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Thermal-Hydraulics and Electrochemistry of a Boiling Solution in a Porous Sludge Pile A Test Methodology

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Abstract

When boiling occurs in a pile of porous corrosion products (sludge), chemical species can concentrate. These species can react with the corrosion products and transform the sludge into a rock hard mass and/or create a corrosive environment. In-situ measurements are required to improve the understanding of this process, and the thermal-hydraulic and electrochemical environment in the pile. A test method is described that utilizes a water heated instrumented tube array in an autoclave to perform the in-situ measurements. As a proof of method feasibility, tests were performed in an alkaline phosphate solution. The test data is discussed. Temperature changes and electrochemical potential shifts were used to indicate when chemicals concentrate and if/when the pile hardens. Post-test examinations confirmed hardening occurred. Experiments were performed to reverse the hardening process. A one-dimensional model, utilizing capillary forces, was developed to understand the thermal-hydraulic measurements.

Introduction

Condensate and feed system corrosion products can accumulate on heat exchanger shellside surfaces such as tube support plates and tube sheets forming a sludge pile. During boiling, chemicals in the water concentrate in the porous sludge piles. These chemicals can react with the corrosion products and transform the sludge into a rock-hard mass. The concentrated chemicals can also create a corrosive environment, leading to intergranular attack, stress corrosion cracking or pitting of the tubing material. Some pressurized water reactor (PWR) steam generators have experienced tubing corrosion in the sludge pile. Previous experimental studies of sludge pile thermal-hydraulic and concentration mechanisms [1, 2] have been performed with either granular sludge from operating plants or with synthetic simulated sludges. Both types had relatively high porosity (35-70%). The synthetic sludges were inert, while some of the plant sludges underwent partial physical and chemical changes during the test period. A thorough review of the thermal effects of deposits and the mass transfer processes in deposits is provided in [3].

In-situ measurements are required to improve the understanding of the environment in the pile. A test methodology has been developed to perform these measurements. It utilizes instrumented tube arrays to investigate (1) the thermal-hydraulic conditions that concentrate chemicals, (2) the location of the concentration zone, (3) when hard sludge formation occurs, (4) the sludge hardening mechanism and (5) methods to soften the hard pile. A discussion of the test method is provided below. The test results are discussed in the sequence the data was taken. Some examples of the data are presented.

Experimental Methods

Equipment

Testing was performed in an 8 liter autoclave that contained two heat transfer test arrays. Each array consisted of three 0.50 inch diameter stainless steel tubes on a 0.75 inch triangular pitch. The tubes were connected by common manifolds at the tops and bottoms of the array. The bottom manifolds were orificed to ensure that the heating fluid (water) was distributed uniformly between each tube. An electric heater was used to heat the fluid. The flow rate was controlled by a pump and several control valves. Since each tube had the same inlet temperature and flow, the heat transferred through each tube to the shellside water was approximately the same. The heat transfer rate was determined by the steam flow from the autoclave, which was controlled by a condensate flow valve and flowmeter. The condensate was stored in a feed tank and pumped back into the autoclave. The feed rate was determined by the secondary water level controller, which maintained a constant water level in the autoclave. A heat exchanger was provided to heat the feed water. A computer model was developed to determine the open tube surface heat flux and

the shellside tube wall temperature at any tube elevation. Each array had a sludge basket with leak-tight seams to ensure water entered and steam left only from the top of the basket. A schematic picture of the test array and autoclave is shown in Figure 1.

Environment

The chemistry tested was a low concentration alkaline phosphate solution, although the methodology can be extended to other chemistries. A phosphate-based chemistry was chosen to demonstrate the test methodology because the chemistry is conductive, finitely soluble and chemically reacts at high concentrations with some of the constituents in the sludge. Also, phosphate-based chemistry has been used in some commercial PWR steam generators. A synthetic powdery sludge was initially placed in each sludge basket. It consisted primarily of magnetite and other spinels, hematite, copper and copper compounds. Basket No. 1 was filled to a height of 19 cm. while No. 2 was filled to 14 cm. Shellside water chemistry was monitored several times a day to maintain it within specified limits.

