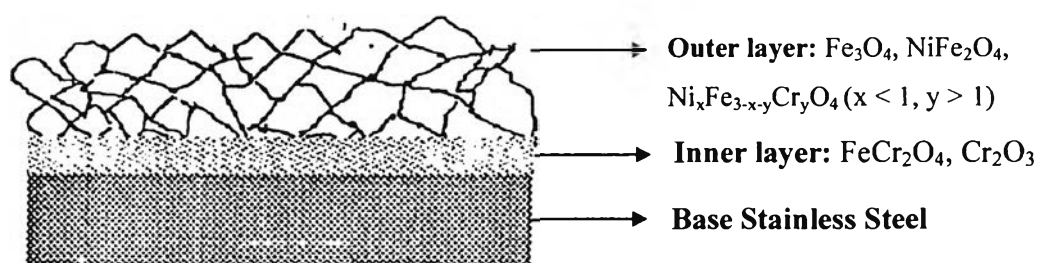


Figure 2.4 Schematic cross-section through oxide film on stainless steel in PWR primary piping (Lister and Venkateswaran, 1995).

The nickel alloys that are used for steam generator tubes in cooling water circuits are the austenitics like Alloy 600 or Alloy 800, in which the former, with about 75% Ni and 15% Cr, is a “true” nickel alloy whereas the latter has less

than half the amount of nickel and more chromium and iron because it has more corrosion resistance. Thus, in some reactor systems, Alloy 600 has been replaced with Alloy 690 which has more chromium and less nickel. These alloys also form oxide films in high-temperature water that are similar to those on stainless steel. In reducing coolant, the protective inner layer next to the metal is chromite but with a nickel content higher than that of the inner layer on stainless steel. In addition, the outer layer, again, is nickel ferrite and is generally less dense than that on stainless steel because of the lower corrosion rate and the fewer corrosion products generated. The typical oxide film formed on Alloy 600 and Alloy 800 is shown in Figure 2.5.

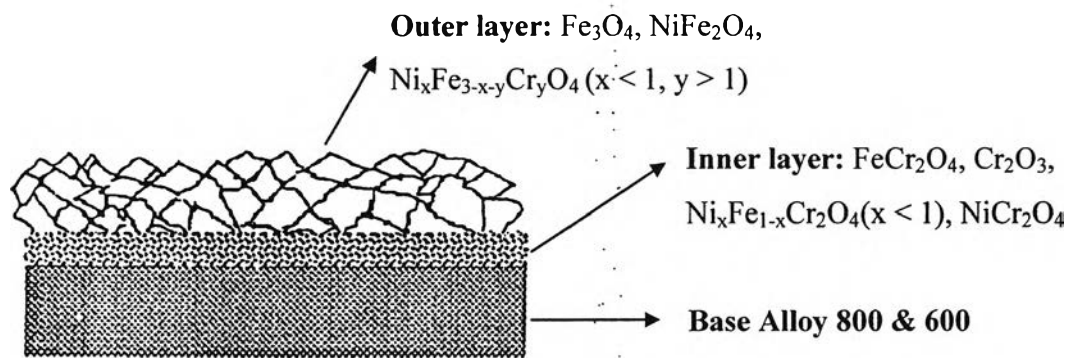


Figure 2.5 Schematic cross-section through oxide film on Alloy 600 & Alloy 800 in PWR & PHWR primary circuits (Lister and Venkateswaran, 1995).

2.3 Heat Treatment

2.3.1 Definition of Heat Treatment

Heat treatment of a metal or alloy is a procedure involving controlled heating and cooling, conducted for the purpose of changing the alloy microstructure and resulting in required properties without changing the product shape (Kopeliovich, 2009).

2.3.2 Objectives of Heat Treatment

Metallic materials consist of a microstructure of small crystals called “grains” or crystallites. The nature of the grains, such as grain size and composition, is one of the most effective factors that can determine the overall mechanical

behavior of the metal. Heat treatment provides an efficient way to manipulate the properties of the metal by controlling the rate of diffusion and the rate of cooling within the microstructure.

There are two general procedures of heat treatment. These are annealing and hardening.

