



Deposit formation in PWR steam generators

Authors: Mikko Vepsäläinen

Confidentiality: Public

Report's title Deposit formation in PWR steam generators		
Customer, contact person, address SAFIR2010, Finnish national research program on NPP safety 2007-2010	Order reference VTT-R-00135-10	
Project name Monitoring of the Structural Integrity of Reactor Circuit	Project number/Short name 32876 / RAKEMON	
Author(s) Mikko Vepsäläinen	Pages 32/	
Keywords Steam generator, deposit, fouling, nuclear energy	Report identification code VTT-R-00135-10	
<p>Summary</p> <p>Fouling in the steam generators of pressurized water reactors can cause significant inconvenience at the nuclear power plants. Accumulation of deposits can lead to corrosion problems, reduce heat transfer and cause tube plugging and flow problems. Secondary-side water chemistry has developed from phosphate-based treatment to all-volatile water treatment, which is based on the use of ammonia and hydrazine. Over the past 10 years, nuclear plants have also used advanced amines to reduce corrosion and deposit precursor formation.</p> <p>Deposits are formed mainly from corrosion products that are transported from the secondary-cycle. Iron oxides are the primary component in the deposits but they may contain significant proportions of copper and copper oxides depending on the construction materials of the secondary-cycle. Soluble species, such as silicates and sulphates, can concentrate and precipitate within deposits.</p> <p>Flow-accelerated corrosion (FAC) on the secondary-cycle is the main source of the iron deposit precursors. On the FAC magnetite layer becomes thin due to enhanced dissolving at the high flow and turbulence. FAC occurs at alkalized and deaerated water. Temperature and pH have significant effect on the FAC, but may be difficult to change in operating plant. Using advanced amines can alleviate FAC, but some amines can be fouling enhancers.</p> <p>The formation of deposits and sludge in the steam generator involve a range of possible physical and chemical phenomena such as turbulent deposition, boiling deposition, gravitational settling and re-entrainment. The deposition process is complex phenomena where multiple factors affect to deposit formation rate. Formed deposits and sludge can be removed from the steam generator by chemical and mechanical means.</p>		
Confidentiality	Public	
Espoo 4.2.2010 Written by	Reviewed by	Accepted by
Mikko Vepsäläinen, Research Scientist	Ari Koskinen Team Leader	Pentti Kauppinen Technology Manager
VTT's contact address Mikko Vepsäläinen, P.O. Box 1000, FI-02044, Finland		
Distribution (customer and VTT) SAFIR2010		
<p><i>The use of the name of the VTT Technical Research Centre of Finland (VTT) in advertising or publication in part of this report is only permissible with written authorisation from the VTT Technical Research Centre of Finland.</i></p>		

Preface

This literature review has been made at VTT Espoo office during year 2009. This research was part of SAFIR2010, Finnish national research program on NPP safety 2007-2010.

Deposit formation in the nuclear power plant steam generators is significant problem that causes corrosion of materials, fluid restrictions and heat transfer reduction. There has been significant effort in the secondary-cycle chemistry area to reduce deposit formation and there are numerous papers published in this field. This review gathers information that is related to composition of deposits, their formation and behaviour in the steam generators and techniques that are used to remove deposits from the surfaces. Objective of this review is to give background for further research work that is related to deposit monitoring and prevention.

Espoo 4.2.2010

Author

Contents

Preface	2
1 Introduction.....	4
2 Goal.....	4
3 Composition of steam generator deposits and their precursors.....	5
3.1 Formation of deposit precursors in the secondary cycle	6
3.2 Steady-state generation of deposit precursors.....	8
3.2.1 Effect of temperature on flow accelerated corrosion	10
3.2.2 Effect of water chemistry on flow accelerated corrosion	11
3.3 Transient generation of deposit precursors.....	14
4 Deposit formation and behaviour in the steam generator	14
4.1 Formation of tube scale.....	17
4.2 Formation of sludge piles.....	20
5 Copper in steam generator deposits.....	21
5.1 Copper oxide formation and stability.....	23
5.2 Factors influencing copper corrosion and release activity.....	25
6 Removing deposits and sludge from the steam generators.....	28
6.1 Chemical cleaning of the steam generator.....	28
6.2 Mechanical cleaning of the steam generator.....	29
7 Conclusions.....	30
8 Summary	30
References	31

1 Introduction

The generation and transport of corrosion products in the feedwater, drain and condensate systems at a pressurized water reactor (PWR) plant results to the formation of deposits on the secondary side of steam generators (SG). These deposits can increase the potential for corrosion of tube materials, cause fluid flow restrictions that increase the pressure drop across the tube supports, reduce the heat transfer efficiency of the units, and prevent a utility from operating a plant at full power [1, 2]. Heavy deposit formation in the steam generators is a pre-cursor for material degradation. Deposits may also interfere with non-destructive evaluation (NDE) of tubes by eddy current or ultrasonic techniques.

Nuclear power plants have changed secondary water treatment from phosphate to all-volatile treatment and "alternative" amines [3]. This has changed deposit related problems from the sludge piles and tube phosphate wastage to deposits on the tube surfaces and reductions on the heat transfer. In order to control deposit formation and steam generator fouling, it is important to minimize the transport of corrosion products into the steam generator. That is the reason to try to control corrosion and corrosion product transport within the steam supply system. But over time, even with careful system cycle water chemistry control, corrosion products will tend to accumulate in the steam generator. They eventually deposit on surfaces, especially on the high-heat-flux surfaces and in the low-velocity regions. During operational thermal transients and hydraulic shock, deposits can break away from these surfaces and re-enter the fluid stream. During these "crud bursts", particulate concentrations in the steam generator can climb dramatically. The deposition of dissolved and suspended species in a fluid is a very complex function of heat flux, species concentration, time, temperature, fluid velocity, surface chemistry and morphology, and pressure.

As mentioned, increased iron concentrations in the feedwater will result in higher steam generator fouling. Less obviously, increased concentrations of non-filterable dissolved iron may result in an increased fouling rate [2, 3]. Some amines used for pH control can enhance fouling, but on the other hand mitigate flow-accelerated corrosion (FAC) rate and lower corrosion product transport.

2 Goal

In this literature review, steam generator deposit formation is gone through in detail. Studies concerning the composition of deposits, the formation of deposit precursors during different stages of plant run and the mechanisms of deposit formation are summarized. Understanding the role of copper in deposits is important, especially when copper compounds are used in the secondary cycle. Progress made on the steam generator deposit removal is summarised at the end of this report.

3 Composition of steam generator deposits and their precursors

The processes, which govern the formation of deposits in PWR steam generators involve multiple steps, which begin with the generation of transportable precursors in the secondary cycle. Once transported to steam generator precursors can be (1) removed by blowdown, (2) transported by steam – “carry over”, (3) removed by chemical or mechanical means or (4) form permanent deposits in the steam generator [1]. The deposit precursors are ionic, particulate and soluble chemical species which are transported to steam generator mainly from elsewhere in the plant. Probably much less than 10% of the deposits in a steam generator are formed in situ due the corrosion of carbon or alloy steel components of the steam generator. Most of the in situ deposits are actually desirable because they passivate the steam generator surfaces and minimize further corrosion. Those in-situ deposits that form on tube support crevices and aggravate concentration of corrosive impurities or cause tube denting are harmful.

Three categories of deposit precursors and examples of impurities which constitute bulk of the material which is carried to steam generators are summarized in Fig. 1. The characteristics and concentration of all three forms of impurities can change inside the steam generator as feed water boils to produce steam [1]. Such transformations could be:

- Particulate impurities can agglomerate, coalesce or grow to form sediment like deposits known as sludge. The large sludge particles settle toward the bottom of the steam generator and collect as piles on the horizontal surfaces, particularly in the regions where flow velocity is low ($< 0,3$ m/s). In addition to forming piles on the horizontal surfaces, particulates can attach to tube surfaces and form scale.
- Ionic species such as sodium, chlorides and sulphates can concentrate in the crevices, within sludge piles and along tube free spans, particularly within and under deposits. Ionic species can then induce tube corrosion and can participate in the chemical mechanisms that consolidate particulate species into tube scale.
- Soluble species such as organics, organic acids and gases can react with other deposits and alter their chemical form.

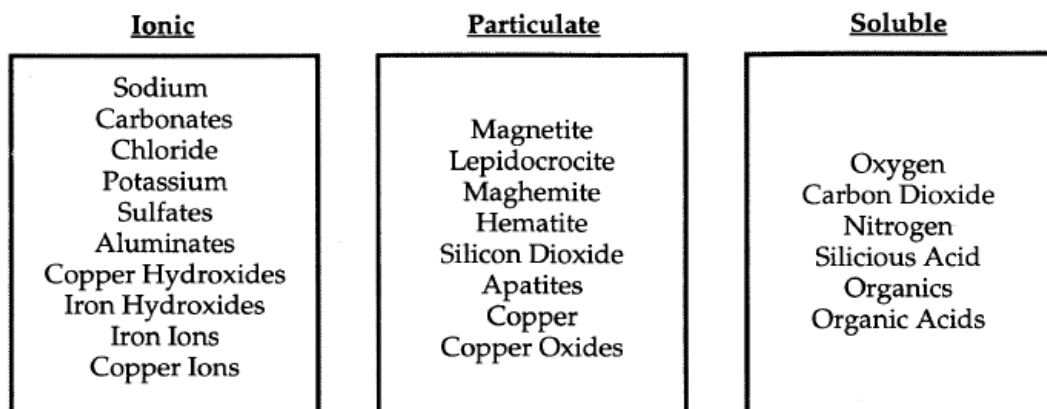


Figure 1: Categories of impurities introduced into PWR steam generators [1].

3.1 Formation of deposit precursors in the secondary cycle

The potential sources of impurities which can be transported to the steam generator along the feedwater are presented in Fig. 2. Included in the Fig. 2 are plant components of a generic plant, which presents major features of operating plants [1]. Precursor materials that are likely to be introduced during normal operation are:

- Ionic and soluble metallic species liberated by dissolution of corrosion films on piping and heat exchanger surfaces.
- Particulate species liberated by flow accelerated corrosion product films on piping and components, particularly in wet steam piping downstream of high pressure turbine.
- Gaseous, ionic, particulate and soluble materials introduced through condenser tube leaks.
- Corrosion products released from condenser tubing.
- Oils and greases used for equipment maintenance and repair.
- Organics not removed by the makeup water treatment.
- Oxygen, nitrogen and carbon dioxide contained in make-up water.
- Resin fines and beads from blowdown demineralizers, condensate polishers or make-up water treatment systems.
- Chemicals used to regenerate resins
- Trace impurities found in resin treatment chemicals.

