LEAD CORROSION AND TRANSPORT IN SIMULATED SECONDARY FEEDWATER

G.B. McGarvey*, K.J. Ross+, T.E. McDougall+ and C.W. Turner*

ABSTRACT

The ubiquitous presence of lead at trace levels in secondary feedwater is a concern to all operators of steam generators and has prompted laboratory studies of its interaction with Inconel 600, Inconel 690, Monel 400 and Incoloy 800. Acute exposures of steam generator alloys to high levels of lead in the laboratory and in the field have accelerated the degradation of these alloys. There is some disagreement over the role of lead when the exposure is to chronic levels. It has been proposed that most of the present degradation of steam generator tubes is due to low levels of lead although few if any failures have been experimentally linked to lead when sub-parts per billion levels are present in the feedwater. One reason for the difficulty in assigning the role of the lead is related to its possible immobilization on the surfaces of corrosion products or iron oxide films in the feedwater system.

We have measured lead adsorption profiles on the three principal corrosion products in the secondary feedwater; magnetite, lepidocrocite and hematite. In all cases, essentially complete adsorption of the lead is achieved at pH values less than that of the feedwater (9-10). If lead is maintained in this adsorbed state, it may be more chemically benign than lead that is free to dissolve in the feedwater and subsequently adsorb on steam generator tube surfaces. In this paper, we report on lead adsorption onto simulated corrosion products under simulated feedwater conditions and propose a physical model for the transport and fate of lead under operating conditions. The nature of lead adsorption onto the surfaces of different corrosion products will be discussed. The desorption behaviour of lead from iron oxide surfaces following different treatment conditions will be used to propose a model for the transport and probable fate of lead in the secondary feedwater system.

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INTRODUCTION

In recent years there has been an interest in the corrosion of lead and lead alloys (1-4), and its participation in the degradation of other metals and alloys (5,6). The chemical aggressiveness of lead compounds is of particular concern in the nuclear industry where the presence of lead has been implicated as a primary contributor to the premature degradation of nickel-based alloys that are used in the manufacture of critical components (7-10). Of particular concern to date has been accelerated attack on Inconel 600, the preferred alloy for the manufacture of steam generator tubes in first generation nuclear plants. Dissolution of one or more biological-shielding lead blankets in boiler 3 of Bruce NGS "A", Unit 2, resulted in the distribution of lead throughout boilers 2 and 3 (8). Deposits in the scallop bar regions were found to contain between 1,000 and 10,000 ppm of lead, and lead was also present in the sludge piles. A similar series of events took place at the Belgian Doel 4 plant where at least one lead shielding blanket was also left in the feedwater circuit. Chemical cleaning of the unit did not remove the quantity of lead that was expected, based on the weight of a blanket (11). In both cases, severe stress corrosion cracking/intergranular attack has occurred at both plants.

While metallic lead may play a key role in the corrosion of the tube alloys, the processes leading to its deposition at tube surfaces are complex and have not been fully elucidated. There is sufficient evidence, however, to implicate the corrosion of lead and lead-containing materials as the first step in the process. There are two most-probable modes for the transport of lead from the low temperature region of the feedwater system to the steam generators; as a dissolved aqueous cation or complex (2), or, as an adsorbed species on the surface of a solid that is suspended in the feedwater. With regard to the possible speciation of lead, Pb(II) species are expected to dominate in the feedwater since the active dissolution or corrosion mechanism will proceed via generation of Pb^{2+} or hydrated Pb(II) ions. Free, aqueous Pb^{2+} species are most stable under strongly acidic conditions with oxide phases possibly precipitating from solution as the pH is elevated if the Pb^{2+} concentrations exceed the solubility limit (12).

In the presence of inorganic oxides, solutions of Pb^{2+} and many other transition metal cations tend to adsorb strongly to these surfaces. This is particularly true as the pH of the aqueous system is raised into the alkaline region ($pH > 8$). Of particular interest with regard to the transport of lead in the feedwater of nuclear generating stations is the adsorption of lead onto iron oxide surfaces. Corrosion product transport (CPT) studies have demonstrated that magnetite, hematite and lepidocrocite are the predominant iron oxides that are generated, and transported in CANDU secondary feedwater systems (13). Under steady state conditions, magnetite and hematite are the principal oxides while a more substantial quantity of lepidocrocite is generated under shutdown conditions and detected during subsequent start-ups. Corrosion product transport studies have also shown that lead is present in low concentrations, particularly in newer stations, and apparently following maintenance outages (14). The latter observations may be attributable to poor control of the water chemistry which promotes the degradation of the lead-bearing materials.