2.3.2.1 Annealing

Annealing involves heating the alloy and holding it at a certain temperature (annealing temperature) followed by controlled cooling. It results in mitigation of internal stresses, softening, chemical homogenizing and transformation of the grain structure into a more stable state. Annealing occurs by the diffusion of atoms within a solid material, so that the material progresses towards its equilibrium state. This results in softening and higher ductility. There are three stages in the annealing process as follows (Kopeliovich, 2009):

Stress relief (recovery)

Stress relief is a low-temperature process of reducing internal mechanical stresses, caused by cold-working, casting or welding. During this process atoms move to more stable positions in the crystal lattice. Thus, vacancies and interstitial defects are eliminated and some dislocations are annihilated.

Typically, recovery heat treatment is used mainly for preventing stress-corrosion cracking (SCC) and decreasing distortions, caused by internal stresses.

Recrystallization

In this process, the grain structure of the metal is changed. When the alloy reaches a particular temperature (recrystallization or annealing temperature), new grains start to grow from the nuclei formed in the cold-worked metal. The new grains absorb imperfections and distortions caused by cold deformation. The grains are equi-axed and independent of the old grain structure. As a result of recrystallization, mechanical properties of the alloy, such as strength and ductility, return to the pre-cold-worked level.

The annealing temperature and the new grain size are dependent on the degree of cold-working. The more cold-working, the lower the annealing temperature and the finer the recrystallization grain structure. Low degrees

of cold-working (less than 5%) may cause formation of large grains. Generally, the annealing temperature of metals is between one-third to one-half of the freezing point measured in Kelvin (absolute) temperature scale.

Grain growth (over-annealing, secondary recrystallization)

In this process, a growth of the new grains at the expense of their neighbors occurs at temperatures above the recrystallization temperature. This process results in a coarsening of the grain structure and is undesirable.

However, the annealing temperature and the controlled-cooling rate depend on the alloy composition and the type of the annealing treatment. The following types of annealing are used in heat treatment of alloys:

- **Full annealing** is a process in which a ferrous alloy (commonly hypoeutectoid steel) is heated to about 100°F (55°C) above the upper critical temperature, followed by soaking and slow cooling in the furnace or in some medium to a temperature below the critical temperature. For the non-ferrous alloys, full annealing means full softening after cold working in contrast to partial annealing meaning partial softening.

- **Subcritical annealing** is annealing of cold-worked steel below the critical temperature on the iron-carbon phase diagram.

- **Recrystallization annealing** is a process of heating a cold-worked metal to a temperature above the recrystallization temperature followed by soaking for a time required for the grain structure transformation. Recrystallization annealing is widely used as an intermediate softening treatment between stages of cold working (cold rolling, drawing). A combination of recrystallization annealing and cold working allows one to control the microstructure grain size.

- **Stress relief (recovery)** is a relatively low temperature process of reducing internal mechanical stresses, caused by cold working, casting or welding. The stress relief temperature is lower than the recrystallization temperature.

- **Spheroidizing annealing** is a process of controlled heating and cooling high carbon steels (tool steels) to produce a spherical (globular)

form of cementite inclusions. This treatment improves the machining characteristics of the steel.

- **Bright annealing** is an annealing treatment which is carried out in furnaces with a reducing atmosphere preventing surface oxidation of the steel.

- **Homogenizing annealing** is a durable high temperature annealing treatment intended to decrease chemical segregation by diffusion. Homogenizing annealing is used for steel and aluminum ingots and castings.

2.3.2.2 *Hardening*

Hardening is a process of increasing the metal hardness, strength, toughness and fatigue resistance. There are many types of hardening as follow:

- **Strain hardening (work hardening)** increases material strength by cold-working (cold plastic deformation). Cold plastic deformation increases the concentration of dislocations, which mutually entangle one another, making further dislocation motion difficult and therefore resisting the deformation or increasing the metal strength.

- **Grain size strengthening (hardening)** increases material strength by grain refining. Grain boundaries serve as barriers to dislocations that raise the stress required to cause plastic deformation.

- **Solid solution hardening** increases metal strength by dissolving an alloying element. Atoms of solute elements distort the crystal lattice, resisting the motion of dislocations. Interstitial elements are more effective in solid-solution hardening than substitutional elements.

- **Dispersion strengthening** increases material strength by addition of a second phase into the metal matrix. The second-phase boundaries resist the dislocation motion, increasing the material strength. The strengthening effect may be significant if fine, hard particles are added to a soft, ductile matrix (composite materials).