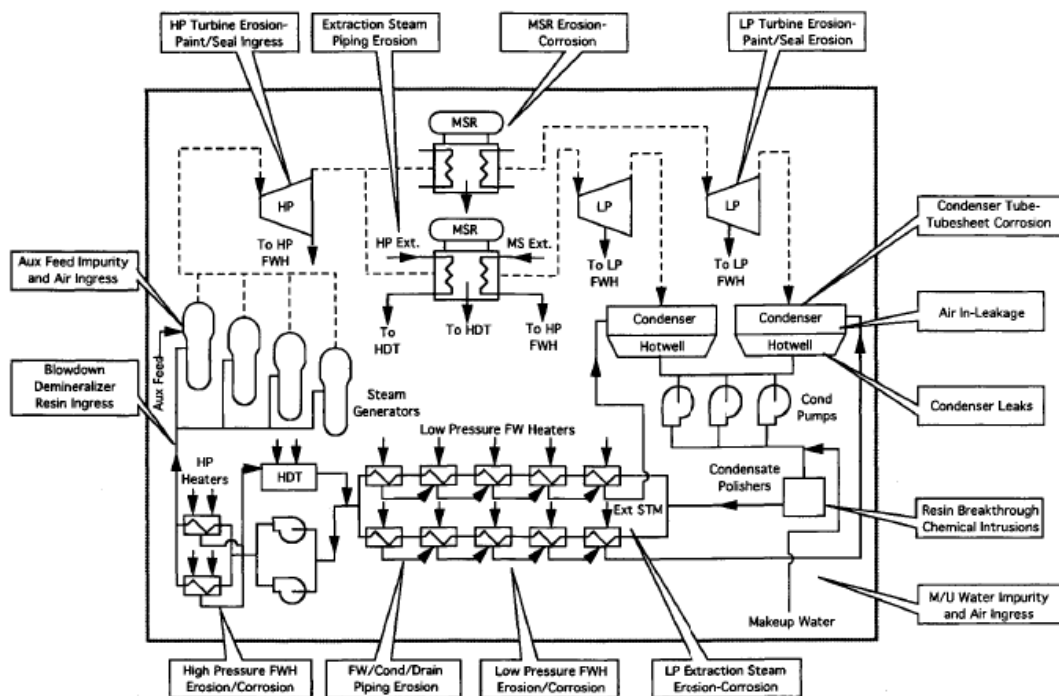


Figure 2: Sources of steam generator deposit precursors [1].

It can be seen that sources of impurities are many and varied and as a result the chemical composition of deposits varies greatly from plant to plant. To roughly illustrate quantity of the precursors from different processes, Fig. 3 presents the flow of different types of species. The widths of the bars that connect the various elements in this figure, are proportional to the mass transport of the deposit precursors [1].

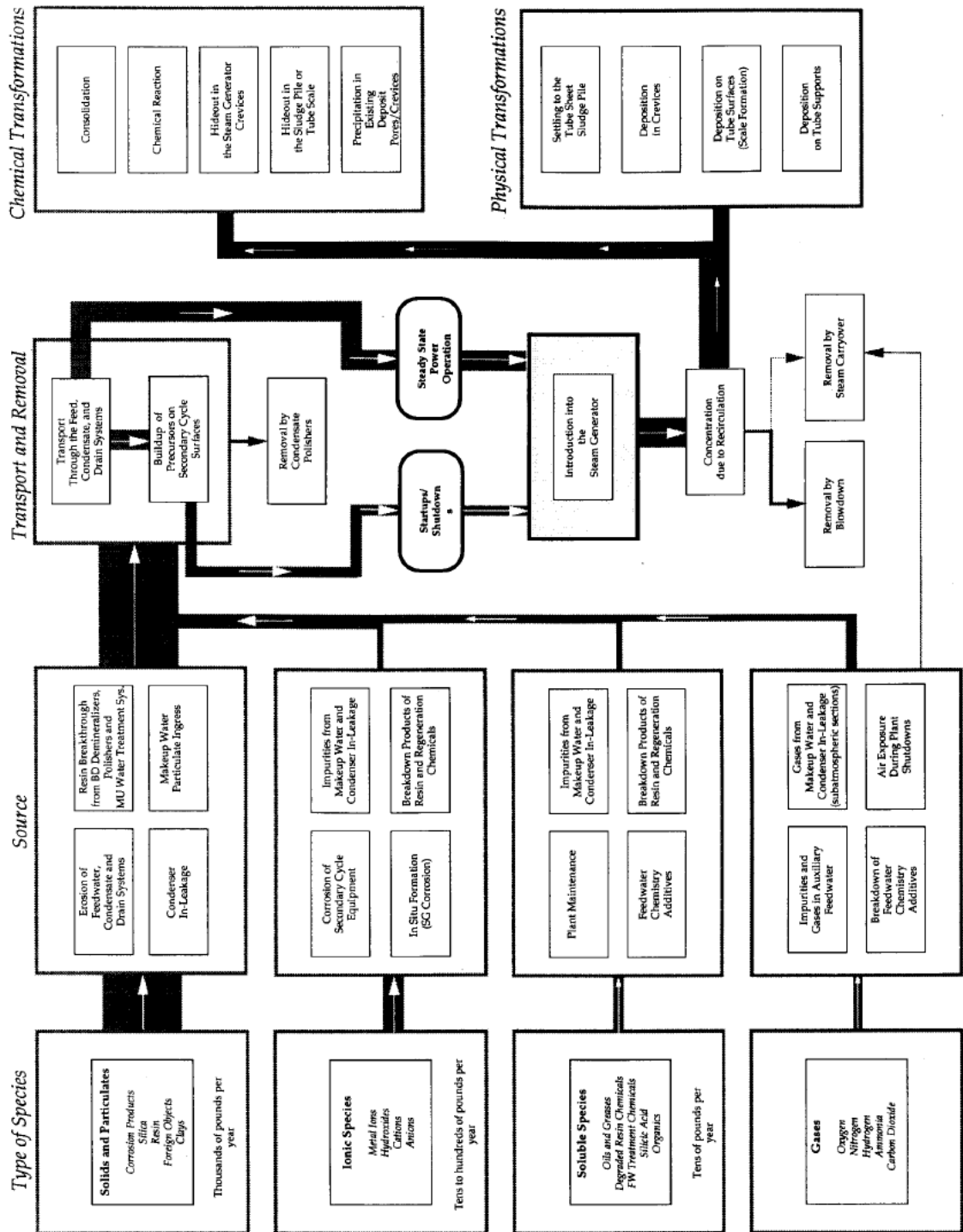


Figure 3: Summary of corrosion product generation and transport [1].

3.2 Steady-state generation of deposit precursors

The greatest source of the material impurities that find their way into steam generators are corrosion products liberated by flow accelerated corrosion (FAC) of carbon steel feedwater, drain and condensate system components [2, 4]. It has been estimated that corrosion products account for approximately 90% of the deposits in the steam generators [5]. This account for that steam generator deposits consist primarily of iron oxides at nearly all PWR. At some plants copper containing alloys are used in condensers and heat exchangers which in turn provide source for the copper and other alloy elements that are found in lesser quantities in the deposits.

The corrosion product films on carbon steel consist of magnetite, hematite, ferrous hydroxides and hydrated iron species. Flow accelerated corrosion (FAC) is a phenomenon that affects this normally protective oxide layer formed on carbon or low-alloy steel. With FAC, the oxide layer dissolves into the flowing stream of water or a water-steam mixture. As the oxide layer becomes thinner and less protective, the corrosion rate increases. Eventually a steady state is reached where corrosion and dissolution rates are equal. It is important to note that in the FAC process, the protective oxide film is not mechanically removed. Rather, the oxide is dissolved. Thus, FAC may be defined as corrosion enhanced by mass transfer between a dissolving oxide film and a flowing fluid that is unsaturated in the dissolving species [2]. FAC affects carbon steel components in deaerated and alkalized flowing water, mainly in the temperature range of 100°C to 300°C. Wall thinning rates are normally less than 0.03 mm/h (0.25 mm/year) but rates as high as approximately 0.34 mm/h (3 mm/year) have already been observed in operating plants [6].

Because the protective layer reaches a near steady-state condition, where the rate of layer formation nearly equals the rate of layer dissolution, the FAC rate tends to have a constant value. The FAC rate is proportional to velocity and turbulence. However, there is no known practical threshold velocity below which FAC will not occur [7].

FAC occurs when the carbon or low alloy steel develops a porous magnetite layer. Soluble ferrous ions are produced at the oxide-water interface. Next, the ferrous ions are transferred across the boundary layer. The concentration of ferrous ions in the bulk water is very low compared to the concentration of ferrous ions at the oxide-solution interface. The FAC rate increases if there is an increase of water flow past the oxide-water interface. One identifying characteristic of FAC of carbon and low-alloy steels is that the magnetite layer that is normally protective is dissolved by the flowing water stream [6]. Importantly, the removal of the magnetite occurs only by chemical dissolution. Flow is responsible for transporting the dissolved iron away from the magnetite and into the bulk water. The FAC mechanism can be described as the action of four simultaneous reactions (Fig. 4) [8].

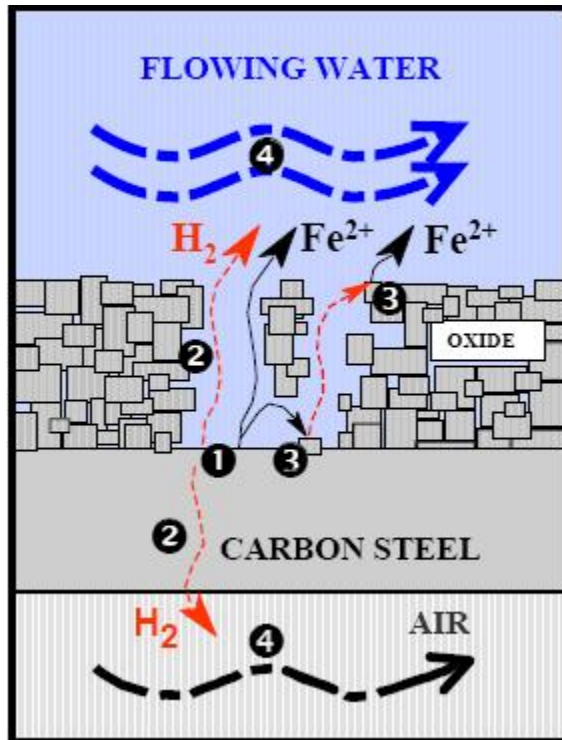
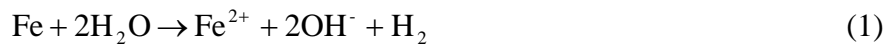
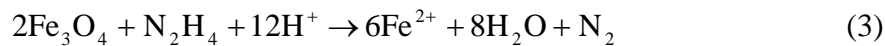


Figure 4: Schematic picture of the flow accelerated corrosion mechanism [8].

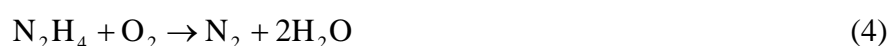
1. Oxidation of iron to soluble ferrous ions and magnetite at the internal interface between the steel and the oxide (Eq. 1 and 2).



2. Diffusion of soluble species (iron and hydrogen) across the porous oxide and diffusion of hydrogen through the carbon steel.
3. Dissolution and reduction of magnetite at the external interface between the oxide and the water (Eq. 3).