The work described here was undertaken to evaluate the adsorption behaviour of magnetite, hematite and lepidocrocite in the presence of aqueous lead (II) at room temperature as the pH of the solution was raised. For magnetite and hematite, desorption profiles were also measured following various treatments. The results of these studies have been used to propose a lead transport model for the secondary feedwater system.

EXPERIMENTAL

Materials

Lead adsorption studies were carried out using the three principal iron oxide phases that are found in CANDU secondary feedwater systems: magnetite (Fe_3O_4), hematite (α-Fe_2O_3), and lepidocrocite (γ-FeOOH). A commercial hematite was used for the adsorption studies (Fisher Certified). Three magnetite samples were used: a synthetic material that was prepared by oxidizing ferrous nitrate with potassium nitrate; Puratronic grade magnetite from Johnson-Matthey (99.999% stated purity); and a Mapico powder material that was determined to be essentially 100% pure by powder X-ray diffraction. All lepidocrocite samples were prepared using methods that have been described in detail elsewhere (15).

Adsorption-Desorption Experiments

The working solution for the adsorption and adsorption-desorption experiments was 10^{-4} M lead nitrate which is approximately 20 mg/l in lead (20 ppm). In a typical experiment, the solution was prepared and left to stir and sparge with argon in a Nalgene vessel for 0.5 h. The adsorption leg of the experiment covered the approximate pH range 3 to 8 or 9.5, depending on the oxide, with pH adjustment accomplished using a 1.0 mol/L solution of morpholine.

Following the completion of the adsorption leg, desorption profiles were measured for some magnetite and hematite samples. Details are provided in the Results and Discussion section.

For each data point on the adsorption or desorption curve, approximately 2.5 mL of solution was removed from the Nalgene reaction vessel and transferred to a plastic 30 mL cup using a disposable plastic pipette. The aliquot was drawn into a 5 mL plastic syringe, a 0.45 μm Millipore syringe filter was attached, and the solution was forced through the filter into a clean 30 mL plastic cup to remove the iron oxide. Duplicate 1 mL samples of the filtrate were diluted to 10 mL in plastic sample vials by adding 9 mL of double-distilled water. The residual filtrate (~ 0.3 mL) was returned to the reaction vessel. Lead determinations were made using atomic absorption spectrometry.

RESULTS AND DISCUSSION

Lead Adsorption onto Lepidocrocite

The adsorption of lead from aqueous solutions was carried out using a series of lepidocrocite samples that varied in morphology and crystallinity. Relevant physical characterization data has been reported (15). For this particular iron oxyhydroxide, surface area changes can be attributed directly to particle size differences since lepidocrocite does not possess an internal pore structure.

Figure 1 shows representative adsorption profiles for lead onto different lepidocrocite samples as a function of pH. In the low pH region (< 3) there was negligible adsorption on any of the lepidocrocite samples but as the pH was raised, lead adsorption was detected. Cation adsorption on the surface of iron oxides is believed to proceed through the formation of a surface complex between the hydrated lead ions and the oxide surface and this process is accompanied by the release of protons from the surface which explains the small, consistent decrease in the measured pH as the equilibration proceeds (16).

While lead adsorption on the different lepidocrocite samples had the same general characteristics and profiles, there were some subtle differences in the shapes and slopes of the curves that were attributed to differences in the number of available surface adsorption sites. The slope of the adsorption profiles gives a semi-quantitative indication of the strength or magnitude of the adsorption of lead onto the oxide surface at a given pH. A direct correlation was measured between the slope of the adsorption curves and the surface area of the substrates.

Maximum adsorption on the lepidocrocite samples was determined to be greater than 90% in all cases and was achieved after the pH was raised to 6, irrespective of which sample was considered. It is not surprising that the different γ-FeOOH samples had approximately the same behaviour, since the differences were primarily associated with the crystallinity and particle size of the materials which will change the number of adsorption sites per gram of material, but not necessarily the affinity of the sites.