- **Hardening as a result of spinodal decomposition.**

Spinodal structure is characterized by strains on the coherent boundaries between the spinodal phases causing hardening of the alloy.

- **Precipitation hardening (age hardening)** increases material strength by precipitation of fine particles of a second phase from a supersaturated solid solution. The second-phase boundaries resist the dislocation motion, increasing the material strength.

2.3.3 Heat Treatment of Nickel Alloys

Nickel alloys may be subjected to one or more of five principal types of heat treatment, depending on chemical composition, fabrication requirements and intended service. These are annealing, stress relieving, stress equalizing, solution treating and age hardening (precipitation hardening). Since the alloys used in this study are subjected to mill annealing (similar to annealing) and thermal treating (similar to stress relieving), only these two processes will be explained in this section.

2.3.3.1 *Mill Annealing (MA)*

Mill annealing is a high-temperature annealing process that usually requires temperatures between 705 and 1205 °C. It is performed to fully recrystallize the grains after cold working. The time required for this type of annealing is generally short, ranging from 0.5 to 60 minutes depending on the alloys and amount of work-hardening (Tillack *et al.*, 1991).

Mill annealing is usually done in closed environments. In the case of Alloys 600, 690, and 800, they are annealed in a hydrogen-purged furnace at a temperature of around 1000 °C ± 100 °C for around 2 minutes, depending on the manufacturer (Sandvik, 2008).

2.3.3.2 *Thermal Treatment (TT)*

Thermal treatment is a stress relieving used to remove or reduce stresses in work-hardened non-agehardenable alloys without producing a recrystallized grain structure. Stress-relieving conditions for nickel and nickel alloys range from 425 to 870 °C (800 to 1600 °F) for 10-15 hours, depending on alloy composition and degree of work hardening (Tillack *et al.*, 1991).

In the case of Alloys 600, 690, and 800, after the annealing process at approximately 1100 °C (2010°F) for some minutes, they are thermally treated at 720°C (1330°F), normally for 10 hours (Sandvik, 2008) or at 704°C for approximately 15 hours produced by Westinghouse (Airey, 1980).

Often Alloy 800 SG tubes are also subjected to a final mill anneal at 950°C min for 2 minutes, a cold drawing for cold work hardening and a final OD surface conditioning by shot peening (Valinox, 2006). Shot peening is a cold working process in which small spheres called shot bombard the surface to create dimples. Therefore, the surface of the material must yield in tension. Below the surface, the material tries to restore its original. Thus, below the dimple it is highly stressed in compression, which increases strength and durability.

Theoretically, one would expect that, for the same material, thermal treating would provide the largest grain size, followed by mill annealing and cold drawing. In addition, a material with a finer grain is harder and has higher yield strength than a coarser-grain material. For the same material, mill annealing should give a higher hardness than thermal treating since thermal treating is performed after mill annealing resulting in softer material.

Intasopa (2008) found that the thermally-treated alloys have a uniform carbide network distributed throughout the grains while carbide precipitates in mill-annealed alloys are distributed within the grain boundaries. This may result in depletion of chromium content in the grain boundaries, making them more prone to intergranular attack (IGA) that has led to intergranular stress corrosion cracking (IGSCC). Thus, thermal treatment has been observed to produce a more stable grain structure than mill annealing, which would result in a higher resistance to SCC attack.

2.4 Crud Induced Power Shift (CIPS)

2.4.1 The Causes of CIPS

Crud Induced Power Shift (CIPS), which is also known as Axial Offset Anomaly, (AOA), can lead to many problems such as loss of shut-down margin, economic penalties, safety consideration and power reduction. Moreover,

there are two other problems that occur in conjunction with AOA. Those are an increased dose rate and a possibility of fuel failure (EPRI, 2003). The cause of AOA is not exactly determined, but there are three things believed to contribute to this anomaly.

First, corrosion products or crud in the coolant deposit on the cladding surface. These are generated from the corrosion of plant systems, especially the steam generator piping, since crud found in the core is mostly nickel-based. For example, the deposit samples from Span 6A of bundles in Callaway Cycle 9 fuel that had experienced AOA were examined by Frattini *et al.* (2001). They found that the deposit samples contained predominantly nickel in a form of NiO, nickel ferrite and bonaccordite, Ni_2FeBO_5 .