4. Transfer of soluble iron species towards the flowing water and transfer of hydrogen towards the air after diffusion through the steel. The influence of several parameters has been studied, such as water chemistry, temperature, hydrodynamic and mass transfer conditions as well as steel composition [6]. As a matter of fact, most of these parameters are well described by models. Nevertheless, the effects of some parameters still require investigation to try to better understand the mechanism of the degradation and to help update guidelines and improve FAC models. Hydrazine is used in plant units to guarantee a reducing environment in the secondary circuit as it is an oxygen scavenger (Eq. 4).



This mitigates secondary side stress corrosion cracking of steam generator tubes. Recent EDF/EPRI results [9] have shown that FAC could be increased in such reducing environments under specific chemistry, temperature and hydraulic conditions.

3.2.1 Effect of temperature on flow accelerated corrosion

Temperature is an important variable affecting FAC of low-alloy steels. FAC usually occurs between 100 °C and 280 °C, with a peak around 150 °C for single phase FAC in water and 180 °C for two phase FAC in wet steam [10, 11]. Numerous studies have resulted the classical “bell graph” relating temperature to FAC rate. Two examples are shown in Fig. 5 in relation to flow rate and amount of alloying elements in the steel. As discussed by Bouchacourt [12], this bell shape is in fact the result of a double dependence. On the one hand, when the temperature increases, the ferrous iron concentration decreases. This signifies that at low temperature, the capacity of water to remove ferrous ions is at a maximum. On the other hand, the temperature effect is very important on the flow viscosity and on the ferrous iron diffusivity, which governs the mass transfer. This explains why on the published curves, the position of the maximum depends clearly upon test conditions [2].

Temperature is an important parameter to consider when modelling the FAC phenomenon. In the actual plant, the temperature of the components are determined by the plant design and operating conditions and is not a parameter that can readily be changed to affect the FAC rate in the plant.

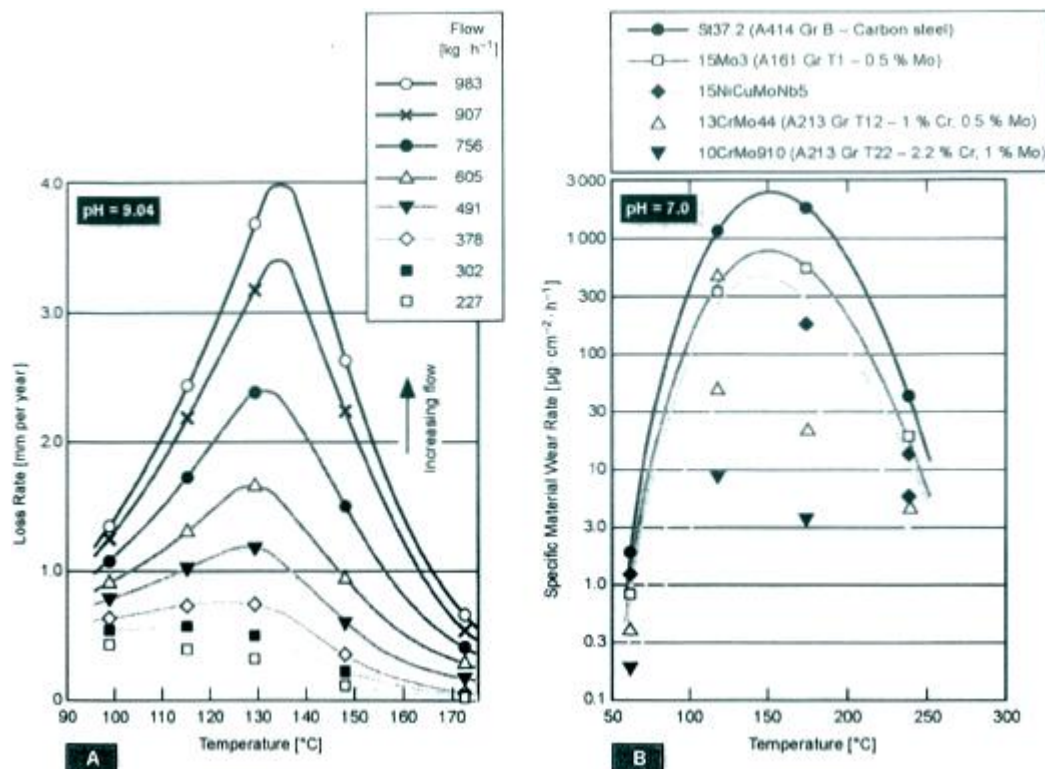


Figure 5: Two examples of temperature dependence of single-phase FAC under different flow and chemistry conditions [11].

3.2.2 Effect of water chemistry on flow accelerated corrosion

Feedwater pH and the distribution coefficient of the amine (or ammonia) used to control pH are the key variables determining the rates of FAC and therefore corrosion product transport. Some studies have shown that for all-ferrous secondary systems, the optimum pH for minimizing overall corrosion product transport is in the range of 9.3 – 9.6. European field studies reveal that even pH 9.8 and greater is required to minimize corrosion product generation in the feed water. Plants, that have used all volatile treatment with the high pH of >9.8 (H-AVT) from the beginning, don't show significant decrease of the heat transfer after 15 years [13]. However, when copper is present in the secondary cycle components, such high pHs will result in increased copper dissolution and transport to steam generators. At plants with copper components, pH is usually maintained below 9.3 [1].

It is well established that the at-temperature pH (pHT) of the high-purity water system has a first-order effect on the FAC rate of carbon steels [6, 10, 12]. This is not surprising, since the FAC rate is directly related to the solubility of iron, which in turn is related to the pH or more specifically the at-temperature pH of the water stream. This is illustrated graphically in Fig. 6 for magnetite in water at 250°C. A pH shift of 0,5 units from the minimum effectively doubles the corrosion rate. The at-temperature pH is a function of the specific amine or combination of amines and ammonia used for pH control [14].

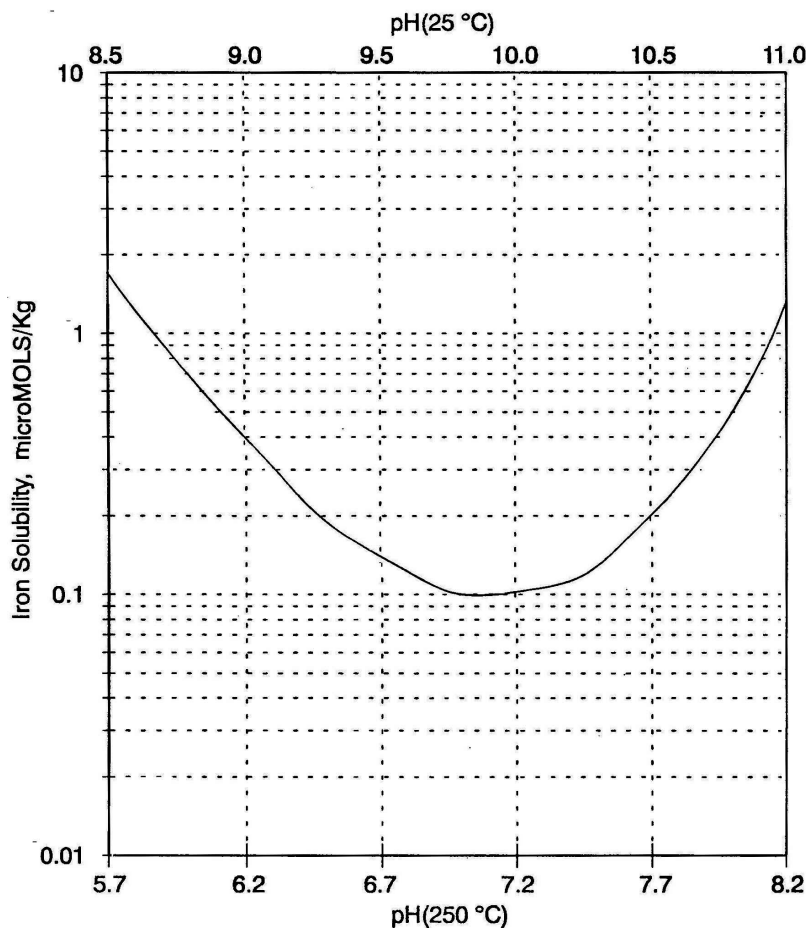


Figure 6: Iron Solubility (Magnetite) at 250°C versus pHT [14].

The effect of elevated pH on the reduction of FAC and corrosion product transport (CPT) is best demonstrated by studies made at operating utilities. One such study discusses the use of alternate amine chemistry at Prairie Island and Beaver Valley Nuclear Plants [15]. The average corrosion product transport at Prairie Island and Beaver Valley are given in Table 1.

Table 1: Average corrosion product transport at Prairie Island and Beaver Valley [15].

Plant/Chemistry	Feedwater pH		Iron Concentration (ppb)	
	pH @ 25°C	pH @ 225°C	Condensate	Feedwater
Prairie Island (NH ₃)	9.2-9.5	6.06-6.29	10	12
Prairie Island (NH ₃)	9.5-9.6	6.29-6.38	4.9	7.4
Prairie Island (Mo)	9.5-9.6	6.60-6.70	2.2	3.0
Beaver Valley (Mo)	9.4	6.50	1.4	6.4

The impact of increasing pH with just ammonia at Prairie Island was a decrease in CPT of a factor of about 2 [15]. An additional factor of about 2 reduction was achieved by the switch to morpholine chemistry with a more favourable distribution ratio and a stronger base at elevated temperature.

Fig. 7 provides an example of the effect of at-temperature pH on the FAC rate of the low-alloy steel at 198 °C. Starting at an at-temperature pH of 5.3, an increase of each 1 unit of at-temperature pH decreases the FAC rate by a factor of 2 or greater [15]. This reduction can be even greater at other temperatures. For example, an increase of the at-temperature pH from 6.7 to 7.1 decreases the FAC rate at 180 °C by a factor of 25 [6].

In addition to effects of pH and conditioning chemicals on the amount of corrosion product transport, water chemistry has been previously shown in loop tests to have a specific effect on SG fouling rate by particles [16]. According to results, average particle size is smaller when compared to ammonia-based AVT chemistry. This has also been verified in later studies [2]. This effect of amines is independent of the effect of chemistry on iron concentration and pH in the feedwater. Klimas et. al [16] found that amines like morpholine and ethanolamine (ETA) appear to be fouling enhancers (compared to amine-free water at the same pH) and produce relatively high fouling rates under SG operating conditions, even though they are beneficial in the means of reducing iron content in the feedwater as shown in Table 1. Whereas, fouling rates can be significantly reduced (by a factor of 5-10) using an optimized amine mixture for pH control [ETA and dodecylamine (DDA)]. Relatively low fouling rates (reduction by a factor of 4) can be also achieved by utilizing DMA (dimethylamine) for pH control.