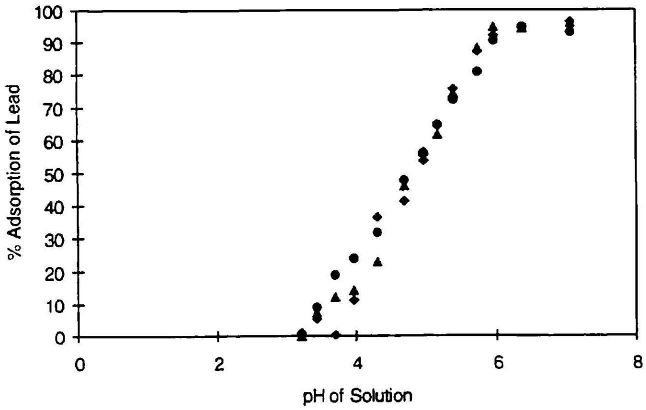

Figure 1: Adsorption profiles for lead on lepidocrocite: ♦ aging time 16 h, temperature 73°C; ▲ aging time 2 h, temperature 50°C; • aging time 24 h, temperature 50°C.

Lead Adsorption onto Hematite

As was observed with lepidocrocite, there was negligible adsorption below pH 3, but as the pH was raised, measurable adsorption was observed. Following a steady increase in the amount of lead adsorbed up to pH 5.5, there was a region covering approximately 1 pH unit where there was negligible additional adsorption. Above pH 6.5, the adsorption proceeded until the maximum was reached at approximately pH 8. The change in the adsorption behaviour was almost coincident with the measured isoelectric point of 6.9. This suggests that the surface charge does play a strong role in the adsorption of lead on hematite from aqueous solution in the presence of morpholine.

Lead Adsorption onto Magnetite

The nature of the lead adsorption onto the surface of magnetite was much different than on the lepidocrocite or hematite. Whereas adsorption onto the lepidocrocite surface proceeded in a relatively smooth manner until the maximum adsorption capacity was reached, there was a definite break in the adsorption profile for magnetite as the pH was raised from 3 to 4.5 (Figure 2).

Between pH 4.5 and 6.5 there was a maximum in the amount of lead that was adsorbed, followed by a shallow minimum. Above pH 6.5, the lead adsorption increased smoothly over a relatively narrow pH range, reaching essentially 100% adsorption at pH 8. This behaviour was similar for the three different magnetite samples, although the trend was more evident on the sintered commercial sample. It is proposed that the difference may arise from the fact that the sintering process yields a more homogeneous surface throughout the sample.

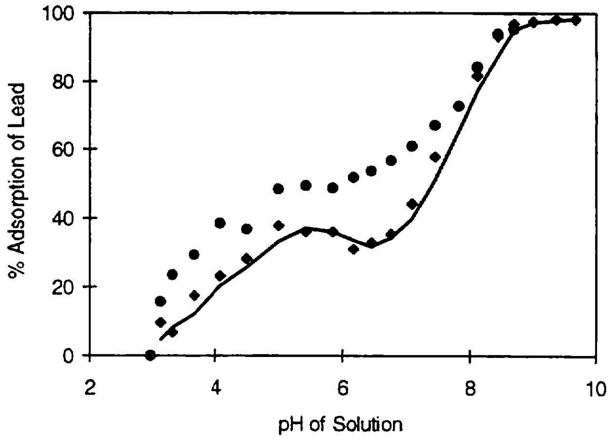

Figure 2: Adsorption profile for lead on the surface of magnetite: ◆pH adjusted with morpholine; ● pH adjusted with sodium hydroxide

The shape of the adsorption profile is attributed to either the adsorption of more than a single monolayer of lead on the magnetite surface, the competitive adsorption between morpholine and lead, or possibly some combination of the two effects. The adsorption of morpholine was suggested from a comparison of the adsorption profile in Figure 2 with a profile that was measured using sodium hydroxide (NaOH) as the pH control agent. Two major differences were noted between the profiles: 1) whereas a distinct minimum was measured for the adsorption of lead onto magnetite in the presence of morpholine, there was no minimum when the adsorption was carried out in the presence of NaOH, although there was an intermediate plateau in the profile; 2) in neutral and alkaline regions ($pH > 6.5$), maximum lead adsorption was approached and achieved under less pH conditions when morpholine was employed.

Previous studies have shown that the adsorption of lead and other divalent metal cations is dependent on both the nature of the oxide and the conditions under which the adsorption occurs. It has been shown that a large fraction of the total quantity of lead in solution is adsorbed onto the oxide surface when the pH is lower than the point of zero charge of the adsorbate. This phenomenon has been rationalized by Rodda et al. (17) who stated that when the oxide surface is positively charged, the surface pH is higher than in the bulk solution because of the attraction of hydroxyl ions which promotes cation adsorption.