Instrumentation

One tube in each array had five vertically aligned thermocouples imbedded in the tube wall. Thermocouples were also imbedded in the sludge at axial elevations identified in Figure 2. The stainless steel sheaths on these ungrounded thermocouples also functioned as electrodes for electrochemical measurements. They were electrically isolated from the autoclave by teflon sheathing, and ceramic insulators located in the fittings at the autoclave vessel penetrations. Two Ag/AgCl external reference electrodes with 0.1N KCl electrolyte were installed through the bottom of the autoclave and were located adjacent to each array. The reference electrodes provided a stable, reproducible voltage to which the potentials of the other electrodes were compared. The second reference electrode served as a backup in case of failure of the primary reference electrode. The potentials of the working electrodes versus the Ag/AgCl reference electrodes were converted to the Standard Hydrogen Scale (S.H.E.). Data was taken periodically on the facility data acquisition system.

Results and Discussion

Phase 1 - Sludge Hardening

The sludge hardened following concentrating the secondary chemicals in the soft sludge. The concentration process was controlled by periodically varying the autoclave steam flow rate over a period of two months. At about 1250 hrs there was an indication that sludge hardening was occurring. Figure 3 shows the response of thermocouple TC22, located in the sludge about 2.5 cm. above the bottom manifold. The superheat increased to 10°C by 2080 hrs. Superheats are relative to the saturated water temperature measured by thermocouple TCBULK, located in the water space above the sludge baskets. While the temperature was elevating, the concentrating phosphates caused the corrosion potential of the TC22 electrode to initially oscillate 100-150 mV cathodic and eventually remain cathodic (Figure 4). Preliminary scoping tests have shown that concentrating an alkaline phosphate solution to high levels produces a more cathodic potential. The final superheat is above the expected boiling point elevation of a highly concentrated alkaline phosphate solution [3] and dryout would be expected. The portion of the thermocouple/electrode tip not sheathed with teflon was about 5-6 mm long when the data was taken. The tip appears to be located at the interface of the wet and dry regions of the sludge pile. A sharp temperature gradient occurs at this interface. The measurements indicate a layer of concentrated phosphate chemistry exists somewhere above the tip of the thermocouple, yielding the cathodic potentials. This was in agreement with the bulk water chemistry measurements, which also indicated that the phosphates were hiding out in the porous sludge.

The thermocouple/electrode TC21 is measuring at 15°C superheat and has a potential comparable to the potential of the bulk water electrode (TCBULK). The high superheat would be expected to preclude the presence of a conductive solution needed to measure a potential. A possible explanation is that the hard sludge contains small amounts of copper providing a conductive path to the test array and autoclave. However, impedance measurements between the electrode and the autoclave showed high impedances, indicating "shorting" was not occurring. Another possibility is that the capillary pressure in the very small sludge pores (~0.1 microns) raised the saturation pressure sufficiently to prevent boiling of the concentrated solution in them, thus maintaining a limited conductive path. Another thermocouple/electrode, MP4, located at the same elevation as TC22, but at a different radial location,

exhibited a 10°C superheat throughout the period, while the potential shifted anodic about 100 mV. This could possibly be due to the sludge height above MP4 increasing during this period, limiting liquid penetration into the hard sludge and the concentrated layer moving above the unsheathed portion of the thermocouple/electrode.

Phase 2 - Extended Steaming

An interim shutdown followed the sludge hardening period and the autoclave was opened. The examination of Basket No. 2 verified there was 3.2 cm. of hard sludge covered by a 0.8 cm. soft sludge layer. Basket No. 1 contained only about 1.3 cm. of soft sludge, indicating much of the soft sludge initially placed in the basket was carried over to the autoclave vessel. Both baskets were refilled with powdery sludge to their initial heights. When testing was resumed, the autoclave was operated at several steaming rates up to 13.8 kg/hr. The tube heat fluxes were controlled by the steaming rate. Figure 2 shows the measured superheat in Basket No. 2 at various elevations and heat fluxes during the steaming period. Temperatures were measured by thermocouples in the soft and hard sludges, and the bulk water. In the soft wet sludge, the superheats were comparable to those measured above the sludge pile, indicating the heat transfer rates were controlled by convection associated with nucleate boiling on the tube surface. In the tightly adherent hard sludge, the superheats were generally much higher. Heat transfer is controlled by conduction through a ceramic medium, which has a relatively low conductivity. The heat transfer rates into the hard sludge above the dryout zone were estimated from tube wall temperatures to be roughly 20% of the rates observed in the soft sludge. The figure shows, as expected, that the superheat increases as the heat flux increases and as the elevation in the sludge pile decreases. The sludge heights shown in the figure were determined at the end of the sludge soaking test phase.