Second, sub-cooled nucleate boiling (SNB) occurs in the upper span of the fuel assemblies. Nucleate boiling will form at nucleation sites (slight imperfections in the cladding surface) that increase the exposure area, allowing more heat to be transferred to the surrounding coolant. SNB is more likely to take place in a high-duty core, where increased coolant temperatures and higher surface heat fluxes make it more likely for localized boiling to occur at the top of the core. SNB promotes the deposition of crud on the cladding surface. Also, because this process occurs while the vapor bubbles are trying to escape from the nucleation sites, small chimneys are formed in these deposits. SNB may be one of the most important contributing factors to AOA; without it the crud may not be able to accumulate in the form of a porous layer with chimneys as observed on AOA fuel assemblies.

Lastly, boron from boric acid in the coolant is concentrated (due to boiling) and deposited within the chimneys, creating an uneven distribution in the core of this high neutron absorber. This results in a depression in power at the top of the core as the boron deposited reduces the local neutron population. There are two possible boron deposition methods considered as causing AOA: precipitation of a soluble boron species and adsorption of boric acid. In a solution of H_3BO_3 and LiOH , the soluble boron species are in the form of lithium borate (lithium monoborate - $\text{Li}_2\text{B}_2\text{O}_3$, lithium diborate - $\text{Li}_2\text{B}_4\text{O}_7$, lithium pentaborate - $\text{Li}_25\text{B}_2\text{O}_3$). In the first and last compound borate refers to the species B_2O_3 , but in the middle one it refers to just the boron, as is the case in lithium metaborate (LiBO_2). Originally, lithium

metaborate was suggested to have been the precipitating species causing AOA (EPRI TR-108320, 1997). The solubility of three lithium borate species is shown in Figure 2.6. From the graph, the solubility of monoborate decreases, while the solubility of pentaborate and diborate may have decreased at high temperatures, so they would precipitate within the crud.

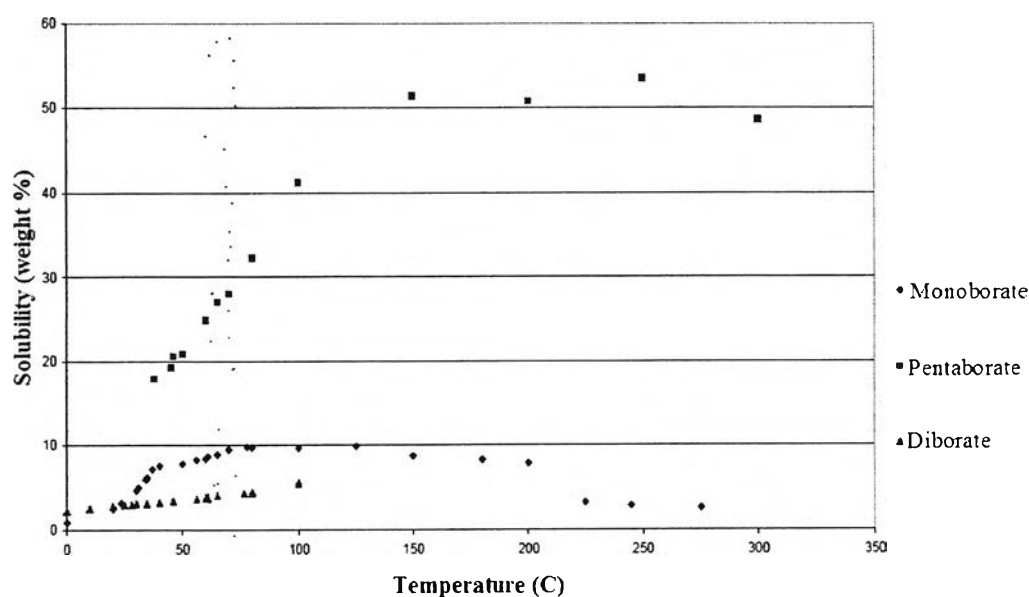


Figure 2.6 Solubility of different borate species (Bouaziz, 1961).