Powder X-ray diffraction investigations of the solid phase(s) that were recovered from the experiments following the completion of the adsorption did not indicate that discrete, bulk lead oxide or hydroxide phases were present. Although lead phases may have been present in a quantity below the detection limit of the XRD technique, a plausible explanation is that lead adsorption continued on the hematite and magnetite surfaces following the completion of the monolayer formation. Gunneriusson et al. (18) have proposed that polynuclear surface Pb(II) species form on goethite when a sufficient number lead ions are present; they proposed the following reaction above pH 6:

$$\text{Surface-Fe-OH} + 6\ \text{Pb}^{2+} + 9\ \text{H}_2\text{O} \rightarrow \text{Surface-FeOPb}_6(\text{OH})^+ + 9\ \text{H}^+$$

Desorption of Lead from Magnetite and Hematite

The adsorption studies with iron oxides indicated that lead will be immobilized on oxide-coated pipe walls, or adsorbed on particulate corrosion products which provides a mode of transport through the feedwater to the steam generators. Studies have been published that demonstrate the correlation between iron and lead concentrations in corrosion product transport studies (14). An important consideration is then to determine the stability of the lead/iron oxide complex under different chemical and thermal conditions. Experiments were undertaken to address issues related to the stability of the complex, particularly the pH at which lead is released from the surface.

In the first series of tests, lead was adsorbed onto magnetite and hematite surfaces up to pH 9.5, followed by desorption after approximately 16 h. In the experiment with magnetite, the desorption leg tracked the adsorption leg with only a minor degree of hysteresis (Figure 3) while in the case of hematite, there was a consistent difference of approximately 0.5 pH units between the two legs. The extent of desorption from the two surfaces suggests that lead was present only as an adsorption complex in which there was little, if any, chemical bond formation between the adsorbate and the substrate.

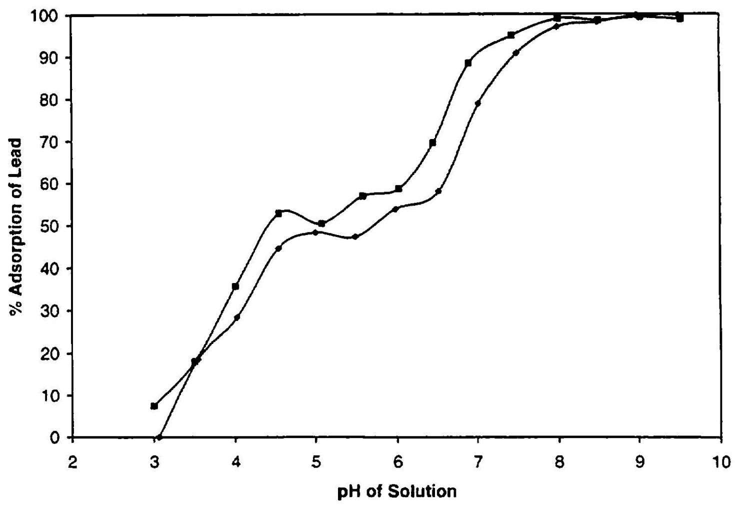

Figure 3: Adsorption-desorption profile for lead on magnetite (25°C): ♦ adsorption; ■ desorption.

A heating experiment was carried out to determine whether lead desorption from magnetite was stimulated by increasing the temperature of the two-phase slurry. Starting at 25°C, the autoclave temperature was increased to 250°C incrementally with liquid samples being drawn off at each temperature and measured for lead. The data in Table 1 suggest that the Pb/Fe_3O_4 complex is stable and that only small quantities of lead are expected to be released from the surface.

Table 1: Effect of heating on lead desorption form the surface of magnetite

Temperature (°C)	Lead Adsorption (%)
25	98.8
100	98.6
150	98.8
200	99
250	98.2

When the lead/iron oxide complexes were heated for 7 d at 250°C in an autoclave, the appearance of the desorption legs was somewhat different. Rather than tracking with the adsorption leg, the desorption leg exhibited a significant degree of hysteresis in the intermediate pH range, followed by essentially complete desorption by the completion of the experiment (pH 3). Interestingly, the magnetite was oxidized to hematite during the course of the experiment. In the complementary experiment with hematite, a similar hysteresis effect was observed; once again, the lead desorption proceeded to completion.