Phase 3 - Sludge Soaking

At the end of the extended steaming period, the test temperature was reduced to 177°C for two weeks and the autoclave maintained in a static condition. The temperature was maintained by electric band heaters on the outside walls of the autoclave. This temperature was chosen because it was expected to promote decomposition of the reaction products [4]. After the soaking period, steaming conditions were resumed and the thermocouple data monitored for changes from similar previous conditions. Temperatures in the hard and soft sludges had not changed. A mass balance of the returning alkaline phosphates was performed by taking shellside water chemistry samples. Phosphate concentrations were measured using an ion chromatograph (IC). It showed only a few grams returned. The post-test hard sludge height measurement in Basket No. 2 (3.3 cm.) was essentially the same as the interim measurement, indicating significant softening did not occur. The soft sludge height was somewhat higher (2.3 cm.), the result of adding more powdery sludge during the interim inspection. It was desired to determine why softening did not occur. Several large pieces of hard sludge were removed from the array, weighed and placed in permeable teflon bags. The specimens were placed in a 1.4 liter autoclave, and maintained at a temperature of 177°C with the same bulk water chemistry as in the previous testing. The autoclave was in a static condition for four days, and then placed in a flowing mode (5 volume changes/day). Initially, high concentrations of phosphates were measured when the autoclave was placed in the flowing mode, indicating decomposition had occurred. This was verified by subsequent sampling which showed no additional phosphate return.

Post-Test Sludge Examinations

The post-test examination showed that some sludge from Basket No. 2 in the 8 liter autoclave had changed substantially, both chemically and physically, from its pre-test condition. X-ray diffraction analyses of the low porosity hard sludge showed it consisted largely of sodium ferric hydroxyphosphate, most likely formed when concentrated phosphates reacted with the spinels in the sludge [5]. Phosphate concentrations in the 10000-20000 mg/l range are needed for the reaction to proceed. Lesser amounts of spinel, copper and copper compounds were also present. The composition of the soft sludge was quite different. It was similar to the pre-test composition, consisting primarily of magnetite, hematite, copper and copper compounds. A high magnification scanning electron microscope (SEM) micrograph of a hard sludge sample (Figure 5) indicates it consists of many reaction product crystals. The crystals have coalesced, causing a reduction in porosity (from a pre-test 70% to a post-test 15%) and increased hardness and strength. Hardness measurements performed on this sample showed an average Knoop hardness of 296, comparable to the tubing material. The reduction in porosity is partially responsible for the increased strength and hardness [6]. The small pores between the crystals allowed liquid to enter. Figure 6 shows a hard sludge sample that has been mounted and polished dry with diamond paste. Many voids are apparent. The

larger voids in the sludge could be chimneys. The post-test exam also showed Basket No. 1 contained only 2 cm. of soft sludge, an insufficient height for a concentration layer to form. It appears that there is some minimum height of soft sludge required to form a hard sludge, probably 3-4 cm.

The specimens from the sludge softening experiment performed in the 1.4 liter autoclave were also examined. They had all been softened to a powdery mass. X-ray diffraction analyses showed that the major species were spinels. No phosphate reaction products were found. Minor amounts of some copper compounds were also present. It appears that the softening is related to the decomposition of the reaction products. The soft sludge layer in the sludge basket seems to have impeded the breakdown process, possibly by controlling the transport of the breakdown products from the hard sludge back into the bulk water.