The other deposition mechanism is adsorption. This process is concerned with the physical attachment of boron or boric acid to the lattice structure of crud. However, the amount of boron or boric acid adsorbed on the surface at PWR operating temperatures is not enough to cause AOA, since the adsorption actually decreases with temperature. Therefore, the adsorption process is most likely not the primary deposition mechanism for boron within the crud layer. The three interrelated causes are shown in Figure 2.7.

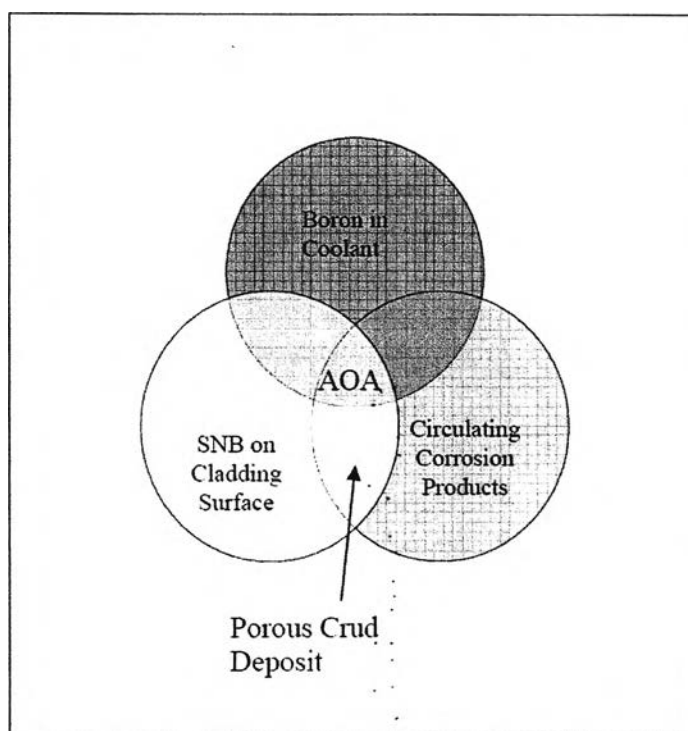


Figure 2.7 Venn diagram of suspected AOA causes (Hawkes, 2004).

2.4.2 Effect of Solubility of Crud

The solubility of substances generally varies significantly with the temperature of the solution as well as with the concentrations of other soluble species. Experiments have been run to determine the solubility of corrosion products such as nickel ferrite and magnetite for the entire coolant temperature range of an operating reactor. Sandler and Kunig (1981) studied nickel and iron solubility and found that they vary with temperature, reaching maxima at 4.1 ppm for iron and 1.0 ppm for nickel at roughly 75 °C. At typical operating temperatures, the solubilities of iron and nickel are 0.2 ppm and 0.1 ppm, respectively, and they decrease at higher temperatures. Moreover, they studied the effect of pH on the solubilities of iron and nickel and found that the temperature coefficient of solubility of iron in solution of 0.06 M B(OH)₃ changes from negative to positive as the LiOH concentration is increased from 10⁻⁴ to 10⁻³ M (at about pH_{25°C}7) so the solubility of iron increases with increasing temperature at pH_{25°C} above 7 but decreases at pH_{25°C} below 7. With a positive temperature coefficient, dissolved iron is most likely to precipitate when

the temperature is decreased during plant shut down. The solubility of nickel is generally lower than that of iron and goes through a minimum in the solution of 0.06 M $B(OH)_3$ and 10^{-3} M LiOH ($pH_{25^\circ C} 7.4$). Later, Chung and Lee (1990) also found that at high pH_T , the iron solubility at temperature less than $250^\circ C$ increases with increasing temperature for both nickel ferrite and magnetite. In addition, they found the effect of pH on the solubility. At each temperature, the solubility is a function of pH_T and goes through a minimum value at some pH_T depending on the temperature. The pH of the non-precipitating coolant should be kept at or slightly above 7 at $300^\circ C$ for the minimum solubility, which agrees reasonably well with Sandler and Kunig. These indicate that the solubility of corrosion products affects the formation of AOA; for example, with increasing temperature, the corrosion products come out of low pH solution; i.e. 0.06 M $B(OH)_3$ and 10^{-4} M LiOH solution ($pH_{25^\circ C} 6.3$) (Sandler and Kunig, 1981), and deposit as crud on the cladding surface.