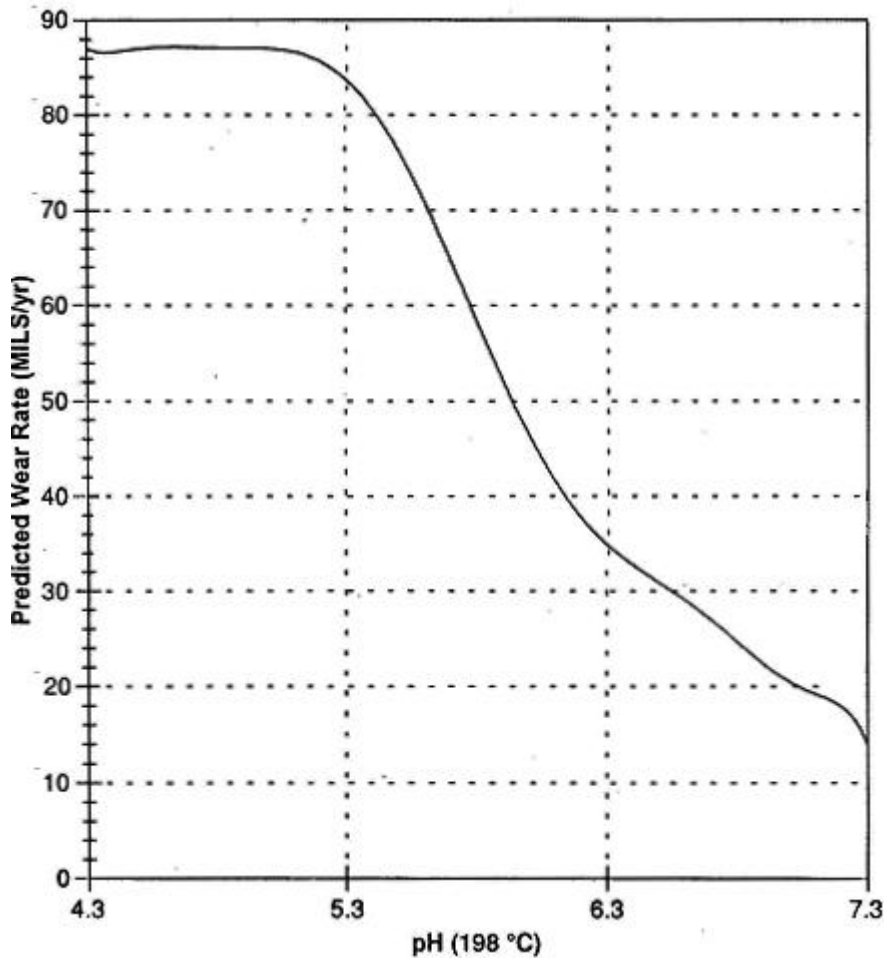


Figure 7: Flow-accelerated corrosion of carbon steel at 198°C versus pHT [14].

To get detailed information of the effect of amines to fouling by magnetite particles, the surface charge properties of the magnetite particles in morpholine, diethylamine and ethanolamine solutions has been studied [17]. According to results, there's no effect of these amines on the magnetite particle surface charge at temperatures of 200 °C and 250 °C. Researchers postulate that pH and ionic strength are surface-charge controlling parameters rather than specific chemical nature of the amine.

When low carbon steel samples were exposed to steam containing amines in low-temperature conditions, similar to condensation stage, clear differences were measured in the oxide layer composition and morphology [18]. The effect of 1,8-diazabicyclo[5, 4, 0]undec-7-ene (DBU), morpholine and dimethylamine (DMA) to the delay in magnetite to hematite transformation on the steel surfaces was evaluated. All amines significantly reduced the metal dissolution rate and DBU appeared to have the highest metal protection properties.

3.3 Transient generation of deposit precursors

In addition to steady state transport of deposit precursors, plant start-ups result in significant transport of the materials discussed in the previous section. These transient events are believed to be results of the following sequence of events [1]:

- Steady build-up of an accumulation of corrosion products on secondary cycle surfaces.
- Slow release of these products during steady state operation of the plant.
- Loss of retention of corrosion products formed during steady state operation during transients, with the release being directly related to the severity of the transient (maximum release during start-up from cold shutdown). In addition, exposure of corrosion products to air during periods of plant shutdown can change their chemical nature, e.g., conversion to magnetite to hematite.

Studies have shown [1] that over time, start-up transport may represent 40 to 70% of the total corrosion product transport of the plant. A single shutdown is roughly equivalent to a full months operation at 100% power in terms of total corrosion product transport. An additional source of transient deposits is the corrosion product generation during shutdowns.

Copper and iron concentrations in the feedwater, condensate and drain systems after start-ups from extended outages can be several orders of magnitude greater than normal [1]. It has also been demonstrated that the amount of corrosion product that is generated during plant startups is highly dependent plant layout practices. This is because exposing fluid systems to oxygenated water or air during shutdowns results in the formation of rust and corrosion product layers on surfaces which are not as adherent as those produced continually during operation. These loose corrosion product films are thought to be easily dislodged during start-up transient.

4 Deposit formation and behaviour in the steam generator

As discussed previously, a wide variety of impurities including metals and corrosion products, suspended solids, oxygen, ionic and colloidal species transported to steam generator with feedwater, with a small amount formed in situ as a result of steam generator corrosion [1]. Once introduced into steam generator, these deposit precursors will: (1) exit the steam generator with blow-down or the steam, (2) transform or breakdown to simpler compounds by chemical reaction, (3) attach directly on surfaces or combine with other species to form deposits, or (4) hideout in crevices or within pores of existing deposits. The formation and behaviour of deposits in steam generator involve a range of possible physical and chemical phenomena, such as turbulent deposition, boiling deposition, gravitational settling and re-entrainment [19].

Turbulent deposition is the convection of particulate species to surfaces by the turbulent action of the fluid in the steam generators, after which the species

remain attached to the surface as deposit [1]. The particulate species are either those carried into steam generator from the feed and condensate system, or particulate species that grow from dissolved chemical precursors within the steam generator. Boiling deposition occurs due to evaporation of the water primarily on the tube surfaces, which causes concentration and precipitation of the deposit precursors. Gravitational settling is the transport of particulates to horizontal surfaces and is thought to be largely responsible for the formation of sludge piles. Re-entrainment is the liberation of the portions of existing deposits by the scrubbing action of the feedwater or by vigorous hydraulic conditions associated with boiling.

The deposition processes as whole are complex and they occur as function of heat flux, species concentration, time, temperature, fluid velocity, surface chemistry and morphology, and pressure [2]. On deposition phenomena a relatively large amount of data has been reported in the literature and Table 2 contains a summary of the parameters that have been shown to have a role in the deposition of corrosion products and impurities from steam and water.

Table 2: Variables that alter deposition rates on heat transfer surfaces [2].

<p>HEAT FLUX has a major influence on the rate of deposition or corrosion products. Investigators report that deposition rate is proportional to (Heat Flux)ⁿ, where $n = 1 - 5$ depending on the design of the hardware and other factors.</p>
<p>FLUID VELOCITY is a factor that significantly influences the rate of deposition. At low velocities, deposition rate can be high as a result of settling from gravitational forces. At intermediate velocities, enhanced static charges between the particles and the surface can enhance deposition rates. At very high velocities, the deposition rate can be decreased by the shearing force of the fluid.</p>
<p>PARTICLE CONCENTRATION, i.e. the concentration of particulate corrosion products, is a factor that significantly influences deposition rates. A first-order function has been proposed by some investigators. As concentration increases, more collisions between the particles and the heat transfer surfaces will enhance the probability of particles adhering to the surfaces. At very high concentrations, the collisions between particles may result in diminishing effects of increasing concentration.</p>
<p>THE ROLE OF SOLUBLE CORROSION PRODUCT CONCENTRATIONS is not completely understood. A shift in chemical equilibrium would be expected as a result of the deposition of particulate corrosion products and would create additional corrosion products. However, the fraction of soluble corrosion products may shift as a result of reduction in temperature during sample collection.</p>
<p>ZETA-POTENTIAL is the electrostatic attraction of the particles in the feedwater to the internal metal surfaces of the steam generator. The greater the difference in zeta-potential between the moving particles and the stationary metal surfaces, the greater the attraction of the particles to the surfaces.</p>
<p>CHEMICAL TREATMENT (pH AND ELECTROCHEMICAL POTENTIAL) AND IMPURITIES alter the rates of general corrosion and/or erosion of carbon steel and other similar metals and, therefore, alters the rates of deposit accumulations in the steam generators. Morpholine and other “alternate amines” have been shown to reduce the amounts of corrosion product transport and resulting deposition in the steam generators relative to ammonium hydroxide.</p>

<p>TIME is a factor in the rate of deposition; a decreased rate of deposition is expected with increasing time. However, the rate is not expected to diminish to near zero within any practical time.</p>
<p>SURFACE ROUGHNESS has been shown to impact deposition on a microscopic scale. Deposits tend to accumulate in machining and polishing marks. As an example, electropolished surfaces tend to accumulate fewer deposits than the other rougher surfaces.</p>
<p>FLOW AND/OR PRESSURE OSCILLATIONS tend to wash away or redistribute deposits.</p>
<p>PARTICLE SIZE DISTRIBUTION AND AGGLOMERATION OF PARTICLES may alter deposition rates.</p>
<p>SYNTHETIC SLUDGE CHARACTERISTICS are a significant limitation on laboratory testing. Although elemental composition is easy to match in laboratory tests, the ability to match laboratory and field deposits is uncertain with respect to porosity, density, molecular/crystalline structure, particle size, heat transfer coefficient, zeta potential, and surface area.</p>
<p>TUBE SIZE primarily alters fluid velocity and does not need to be considered separately.</p>
<p>TEMPERATURE may be partially accounted for in heat flux, but it is known that heat transfer surfaces have higher rates of deposition than other surfaces at the same temperature.</p>
<p>STEAM QUALITY is not an independent variable and is accounted for in heat flux and velocity; however, most corrosion products tend to deposit below 100% steam quality.</p>

Jevec et. al. comment in their review that table 2 omits more complex, dependent variables, and that the following two variables deserve to be mentioned because of their potential fundamental effect on fouling [2].

- Mode of heat and mass transfer is not an independent variable but depends on flow velocity, temperature, pressure, heat flux, surface properties, etc. Under steam generator operating conditions, the most important regime is that of fully developed nucleate boiling. However, two-phase forced convection and single-phase forced convection are also present. Fouling rates under nucleate boiling conditions are typically substantially higher than those under single-phase forced convection. However, two-phase forced-convective fouling rates can be either higher or lower than those under nucleate boiling, depending on the character of the fouling particle, with potential consequences to fouling rates in the upper tube bundle, broach holes, and steam separators.
- Flow pattern in two-phase flow is not an independent variable, but a function of the properties of water and steam, their flow rates, channel geometry, and flow history. “Elevated” fouling rates have been reported when the content of steam in the steam-water mixture exceeded a threshold of about 35% - 45%. These high fouling rates were associated with “mist” flow pattern.

4.1 Formation of tube scale

The deposition mechanism is different for soluble and particulate oxides [20]. Several theories have been proposed to explain deposition phenomena and in general, they can be divided in two groups [1]:

- Chemical processes involving crystallization from solutions.
- Physical processes which depend on adhesion of solid particles to the surface.