Model

A physical model of the boiling mass transfer in a porous sludge pile was developed that expands on the model formulated by MacBeth [7]. It was applied to a sludge pile consisting of two layers, each with different physical properties. MacBeth's original model only considered the capillary and frictional forces, and assumed all vaporization occurred at the inlet to the chimneys. The proposed model consists of a cell containing a vapor chimney of relatively large diameter and an ensemble of smaller diameter channels containing two phase flow that communicates with the chimney. The heat supplied produces the vaporization in the channels, which is complete when the vapor enters the chimney. The vapor moves along the dry chimney and exits the sludge pile into the bulk fluid. Circulation within the loop is provided by the channel capillary pressure and the elevation head, which have to overcome the frictional forces in the channel pores and chimney, and the capillary pressure at the chimney exit. The model assumes laminar flow in both the pores and chimney. The inertia forces can be neglected and the motion in the loop can be expressed by the following equation:

$$4\sigma \cos \theta \left(\frac{1}{D_p} - \frac{1}{D_c} \right) = 32L \left[\left(\frac{\beta \mu_p V_p}{D_p^2} \right) + \left(\frac{\mu_v V_c}{D_c^2} \right) \right] - L(\rho_p - \rho_v) \quad (1)$$

- σ = surface tension
- D_p = pore diameter
- D_c = chimney diameter
- L = liquid penetration into sludge pile
- μ_p = average viscosity of the two phase fluid in the pores
- V_p = average velocity of the two phase fluid in the pores
- μ_v = viscosity of the vapor in the chimney
- V_c = velocity of the vapor in the chimney
- ρ_p = average density of two phase fluid in the pores
- ρ_v = vapor density in the chimney
- θ = contact angle at the liquid-vapor interface
- β = tortuosity factor to account for the circuitous pore flow paths

For small pores, such as those that exist in a sludge pile, the flow will be capillary bubble [8]. In this regime, the vapor bubble completely fills the pore cross section, leaving the wall at that location completely dry. Both phases move at the same velocity. The void fraction (α) in the channel can be expressed as:

$$\alpha = \frac{x v_v}{(1-x)v_l + x v_v} \quad (2)$$

- x = quality
- v_v, v_l = specific volume of the saturated vapor and liquid in the pores

The average void fraction ($\bar{\alpha}$) in the pores, with an inlet quality of (x_i) and an exit quality (x_e) is:

$$\bar{\alpha} = \frac{1}{x_e - x_i} \int_{x_i}^{x_e} \alpha(x) dx \quad (3)$$

The average fluid density (ρ_p) and viscosity (μ_p) in a pore are:

$$\rho_p = \rho_l (1 - \bar{\alpha}) + \rho_v (\bar{\alpha}) \quad (4)$$

$$\mu_p = \mu_l (1 - \bar{\alpha}) + \mu_v (\bar{\alpha}) \quad (5)$$

ρ_v, ρ_l = saturated vapor and liquid density
 μ_v, μ_l = saturated liquid and vapor viscosity in the pores

For a sludge pile consisting of a single homogeneous layer, the number of pores in the array (N_p) is:

$$N_p = \frac{4\varepsilon(I-\gamma)A_A}{\pi D_p^2} \quad (6)$$

and the number of chimneys in the array (N_c) is:

$$N_c = \frac{4\varepsilon\gamma A_A}{\pi D_c^2} \quad (7)$$

ε = porosity
 γ = chimney fraction of porosity
 A_A = cross sectional area of test array
 D_p = pore diameter
 D_c = chimney diameter

Cohen [9] reports that chimneys in boiling crud deposits on heat transfer surfaces are typically about 10% of the porosity. Although this data is limited, it is the best available and was used in subsequent parameter studies.

The total heat transfer to the pores (Q) is:

$$Q = N_p (\pi D_p L) \phi \quad (8)$$

ϕ = average pore heat flux.

The total heat transfer can also be expressed as:

$$Q = M_p (h_v - h_l) \quad (9)$$

M_p	=	total mass flow rate through pores
h_v	=	saturated vapor enthalpy leaving pores
h_l	=	saturated liquid enthalpy entering pores

Therefore:

$$M_p = \frac{N_p (\pi D_p L) \phi}{h_v - h_l} \quad (10)$$

Under steady-state conditions, the mass flow rate of liquid entering the pores equals the mass flow rate of vapor exiting the chimneys. Therefore, continuity requires that:

$$V_c = \frac{4 N D_p L \phi}{(h_v - h_l) \rho_v D_c^2} \quad (11)$$

and

$$V_p = \frac{4 L \phi}{(h_v - h_l) \rho_p D_p} \quad (12)$$

N = ratio of number of pores to number of chimneys.