2.4.3 Effect of Heat Flux of Fuel Element

An increase in thermal duty causes an increase in SNB. This most likely promotes AOA, either directly or indirectly. Kawaguchi *et al.* (1983) found that increased heating will increase the rate of deposition of particulate matter. This is consistent with the observation that the higher heat flux in the upper portions of reactors has resulted in more crud deposition, very likely resulting in AOA. It was observed by EPRI (EPRI NP-1254, 1979) that the weight of deposited iron was greater at higher surface heat fluxes. The deposition mechanisms were believed to depend on the change in solubility of crud induced by evaporation and temperature changes in the coolant.

2.4.4 Mitigation Strategies for CIPS or AOA

Several mitigating strategies have already been proposed to treat AOA, such as adding zinc to the coolant, operating the plant at an elevated pH, using enriched boric acid, and cleaning fuel assemblies that are to be re-inserted for second and third cycles, which can be described as follows:

2.4.4.1 *Adding Zinc*

Zinc is added to the coolant since it forms a more protective oxide layer on system surfaces that will prevent corrosion product release and stress corrosion cracking (SCC) (Byers and Jacko, 1993). The ability for zinc to limit the amount of corrosion product release helps reduce AOA by limiting the crud source term. Byers and Jacko (1993) studied the effectiveness of zinc additives in simulated PWR environments by varying the amounts of zinc added to an aqueous solution by up to 20 ppb at 330°C. The results showed that zinc limited the corrosion product release rate by as much as a factor of five as compared to the same coolant without the added zinc.

2.4.4.2 *Operating the Plant at an Elevated pH*

Operating the plant at an elevated pH is one method of reducing AOA. The benefit from increasing pH and maintaining it constant during the operating cycle are reductions in the specific activity of deposits, resulting in lower radiation fields as well as reductions in the amount of crud deposited on fuel. For a long time, PWRs operated with a coordinated $\text{pH}_{300^\circ\text{C}}$ of 6.9 which was based on the assumption that the bulk of deposits consisted of magnetite (Fe_3O_4). The magnetite assumption was used in models to determine an optimum pH for the coolant to minimize corrosion product deposition. Later, the pH was increased when data showed that the bulk of the deposits on the cladding actually consisted of a compound with a nickel component such as nickel ferrite ($\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$). With the assumption that nickel ferrite is the major corrosion product, the pH recommendation was increased to 7.4. There is evidence of the effect of pH on crud deposition. It was observed by EPRI (EPRI NP-1254, 1979) that operation under low pH chemistry conditions led to heavier deposits on heated surfaces than that under higher pH conditions. However, exposure to too high a lithium concentration could lead to stress corrosion cracking of core elements and fuel cladding failures (Hawkes, 2004).

2.4.4.3 *Using Enriched Boric Acid*

In some PWRs, the use of enriched boric acid (EBA) and ultrasonic fuel cleaning have been suggested to reduce AOA. EBA consists of boric acid that is more abundant in the ^{10}B isotope, which is the main neutron absorber with a much higher neutron absorption cross section than the other isotope ^{11}B . There

are two advantages to using EBA. The first is that it may reduce the amount of boric acid deposition in crud because the overall boric acid concentration is lower; the concentrations of depositing species may be reduced to below the solubility limit. The other advantage is that it can allow for more efficient control of the pH of coolant because the amount of boric acid required would go down while the lithium concentration would be the same, so the reactor may possibly be able to run at a pH of 7.4 for the entire cycle, depending on the boron enrichment. However if precipitation and adsorption could still occur, there may be even more flux depression because of the enhanced level of the ^{10}B isotope. Therefore, the net effect of EBA on AOA could be either positive or negative, depending on the relative amounts of deposition reduction and ^{10}B increase (Frattoni *et al.*, 2001).

2.4.4.4 *Cleaning Fuel Assemblies*

Ultrasonic fuel cleaning (UFC) is a process to remove the crudded fuel assembly from the reactor, place it in a UFC bath, clean it, and then place it back in the core for the next cycle (Frattoni and Moser, 2000). The problem with UFC is that it is time-consuming during an outage when plants try to get the core back online as soon as possible, and it is expensive.