Tube scale formation in steam generators probably involves contribution from both of the phenomena. Chemical deposition involving crystallization can occur in non-boiling, boiling, steaming, or other two phase environments. Soluble iron is deposited on the surfaces when temperature increases and solubility of the iron decreases [20]. Particulate matter is deposited when hydrate shell surrounding particle is removed. Physical deposition involving particle adhesion involves convective transport of particles to the tube surfaces and is influenced by a number of factors [1]:

- Particle size, where particles present in steam generator systems range from 0.1 to 10 μm , with typical sizes in the range of 0.1 to 3 μm . Models of deposition and re-entrainment indicate that particles in the range of 0.1 to 1 μm will result in the formation of heavier deposits, while large particles greater than 10 μm do not appear to have a tendency to contribute to the formation of the scale. Higher molecular weight amines, such as morpholine and ETA, have been shown to produce a greater population of magnetite-based particles in the 0.1 to 0.5 μm range as opposed to larger size particles found in ammonia-based AVT chemistries, where the average particle size is in the range of 1 to 3 μm . This suggests that switching to morpholine or some other amine could result in the formation of thicker tube scale in the steam generator.
- Particle concentration, where deposition rates increase in proportion to the particle concentration, sometimes raised to a power.
- Velocity of the fluid and nature of the surface, with higher deposition rates at higher velocities and greater surface roughness of substrate. However, above a certain velocity, the formation of deposits is hindered or prevented due to re-entrainment of deposit particulates. This critical velocity has been estimated to be on the order of 30 to 60 cm per second.
- Higher deposition in areas with cross flow as opposed to purely axial flow.
- Faster deposition on tubes with higher temperature, such as on the hot leg side of the tube bundle.
- Boiling regime, with nucleate boiling promoting faster rates of deposition compared to film boiling.
- Particle and deposit/substrate charge based on the zeta-potential.
- Fluid pH as the acidity-basicity of the fluid influences the zeta-potential of the particle as well as the deposit surface, and further affects which species are likely to precipitate within the porous structure of the deposits, e.g. hardness species, silicates, iron and nickel-iron oxides.

Regardless of whether tube scale formation is a chemical or physical process (or both) it occurs in several stages including (1) incubation, (2) initiation, (3) growth, (4) growth limiting stage and (5) spalling and re-deposition [2]. The Charlesworth model is the generically accepted model for steam generator deposition presenting the formation processes. The Charlesworth model is shown schematically in Fig. 8. Charlesworth showed that deposit growth is a dynamic process involving both deposition (i.e. scaling and particulate fouling) and release or re-entrainment (i.e. spalling, erosion, and dissolution) mechanisms. This basic concept of deposition and release is the basis for most of the computer codes in use today for sludge deposition.

Work done by AECL [21] introduced an additional factor in the fouling models - ageing or consolidation. Consolidation is the process where particles become chemically bonded to either the heat-transfer surface or to the pre-existing deposit. Deposit that has aged, or become consolidated, is strongly bound to the surface and is therefore not removed by the fluid at an appreciable rate. It has been demonstrated that the process of sludge consolidation involves the precipitation or recrystallization of solid material within the pores of the sludge deposit [22]. The mechanisms proposed for consolidation include Ostwald ripening, dissolution and re-precipitation of corrosion product in a temperature gradient, and boiling induced precipitation of dissolved species.

Ostwald ripening is the process where smaller particles or crystals dissolve and re-precipitate onto the surfaces of larger ones [2]. This process is thermodynamically favoured because it is accompanied by a reduction in surface area and, therefore, of surface energy. Deposit, which resides in a temperature gradient, is subject to consolidation by dissolution and re-precipitation. The temperature gradient gives rise to a solubility gradient, which results in a material being transported from a region of higher solubility to one of lower solubility, with a corresponding reduction of porosity and increase in deposit strength.

The third mechanism proposed for consolidation is the boiling-induced precipitation [2]. It is due to the evaporation of water on the heat transfer surface (e.g., the “microlayer” evaporation), which leaves residues of dissolved species and very small particulates acting as a cement for the larger particles.

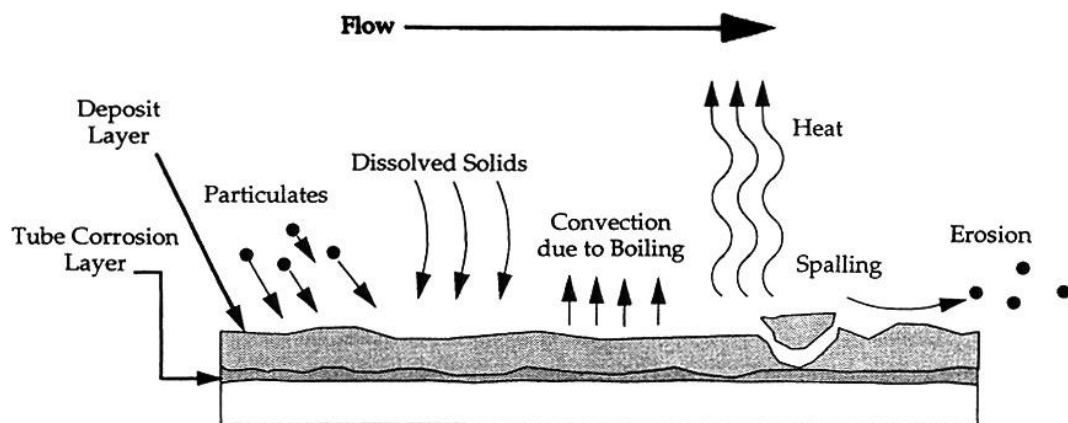


Figure 8: Schematic of the deposition and release mechanisms for the Charlesworth fouling model [2].

Ostwald ripening is the only consolidation mechanism that is active on unheated surfaces [2]. Ostwald ripening and dissolution /re-precipitation take place under forced convective heat transfer and are potentially active under nucleate boiling as well as boiling induced precipitation.

The basic premise of the AECL model is that once consolidation occurs, re-entrainment cannot readily occur (Fig. 9) [21].

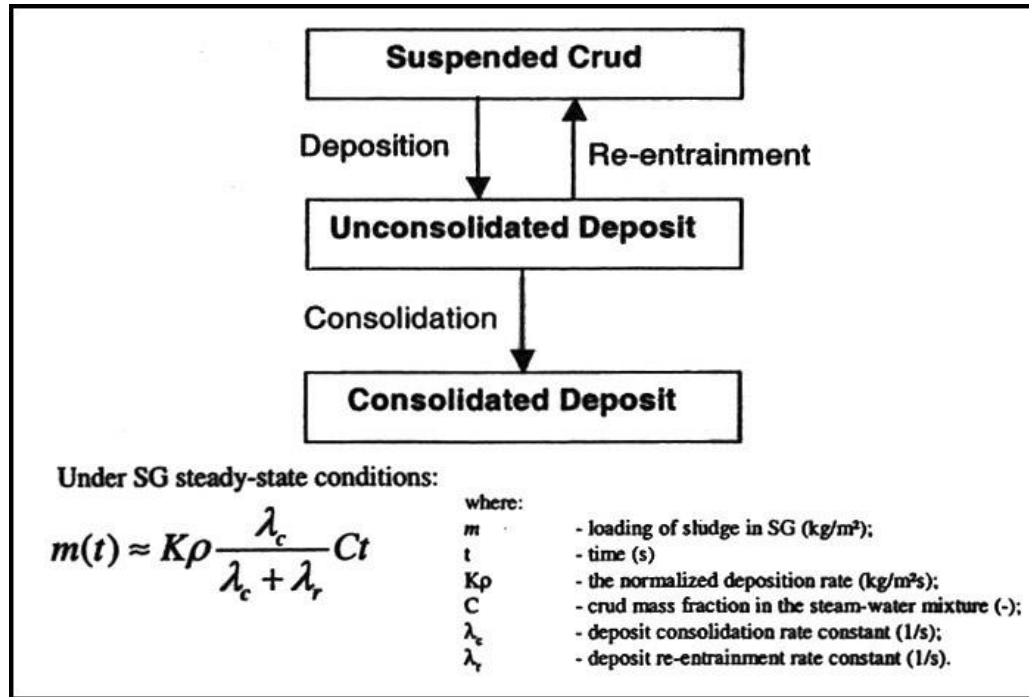
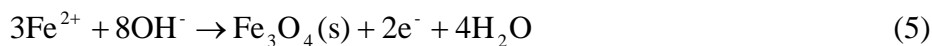


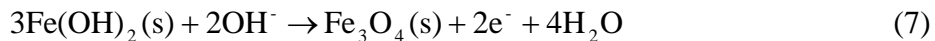
Figure 9: Flowchart of the AECL fouling model [21].

Also the ratio of particulate to dissolved iron can be important to deposit formation and consolidation. Dissolved iron can work as a binder of the transported particulate oxides [2]. King et. al. [4] measured normalized fouling rates by dissolved iron and fresh ferrous precipitates and found values very high, between 0.01 and 0.6 kg/m²s. Klimas et. al. [23] also observed fouling rates between 0.03 and 0.5 kg/m²s for dissolved iron and fresh ferrous precipitates. Observed fouling rates were approximately two orders of magnitude higher than those for pre-formed magnetite particles (0.2 - 0.5 μm diameter) at similar concentrations.

For fouling from dissolved ferrous species under SG conditions, a redox reaction is likely to take place to convert the dissolved ferrous species into magnetite [5]. Fouling by dissolved iron is a reverse of the reaction in Eq. 5, e.g., under alkaline and reducing conditions:



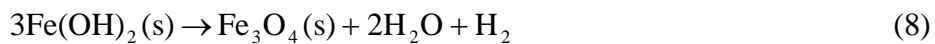
The concentration of Fe²⁺ in equilibrium with magnetite is expected to depend on the solution pH and the surface potential (and temperature). However, one cannot exclude fouling by a sequence of Eq. 6 and 7.



Thus, fouling by dissolved ferrous species is, in principle, an electrochemical process, because it can generally involve transfer of charge across an electrified interface and an electron transfer. The driving force for fouling (the supersaturation at the surface) may depend on the potential of the fouling substrate; however, the fouling rate by dissolved iron does not have to depend on the substrate potential for kinetic reasons (for example, it may be governed by the rate of transport of ferrous species to the surface).

4.2 Formation of sludge piles

Sludge piles form on horizontal surfaces in steam generators due to the gravitational settling, entrapment and consolidation of particulate and chemical species from the feedwater [1]. Sludge pile integrity is thought to be maintained and improved by reactions among the sludge pile species or by chemical reactions with dissolved species that tend to consolidate the sludge pile matrix. Two examples of such consolidations are: (1) the cementation of iron oxide particles such as magnetite by ferrous hydroxides according to the Schikorr reaction (Eq. 8), and (2) the reaction between the dissolved iron species or magnetite and phosphate to form sodium iron phosphate.