In the tightly adherent hard sludge, heat (Q) is transferred from the tubes to the liquid in the pores by conduction. In the soft sludge, the heat transfer mechanism from the tube wall to the sludge is convection enhanced by boiling, resulting in much higher heat transfer rates into the soft sludge. A simplified model assuming the heat transfer is uniform and one-dimensional is proposed. Heat that is not removed by vaporization in the pores, is transferred by conduction to the sludge basket wall, and subsequently into the autoclave bulk fluid. The total heat transfer area of the pores, for a sludge height (H) is:

$$HTA_p = H N_p \pi D_p \quad (13)$$

The average pore heat flux is approximated by:

$$\phi = \frac{Q}{HTA_p} \quad (14)$$

From Darcy's Law [10] an equivalent permeability (K) can be determined:

$$K = \frac{\varepsilon \mu_p V_p L}{32L \left[\left(\frac{\beta \mu_p V_p}{D \rho^2} \right) + \left(\frac{\mu_v V_c}{D_c^2} \right) \right]} \quad (15)$$

By combining equations 11, 12 and 15, the permeability can also be expressed as:

$$K = \frac{\varepsilon \mu_p D_p^2 D_c^4 \rho_v}{32(\beta \mu_p \rho_v D_c^4 + N \mu_v \rho_p D_p^4)} \quad (16)$$

Experiments with irregular powders [11] showed that a reasonable value for the tortuosity factor (β) should be approximately 2.5. The semi-empirical Ergun correlation is frequently used to predict permeability [10] in laminar flow with a Reynolds number <20 .

$$K = \frac{\varepsilon^3 d^2}{150(1-\varepsilon)^2} \quad (17)$$

This correlation is a function of only the physical properties of the sludge (porosity (ε) and mean particle size (d)), while equation (16) is also a function of the properties of the fluids flowing in both directions through the porous pile. Surprisingly, a comparison of the predictions by the two methods over the range of interest showed reasonable agreement. For example, a hard sludge permeability of .007 Darcy was predicted using equation 16, while .009 Darcy was predicted using equation 17. This is comparable to a low porosity brick.

When the sludge pile consists of two distinct layers, with different permeabilities, porosities, and heat addition rates, it is assumed that the equations are applied to each layer, while maintaining continuity of flow and conserving momentum. The number of chimneys in the soft sludge is set equal to the number of chimneys in the hard sludge. An iterative procedure was used to solve for the pore quality at the soft/hard sludge layer interface and the liquid penetration into the hard sludge.

Pore and chimney sizes used in the model were estimated from SEM photographs of the hard sludge, or from measurements of the soft sludge. The predicted liquid penetration line in Figure 2 lies just above the points of high superheat, and thus agrees reasonably well with the data. If one allows for the effect of boiling point elevation of a saturated alkaline phosphate solution and the additional temperature rise due to capillary pressure of the voids inside the hard sludge pores, one would expect the solution would penetrate much deeper into the sludge pile than predicted. If the combined effect were a 6°C elevation in boiling point [3], the liquid could penetrate all the way to the bottom of the pile at heat fluxes up to 1.6 watts/cm² and possibly higher. At higher heat fluxes, liquid penetration is less sensitive to the effects of boiling point elevation and capillary pressure.

Conclusions

The test methodology was successful in providing insight into the formation of hard sludge, and the thermal-hydraulic and chemical environment in the sludge. Temperatures and corrosion potentials were significantly different from the bulk water and indicated when and where chemicals were concentrating. This type of testing might aid in assessing corrosion susceptibility. This method utilized an alkaline phosphate water chemistry, but can be applied to other water chemistries. A one-dimensional analytical model, utilizing capillary forces, was applied to understand both the thermal-hydraulic and electrochemical data. The model can be reasonably used in parametric studies to predict the liquid penetration into sludge piles.

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Figure 1 - Test array (left) and autoclave (right) arrangement

Figure 2 - Superheat temperature vs. heat flux in the soft sludge layer in Basket No. 2
(Superheat = $TC_T - TC_{BULK} (^{\circ}C)$)

Figure 3 - Changes in superheat temperature as sludge hardening occurs.

Figure 4 - Changes in corrosion potential as sludge hardening occurs

Figure 6 - Optical micrograph of polished cross-section of heterogeneous hard sludge. The dark areas are relatively large pores which could be functioning as chimneys (200X)

Figure 5 - SEM micrograph of hard sludge showing crystal growth and coalescence. (There are many small pores between the crystals).