2.5 Zinc Addition

The key parameter that controls corrosion release and reduces radiation build-up on PWR primary system materials is the oxide film on the material. One of ways in which oxide films can be modified is the selective addition of small quantities of metal ions to the coolant. Zinc is an effective additive because its incorporation makes the protective oxides on the Fe-Cr-Ni alloy surfaces more compact and tenacious, being based on ZnCr_2O_4 . It reduces corrosion release and inhibits the incorporation of radioactive elements such as ^{60}Co by decreasing the quantity of oxide (by making it more protective) on the surfaces of these alloys and by occupying the available sites in preference to ^{60}Co (Lister and Venkateswaran, 1995).

The beneficial effect of zinc on corrosion release and on radiation build-up control can be explained by applying the site preference energy and the net lattice

energy concepts (Lister, 1994). In austenitic alloy/high-nickel-alloy systems without zinc addition, iron chromite (FeCr_2O_4), which is a major constituent of the very protective inner layer, can be receptive to cobalt since CoCr_2O_4 is about as stable as FeCr_2O_4 as can be seen from their net lattice energies in Table 2.4. The spinels are arranged in the Table in order of apparent stability, from most stable to least stable. When zinc is added to the primary coolant, zinc chromite (ZnCr_2O_4), which is the most stable species of the various spinel/inverse-spinel oxides of interest as shown in Table 2.4, is formed. Table 2.5 shows the site preference energies of certain cations, Cr^{3+} in chromite has the highest octahedral site preference energy. The Cr^{3+} ions therefore occupy the octahedral sites in the spinel lattice and the divalent ions fill the tetrahedral sites. Since the tetrahedral site preference energy of Zn^{2+} is more than that of Co^{2+} , this means that it is energetically more favourable to form ZnCr_2O_4 than CoCr_2O_4 . Thus, ZnCr_2O_4 not only can be a highly protective inner layer, but also, unlike FeCr_2O_4 , can reject the entry of cobalt into the oxide lattice (Lister and Venkateswaran, 1995).

Marble and Wood (1985) found that zinc in the form of ZnO significantly reduces the amount of oxide formed on stainless steel pipes and the amount of ^{60}Co incorporated in the system. This is because zinc cations will tend to modify the normal magnetite and chromite crystal defect structures, so that a more protective film is formed and corrosion significantly inhibited. Generally, zinc cations prefer to modify the chromite structure than the magnetite structure because ZnCr_2O_4 is more stable than ZnFe_2O_4 as can be seen in Table 2.4.

A drawback, however, is that natural zinc contains 48% ^{64}Zn , which can be activated to ^{65}Zn in the reactor core. ^{65}Zn is a γ -emitter with half-life of 244 days. Therefore, full benefit of zinc addition can only be obtained by using zinc depleted in ^{64}Zn . Due to the fact that separation of isotopes is a complicated process and associated with high costs, it is not always reasonable to use depleted zinc. However, using undepleted zinc still enables the radioactivity to be reduced because ^{65}Zn has a considerably shorter half life than ^{60}Co , which is a γ -emitter with half-life of 5.27 years.

This research aims to study the effect of SG alloy composition and heat treatment and concentrations of boron and zinc on oxide film formation on Alloy 600, Alloy 690 and Alloy 800. The results should increase our understanding of crud transport and lead to methods for reducing AOA.

Table 2.4 Net lattice energies of some spinels (Lister, 1994)

Normal spinel	Inverse spinel	Lattice energy (kcal/mole)
ZnCr ₂ O ₄		64.8
CoCr ₂ O ₄		43.7
FeCr ₂ O ₄		43.1
MgCr ₂ O ₄		38.2
NiCr ₂ O ₄		24.2
	NiFe ₂ O ₄	9.0
ZnFe ₂ O ₄		5.0
	MgFe ₂ O ₄	-5.0
	Fe ₃ O ₄	-9.9
	CoFe ₂ O ₄	-10.5

Table 2.5 Site preference energies of certain cations (Miller, 1959)

Ion	Site Preference Energy (kcal/g at.wt.)	
	Octahedral	Tetrahedral
Fe ²⁺	-9.9	9.9
Co ²⁺	-10.5	10.5
Ni ²⁺	9.0	-9.0
Zn ²⁺	-31.6	31.6
Mg ²⁺	-5.0	5.0
Cr ³⁺	16.6	-16.6
Fe ³⁺	-13.3	13.3