Sludge piles form in regions where the fluid velocities are lowest [19]. The piles tend to be much more predominant on the hot leg side of the tube bundle. In simplest terms, a deposit particle is able to settle to a horizontal surface, if its terminal settling velocity, as dictated by the force of gravity on the particle (its weight), can overcome the imposed velocity due to convective transport away from the horizontal surface. However, analyses of steam generator fluid mechanics have shown that sludge pile formation is actually more complex phenomenon that is governed by [1].

- Gravitational settling of particles with diameters approximately 10 μm or greater. These particles are supplied to the surface from a thin layer of fluid above grooving sludge pile which is replenished with particulates from the well-mixed bulk fluid above.
- Chance incorporation of particles into sludge pile which can be predicted by use of "sticking probabilities" which are function of physical effects and chemical reactions between and among the particles and the sludge pile surface.
- Continual re-entrainment of particles due turbulent bursts at the pile surface.

Each of the above processes in itself involves complex chemical and physical phenomena. The principal conclusions of several computer modelling efforts which have attempted to predict formation of sludge piles have been as follows [1].

- The growth of the sludge pile is not self limiting; that is the piles will continue to grow through the life of the plant and therefore should be periodically reduced in size by means such as sludge lancing.
- The size of the sludge pile as dictated by its rate of growth can be greatly reduced by increasing the fluid velocity from 30 to 60 cm/s to greater than 90 cm/s.

Calculations of settling velocity and settling mass flux of particles of variable diameter suggests that if sludge piles are not held in place by inter-particle attraction or some other means of consolidation, the minimum particle size of the material in the piles would have to be between 10 and 20 μm in diameter [1]. This is seven to twenty times the diameter of the particulates measured in the feedwater, which are typically 0.25 to 1 μm . This analysis suggests that for particles to settle on horizontal surfaces, they must either grow within the steam generator, or individual particles must coalesce or agglomerate to a point where they have sufficient weight to settle out of the feed water flow.

Summarizing it would appear probable that for sludge piles to form, several processes must take place [1].

- The small diameter iron oxide particles which enter the steam generator grow, coalesce or agglomerate to form, heavier, larger groups which have sufficient weight to settle to the tube sheet sludge pile.
- Having arrived at the sludge pile, the agglomerated particles fuse with the pile by chemical reaction or some other means thereby promoting growth of the pile over time.
- Whether or not an individual particle which comes in contact with the sludge pile surface tends to stick or be re-entrained is likely to be related to the specific morphology and size of the particle in question.

5 Copper in steam generator deposits

Although SG deposits typically consist mostly of iron oxide (generally magnetite, Fe_3O_4), metallic copper is often a significant constituent species. Copper is found in the deposits of corrosion products in all nuclear power plants [20, 24]. Copper in the deposits encourages pitting corrosion on the outer surfaces of the steam-generator pipes [25]. Following observations are made from SG deposits [26]:

- Deposits contain >85% by weight magnetite.
- Deposits contain ~5% by weight metallic copper.
- Even in nominally “copper-free” plants, copper can account for ~0.3% by weight of the deposits.

- Copper can account for as much as 50% by weight of the deposits in some PWR steam generators.
- Copper in deposits is generally found as copper metal, but minor amounts of cuprite (Cu_2O) and tenorite (CuO) have also been found.

Average amount of iron and copper compounds washed from 46 steam generators of VVER-1000 and VVER-400 reactors was 1288 kg [24]. The deposits contained on the average 27% copper. The ratio of copper and iron compounds varies between NPP and general trend is that those units which have operated longer have higher amount of copper compounds in the corrosion products. The main-sources of copper entering to the steam generators at VVER-1000 and VVER-400 reactors secondary loops are the low-pressure heaters.

As mentioned, copper tends to be found in scale as metallic inclusions, which appear close to the tube scale-tube wall interface [1, 26]. This is consistent with a fact that the solubility of the copper $\text{Cu}(\text{OH})^+$ or as an amine complex is much larger than that of iron species. Accordingly, copper would not precipitate or crystallize along the tube wall, but would at the base of the scale near the boiling interface. Also solid phase diffusion coefficients for copper are typically large in comparison to those of other metallic species. Copper ions in solution could be: (1) crystallizing preferentially on existing copper metal sites since the lattice parameter and energy of adsorption/crystallization is much lower than that associated with the formation of copper-iron-oxide spinels, which are rarely seen in tube deposits or (2) precipitating on the magnetite based scale and diffusing in the solid phase until arrival at a local inclusion. Cu^{2+} may also contribute to the hardness of the tube scale since Cu^{2+} has been found to produce hard sludge pile deposits while Cu^+ does not.

Events of transient periods might affect the copper in deposits and Marks and Varrin [26] have presented a qualitative working hypothesis of the effects of shutdown, layup and startup (SLS) on SG chemistry. The hypothesis postulates four steps.

1. During normal operation, some corrosion in the secondary water loop occurs, introducing dissolved metal into the feedwater in minute quantities.
2. Normal operation of the SG concentrates these metal ions, forcing precipitation of metal and oxides in the SG.
3. During SLS, the deposits in the SG are oxidized and serve as an oxygen reservoir, and oxides are also formed in other parts of the secondary system.
4. During the initial phases of operation, these oxides—together with oxides introduced from the secondary plant by the feedwater—are reduced, either by directly oxidizing the metal of the SG tubes or through introduction of oxygen into the SG secondary bulk via various possible reactions.

A flow diagram showing the sequence of events postulated in this hypothesis is shown in Figure 10.

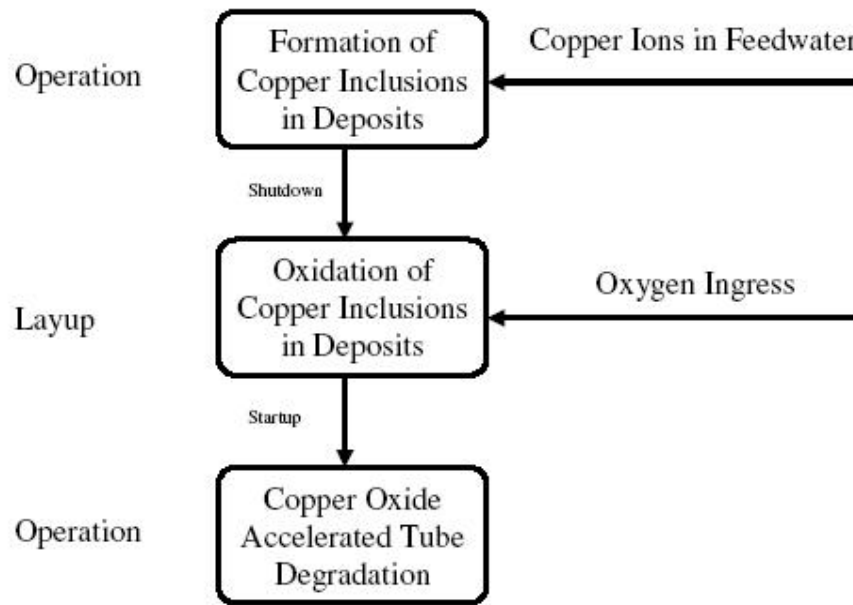


Figure 10: Copper deposition and oxidation in transient situations [26].

5.1 Copper oxide formation and stability

Copper forms two common oxides (Cu_2O - cuprous oxide and CuO - cupric oxide) and one common hydroxide ($\text{Cu}(\text{OH})_2$ - cupric hydroxide) in aqueous feedwater environments. Numerous studies have shown that the passive film on copper (alloys) is a bilayer structure comprising an inner defective Cu_2O layer that grows into the metal, and an outer $\text{Cu}(\text{OH})_2$ or CuO layer that incorporates species from the solution.

The oxide formation process on copper alloys in feedwater environments initiates with the oxidation of metallic copper to cuprous oxide (Eq. 9 and 10) by the following possible reactions [27].



Eq. 9 is thermodynamically favourable at 25°C ; the thermodynamic feasibility of Eq. 10 is questioned by some investigators and is rarely cited as the predominant corrosion reaction.

Cuprous oxide formed as a result of Eq. 9 and 10 may be further oxidized to cupric oxide [27].



Again reaction (11) is questioned by some workers and is rarely cited as the predominant corrosion reaction. It is appropriate to consider the possibility that cupric hydroxide $[\text{Cu}(\text{OH})_2]$, another valence 2 compound, will form instead of cupric oxide.

The conversion of $\text{Cu}(\text{OH})_2$ to CuO can be described by the Eq. 13.



At the temperatures of condensate and feedwater train ($<200\text{ }^\circ\text{C}$), the standard Gibbs energy is negative, showing that CuO is stable relative to $\text{Cu}(\text{OH})_2$ [27]. Thus, at feedwater temperature, $\text{Cu}(\text{OH})_2$ is not stable relative to CuO . This is important because it implies that any $\text{Cu}(\text{OH})_2$ that is observed in contact with the feedwater cannot form by the hydration of CuO , but must form from a less stable species (such as Cu^{2+} , Cu^+ , or possibly Cu_2O , depending on the specific conditions).

When oxygen concentrations are high enough, both Cu_2O and CuO will form on a copper or copper alloy surface [27]. The proportion of cupric oxide present increases with the distance from the base metal. For feedwater conditions within typical guidelines (Table 3), (reducing conditions, low oxygen, oxygen scavenger/reducing agent, proper pH range) the oxide layer has been observed to consist mainly of cuprous oxide. However, when cycle conditions are changed by allowing oxidizing conditions ($\text{ORP} > 0\text{ mV}$) to exist by eliminating the oxygen scavenger or because of air-inleakage, then the proportion of cupric oxide in the outer layers increases. There is a concomitant increase in the amount of porosity, which facilitates the mechanical disruption and release of the CuO into the feedwater.

Table 3: Normal Cycle Chemistry Limits at the Economizer Inlet for Units with Mixed-Metallurgy Feedwater Systems [27].

<u>Cycle Chemistry Parameter</u>	<u>AVT Mixed-Metallurgy</u>
pH	8.8 - 9.1
Ammonia, NH_3 , ppm	0.15 - 0.4
Cation Conductivity, $\mu\text{S}/\text{cm}$	< 0.2
Fe, ppb	< 5 (<5)*
Cu, ppb	< 2 (<2)*
Oxygen, ppb	< 5 (<2)*

*Values in parenthesis represent the achievable and desirable limits. These values are achieved on mixed metallurgy units without any copper problem.

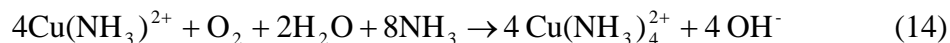
In general, the surface oxide layer found on copper and its alloys tends to be less stable, less passive, and less protective than the iron oxide films found on ferrous alloys [27]. Destabilization of the copper oxide film involves both chemical and physical/mechanical processes. Both cuprous and cupric oxides are subject to dissolution, with higher solubility noted for the latter, at least under reducing chemical conditions. However, as already noted, CuO predominates under oxidizing conditions and the solubility of CuO under such conditions appears to be lower than the solubility of Cu_2O under reducing conditions. Nevertheless,

solubility does not necessarily control release rate, so care is needed in interpreting this information. Mechanical strain present in the oxide layer renders it subject to fracturing as distance from the parent metal increases. As a consequence of these processes, the diffusion rate of copper increases, leading to higher release rates. Porous oxide layers will be subject to high rates of corrosion, while tighter layers will restrain corrosion and release of copper to the feedwater.

Typically, approaches to minimize copper corrosion and release have focused on control of those species known to promote dissolution of metallic copper [27]. Under reducing chemistry conditions, the process is generally expected to consist of two steps, oxidation of copper and production of copper ions. Dissolved oxygen in the water serves as the oxidant while ammonia and, perhaps, certain neutralizing amines, serve to form stable complexes with copper ions. Complexes are distributed in secondary water system due to high solubility [25].

This concept is supported by research which demonstrates that the principal cathodic reaction for copper alloys in solutions containing ammonia is cupric ion reduction, although dissolved oxygen or ferric iron will also serve as cathodic depolarizers [27]. It should be noted, however, that the presence of ferric ion and cupric ion in mixed metallurgy systems invariably implies the presence of oxygen, although the possibility that hydrogen evolution becomes a viable cathodic reaction must also be recognized.

Initially, in the absence of cupric ion, copper corrodes at a slow rate that is governed by the kinetics of oxygen reduction [27]. The cuprous ion in solution is then complexed by ammonia to form $\text{Cu}(\text{NH}_3)^{2+}$ which, in turn, reacts with oxygen to form the cupric complex ion according to Eq. 14.



This reaction of oxygen with the cuprous complex ion in the bulk occurs much more rapidly than reaction of oxygen at the metal surface because the bulk reaction is homogeneous in nature (i.e., it occurs uniformly throughout the solution) while the reaction at the metal surface is heterogeneous. When sufficient quantities of the cupric complex ion are generated, they become the primary oxidizing species and rapidly accelerate corrosion of susceptible copper-base alloys with the concomitant production of cuprous complex ions, $\text{Cu}(\text{NH}_3)^{2+}$. These reduced species are then regenerated by oxygen in the solution and thus the dissolution process is autocatalytic in the presence of oxygen.

5.2 Factors influencing copper corrosion and release activity

As indicated above, corrosion of copper and its alloys is strongly influenced by the presence of dissolved oxygen and ammonia in solution. However, the body of research available indicates that several other factors are also important. The interaction of all these factors is not fully understood [27].

Effect of Oxygen

Most published laboratory investigations and field research indicate increasing rates of metal release from brasses and copper-nickel alloys as oxygen concentration is increased from <30 ppb to 100-500 ppb [27].

The various research studies and field investigations show that oxygen is an important but not necessarily dominant factor in the corrosion of copper alloys [27]. However, they also indicate the complexity of the situation and identify other factors which will affect rates of copper corrosion and release under fossil plant operating conditions. In a properly operated unit, these would appear to include pH (or concentration of additive applied for pH control), presence and concentration of oxygen scavenger, service temperature, and feedwater velocity. The effect of a selected feedwater condition will be different for each copper alloy to which it is applied. Corrosion/release rates would be affected further during periods of dissolved solids contamination which occur when the condenser leaks.

Oxygen scavengers appear to be beneficial since they react with dissolved oxygen and establish a reducing environment which has been shown to reduce copper corrosion/release rates under some laboratory and field conditions [27].

Effect of pH

In many plants feedwater pH is controlled by addition of ammonia or neutralizing amines. Other species which, if present, will influence feedwater pH include carbon dioxide (present as a consequence of condenser air inleakage), oxygen scavengers, and organics (present in the treated makeup or as breakdown products of proprietary treatment chemicals). Laboratory investigations of copper alloy corrosion typically control pH with ammonia or an amine. The other influencing species are either assessed individually or excluded entirely. The opposite situation exists in the power plant, where all species may be present but are less effectively controlled and may not be measured.

As indicated in Fig. 11, corrosion/release rates for copper alloys appear to decrease and then increase over the pH range of 5 to 10 [27]. The pH at which corrosion is minimal appears to fall between pH values of 8.0 and 9.0, but is sensitive to temperature and possibly to other factors.

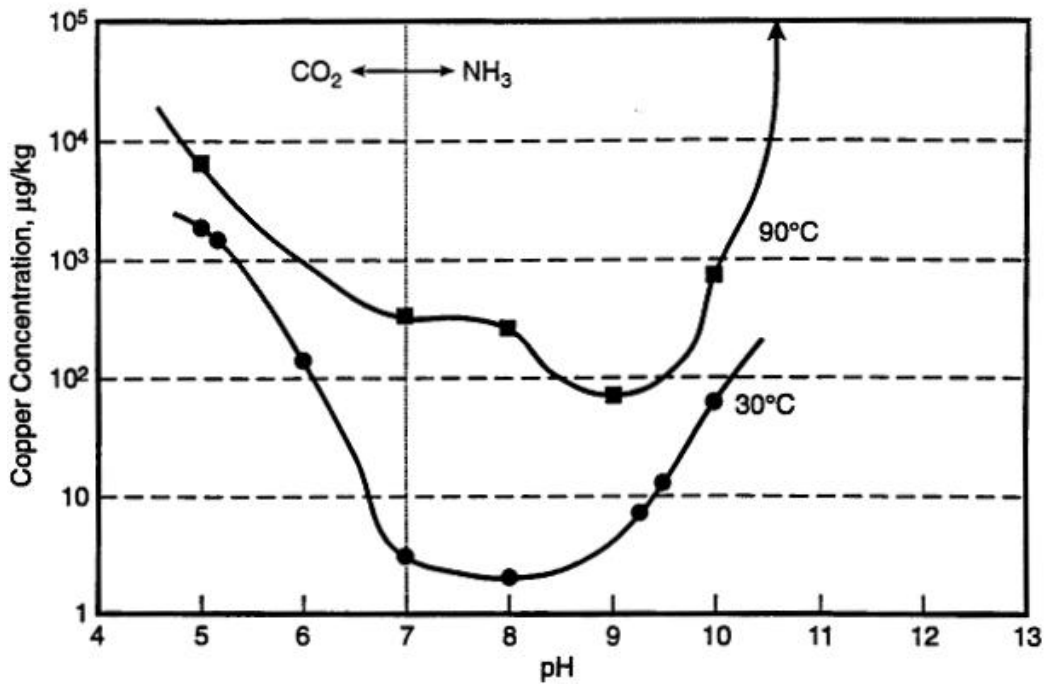


Figure 11: Effect of pH on Copper Release Rate From 71Cu/28Zn/Sn (SoMs-71 brass, or Admiralty brass) Exposed to Water Containing Carbon Dioxide (for pH < 7) or ammonia (for pH > 7) at Temperatures of 30°C and 90°C [27].

Copper release rates for feedwater treated with neutralizing amines would probably be different than for feedwater dosed with ammonia due to presumed differences in copper complexing abilities, which are not well defined [27]. Copper-cyclohexylamine complexes tend to precipitate from solution which may form a protective film on the base metal. Laboratory evaluations have shown that copper release rates increase following a change from cyclohexylamine to ammonia; whereas the release remained stable when switching from ammonia to cyclohexylamine. Use of volatile neutralizing amines instead of ammonia to control condensate and feedwater pH is sometimes implemented to control corrosion of copper alloys. This strategy has failed in virtually every case where no effort was made to improve dissolved oxygen control. Although some amines exhibit better thermal stability than others, in-service degradation of these treatments will produce some ammonia in addition to other breakdown products, including carbon dioxide and organic acids. Another concern is the tendency of some amines to liberate pre-existing deposits. As a precaution, system cleanliness should always be evaluated as part of efforts to consider any proposed change in feedwater treatment.

Effect of Temperature

Generally, rates of copper alloy corrosion and release increase as temperature is elevated. A Japanese study of various copper-nickel alloys (Fig. 12) indicates also this result, with the influence of temperature becoming relatively minor as nickel levels increased.

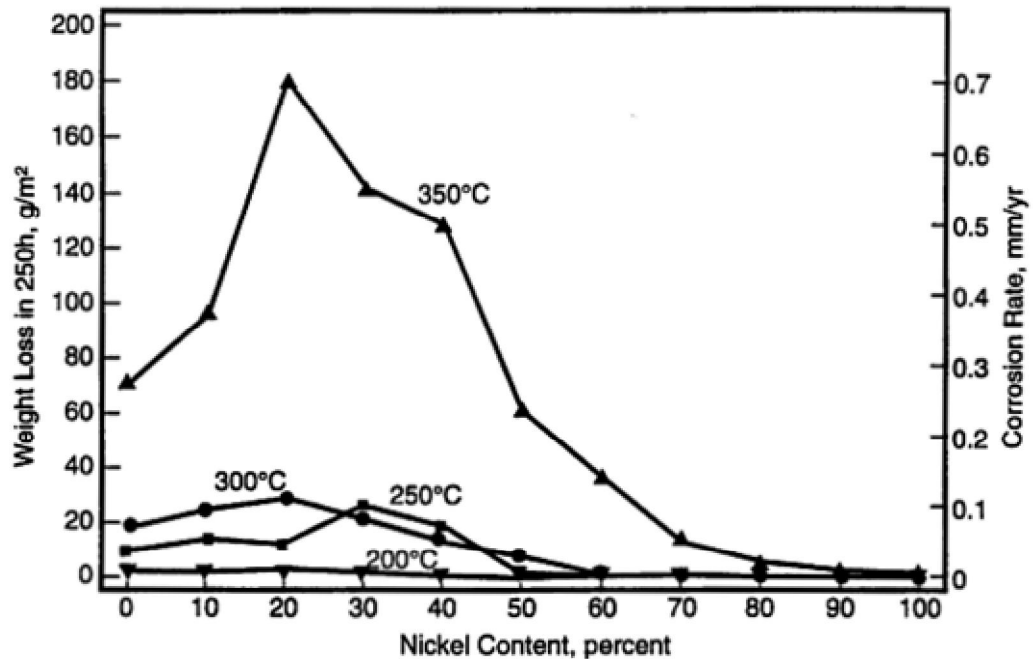


Figure 12: Effect of Nickel Content (0-100%) and Temperature (200° to 350°C) on the Corrosion Rate of Copper-Nickel Alloys Exposed for 250 Hours to Oxygen-Bearing Water Under Saturated Pressure Conditions [27].

6 Removing deposits and sludge from the steam generators

As stated in earlier, there are several means to reduce the deposit formation. Demineralizers and good feedwater quality can decrease sludge build-up by a factor of 2-10 [3]. Increasing the pH of the feedwater in all-ferrous systems can also reduce iron carry to steam generators by one third. However, deposits and sludge can still accumulate over time and cleaning of SG is needed to reduce problems associated to them. There are several chemical and mechanical ways to remove sludge from the steam generator. Mechanical techniques are more common but chemical cleaning can be good option when more thorough cleaning is needed.

6.1 Chemical cleaning of the steam generator

Chemical cleaning is efficient technique if steam generator has to be completely cleaned [28]. It can be used for restoring the heat flux on the tube surfaces. However, NPP are unwilling to perform chemical cleaning for a number of reasons such as cost of cleaning, undesired waste and possible corrosion of SG during chemical cleaning. The goal of chemical cleaning is to maximize the dissolution of deposits and simultaneously minimize the corrosion of steam generator materials. Chemical cleaning is the most effective of the deposit removal techniques but it is also most expensive [1]. Off-line cleaning is done during scheduled outages. On-line cleaning can be done during shutdown or start-

up when chemical solutions can be heated with the primary to secondary side heat transfer.

Chemical cleaning can be done in low temperature, 93 °C, with 10-20% ethylenediaminetetra-acetic acid (EDTA), hydrazine and corrosion inhibitor at pH 7 [29, 30]. At high temperature, above 140 °C, formula contains 2-6% nitriloacetic acid (NTA) or EDTA and hydrazine at pH 9.5. Higher temperature has been found to accelerate magnetite deposit dissolution. Hydrazine effects on the dissolution of the magnetite and corrosion rate of materials. Small amounts (1%) of hydrazine reduce ferric ions which decrease corrosion of the base material and simultaneously dissolution of magnetite increases. Higher concentration of hydrazine increases corrosion of the materials but doesn't increase deposit removal rate. Corrosion inhibitor in the solution doesn't have effect on the dissolution rate of the magnetite but decreases corrosion rate.

Rufus et al studied different formulations for iron and copper oxide deposit removals using real deposits and synthetic oxides [30]. Formulations containing EDTA, hydrazine and pH additives were used for dissolving oxides of iron. This formulation can only dissolve copper that exists as cupric oxide or cuprous oxide. In the presence of a carbon steel surface a part of the copper that was dissolved will be plated out on the carbon steel surface according to Eq. 15.



Dissolution of copper and its oxides are done at high pH with complexing chemical and oxidizing environment [30]. Oxidizer can be air, oxygen or hydrogen peroxide. With air dissolved oxygen concentration is low compared to oxygen. Hydrogen peroxide was found to be the best oxidizing agent for the dissolving of copper and its oxides. Nickel dissolving was found to be slow when compared to iron and copper. Some calcium and magnesium silicates can remain undissolved from the surfaces after chemical cleaning.

6.2 Mechanical cleaning of the steam generator

The three most common mechanical methods for removal of sludge from the steam generators are blowdown, gas pressure and lancing [3]. The blowdown method usually removes only sludge that exists as suspended particles and is ineffective at removing hardened sludge. It is used only for recirculating steam generators and uses draining system built into the steam generator.

Two gas pressure methods utilize quick acting valves which release nitrogen below the water surface at approximately 60 bar pressure [3]. Violent displacement of water with gas flushes and dislodges deposits. Deposits removed from the steam generator are extracted using filters or special draining procedures.

Sludge-lancing uses high-pressure water jets to remove sludge from steam generator [3]. In this method device with water nozzles is inserted in to the steam generator through inspection ports and high-pressure jets of water are used to dislodge the sludge. Sludge-water mixture is pumped out from the steam

generator and filtered to remove suspended sludge particles. Sludge-lancing can remove soft and some sticky sludge from the steam generators. Consolidated sludge may be difficult to remove with lancing techniques. Tube sheet lancing technique has also been extended to reach locations higher in the tube bundle [1].

7 Conclusions

Deposit formation on the PWR steam generator is costly problem, which has been extensively studied, according to literature survey. However, due to the complex nature of the fouling, there are still open questions related to the mechanisms of deposit formation. Especially problematic situation is in the facilities that have copper compounds in the secondary cycle that limits the possibility to increase water pH. The most interesting topic for further research is the role of different amines on the flow-accelerated corrosion and deposit formation.

8 Summary

Fouling in the steam generators of pressurized water reactors can cause significant inconvenience at the nuclear power plants. Accumulation of deposits can lead to corrosion problems, reduce heat transfer and cause tube plugging and flow problems. Secondary-side water chemistry has developed from phosphate-based treatment to all-volatile water treatment, which is based on the use of ammonia and hydrazine. Over the past 10 years, nuclear plants have also used advanced amines to reduce corrosion and deposit precursor formation.

Deposits are formed mainly from corrosion products that are transported from the secondary-cycle. Iron oxides are the primary component in the deposits but they may contain significant proportions of copper and copper oxides depending on the construction materials of the secondary-cycle. Soluble species, such as silicates and sulphates, can concentrate and precipitate within deposits.

Flow-accelerated corrosion (FAC) on the secondary-cycle is the main source of the iron deposit precursors. On the FAC magnetite layer becomes thin due to enhanced dissolving at the high flow and turbulence. FAC occurs at alkalinized and deaerated water. Temperature and pH have significant effect on the FAC, but may be difficult to change in operating plant. Using advanced amines can alleviate FAC, but some amines can be fouling enhancers.

The formation of deposits and sludge in the steam generator involve a range of possible physical and chemical phenomena such as turbulent deposition, boiling deposition, gravitational settling and re-entrainment. The deposition process is complex phenomena where multiple factors affect to deposit formation rate. Formed deposits and sludge can be removed from the steam generator by chemical and mechanical means.

References

1. Varrin, R., Characterization of PWR Steam Generator Deposits, EPRI, Palo Alto CA, 1996. TR-106048.
2. Jevec, J.M., Klimas, S.J., King, P., Fruzzetti, K., Multivariable Assessment of Flow Accelerated Corrosion and Steam Generator Fouling: Literature Review, EPRI, Palo Alto, CA: 2003. 1003619.
3. Green, S. J., Hetsroni, G., PWR steam generators, *Int. J. Multiphase Flow*, 21 (1995) 1-97.
4. King, P. and Jevec, J. M., Multivariable Assessment of Flow-Accelerated Corrosion and Steam Generator Fouling: Loop Tests to Investigate the Role of Dissolved Iron in Steam Generator Fouling. EPRI, Palo Alto, CA: 2006. 1013383.
5. Patel, B., Investigation of steam generator corrosion products under typical operating conditions, EPRI report NP-3068, May 1984.
6. Flow-Accelerated Corrosion in Power Plants, EPRI, Palo Alto, CA: 1998, TR-106611R1.
7. Laronge, T.M. and Ward, M.A., "The Basics and Not so Basics of Water Corrosion Processes Altered by Flow Changes," CORROSION/99, paper 99345, NACE International, Houston, TX, (1999).
8. Pavageau, E.M., Effect of Hydrazine on Flow Accelerated Corrosion, EPRI, Palo Alto, CA, and EDF Electricité de France, Moret Sur Loing, France: 2005. 1008208.
9. De Bouvier, O., Effect of Redox Conditions on Flow Accelerated Corrosion: Influence of Hydrazine and Oxygen, November 2002. EPRI Report 1002768.
10. Dooley, R.B. and Chexal, V.K., "Flow-Accelerated Corrosion," CORROSION/99, paper 99347, NACE International, Houston, TX (1999).
11. Dooley, R.B., Flow-Accelerated Corrosion in Fossil and Combined Cycle/HRSG Plants, *Power Plant Chemistry*, 2008 vol.10 (2), s. 68-86.
12. Bouchacourt, M., "Impact of Water Chemistry on Corrosion-Erosion in One-Phase and Two-Phase Flow," *Proceedings of water Chemistry in Nuclear Reactor Systems 5*, BNES, London, 1989 p.135.
13. Schwartz, T., Heat transfer and fouling behaviour of Siemens PWR steam generator - long-term operating experience, *Exp. Therm Fluid Sci.* 25 (2001) 319-327.
14. Advanced Amine Application Guidelines, EPRI, Palo Alto, CA: 1993, TR-102952.
15. Effects of Alternate pH Control Additives on PWR Secondary Cycle Chemistry, EPRI, Palo Alto, CA: 1988, NP-5594.
16. Klimas, S.J., Guzonas, D., Turner, C.W: and Fruzzetti, K., Identification and Testing of Amines for Steam Generator Chemistry and Deposit Control, EPRI, Palo Alto, CA and Atomic Energy of Canada Limited, Chalk River, Ontario, Canada: 2002. 1002773.
17. Bénézeth, P., Wesolowski, D. J., Palmer, D. a., Machesky, M. L., Effect of amines on the surface charge properties of iron oxides, *J. Solution Chem* 38 (2009) 925-945.
18. Nasrazadani, S., Diaz, J., Stevens, J., Theimer, R., Effects of DBU, morpholine, and DMA on corrosion of low carbon steel exposed to steam, *Corros. Sci.* 49 (2007) 3024-3039.

19. Srikantiah, G., Chappidi, P. R., Particle deposition and fouling in PWR steam generators, *Nucl. Eng. Des.* 200 (2000) 285-294.
20. Oleinik, s. G., Effect of the quantity, composition, and thickness of deposits on the damage to the pipes of steam generators in nuclear power plants with VVÉR reactors, *At. Energ.* 96 (2004) 228-233.
21. Identification and Testing of Amines for Steam Generator Chemistry and Deposit Control, EPRI, Palo Alto, CA and Atomic Energy of Canada Limited, Chalk River, Ontario, Canada: 2002.1002773.
22. C.W. Turner, M.E. Blimkie, P.A. Lavoie, "Physical and Chemical Factors Affecting Sludge Consolidation," Report AECL-11674/COG-96-492-1, Atomic Energy of Canada Ltd., Chalk River, Ontario (1997).
23. Klimas, S.J Strati, G.L., Balkrishnan, B.V: and Fruzzetti, K Identification and Testing of Amines for Steam Generator Chemistry and Deposit Control: Part 2, EPRI, Palo Alto, CA, and Atomic Energy of Canada Limited, Chalk River, Ontario, Canada:2003. 1003624.
24. Oleinik, s. G., Influence of various factors on damage to steam-generator tubes in nuclear power plants with VVÉR reactors, *At. Energ.* 96 (2004) 399-402.
25. Parfenov, V. V., Gorbatykh, V. P., Kinetics of pitting formation in the presence of copper in deposits, *Ther. Eng.* 53 (2006) 1017-1020.
26. Marks, C. and Varrin, R. Jr., Oxidation and Reduction of Copper in Steam Generator Deposits: Under Shutdown, Layup and Startup Conditions, EPRI, Palo Alto, CA: 2000. 1001204.
27. R. B. Dooley, B. C. Syrett, T. H. McCloskey, J. Tsou, K. J. Shields, D. D. Macdonald, State-of-Knowledge of Copper in Fossil Plant Cycles, EPRI, Palo Alto, CA, 1997, TR-108460.
28. Nordmann, F., Fiquet, J.-M., Selection criteria for the best secondary water chemistry, *Nucl. Eng. Des.* 160 (1996) 193-201.
29. Hur, D. H., Choi, M. S., Chung, H. S., Kim, U. C., Optimum EDTA solvent chemistry for iron oxide removal at 150 °C, *J. Nucl. Mater.* 305 (2002) 220-223.
30. Rufus, A. L., Sathyaseelan, V. S., Srinivasan, M. P., Kumar, P. S., Veena, S. N., Velmurugan, S., Narasimhan, S. V., Chemistry aspects pertaining to the application of steam generator chemical cleaning formaultion based on ethylene diamine tetra acetic acid, *Prog. Nucl. Energy* 39 (2001) 285-303.