The final set of trials was carried out by heating the adsorption complex at 250°C in the presence of 2 ppm hydrazine (initial concentration) for 7 d. Following the heating step, there was a significant delay in the desorption of lead from the surface of magnetite, similar to that observed for the experiment carried out in the absence of hydrazine. In this case however, there was incomplete desorption of lead from the surface, even after the pH was lowered to 2.5. Similar behaviour was measured in the hematite system with approximately 40% of the lead remaining on the oxide surface (Figure 4).

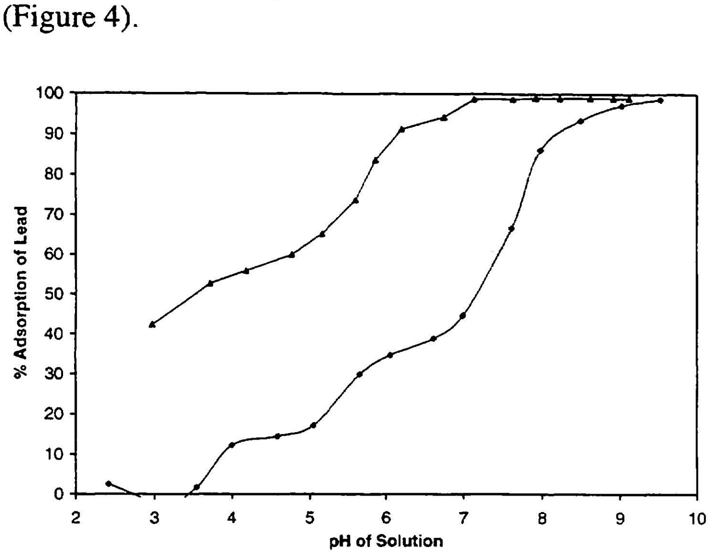

Figure 4: Adsorption-desorption profile for lead on hematite that had been heated for 7 d in 2 ppm hydrazine at pH 9.5: ◆ adsorption; ▲ desorption

The results of these desorption studies reveal several features of lead/iron oxide complex behaviour that are relevant to the chemistry in the feedwater and steam generators. Heating has a marked influence on the desorption of lead from the oxide surfaces. At low temperatures, even relatively small fluctuations in pH, such as those experienced when the feedtrain is filled with fresh demineralized water following a maintenance outage, may cause lead to be released from the oxide surfaces. Under the more aggressive conditions of the steam generator, heating in the presence of hydrazine appears to have an immobilizing effect as shown by the partial retention of lead in Figure 4.

Proposed Mechanism for Lead Transport in Secondary Feedwater

In all cases that were studied here, the maximum adsorption on each of the oxides was achieved well below the feedwater pH that is used in either mixed alloy (pH 9.2) or all-ferrous (pH 10) feedtrains. This suggests that iron oxides present in the feedtrain, either suspended particulate or corrosion products on pipe surfaces, will readily adsorb any aqueous lead that is present.

Several plausible mechanisms that can explain the dissolution process under normal operating or shutdown/start-up conditions have been identified. Oxygenated, neutral water of the type used to fill the feedwater system following dry lay-up has been shown to be a very aggressive fluid for lead (19). The following reaction describes one scheme through which dissolved oxygen can participate in the corrosion of lead:

$$2\ Pb + 2\ H_2O + O_2 \rightarrow 2\ Pb^{2+} + 4\ OH^-$$

One of the other possibilities is the reaction of lead with copper which is generally present at trace levels in all secondary feedwater systems. The reaction

$$Pb + Cu^{2+} \rightarrow Pb^{2+} + Cu$$

has an E^o value of +0.463 V and an equilibrium constant of 10^{16}, suggesting that this reaction may be one of the principal modes for release of lead.

At the feedwater pH, free Pb^{2+} concentrations are not expected to be significant (12,18). In fact, the monomeric and polymeric hydroxy complexes are predicted to be the equilibrium species, and these are expected to be soluble at the low total lead concentrations (< 1 ppb) that exist in the feedwater. Gunneriusson et al. (18) also predicted the formation of a series of lead adsorption complexes on the surface of goethite. Assuming that other iron oxides possess similar characteristics in adsorption behaviour, it can be generalized that many of the same surface complexes will form on the iron oxide surfaces of interest in feedwater systems. The studies of the Pb/α-FeOOH system showed that as the pH was raised above 3, the fraction of free Pb^{2+} in solution began to decrease with the onset of the formation of $FeOHPb^{2+}$, and later the $FeOPb^+$ complex above pH 5. As the pH passes into the alkaline region, the concentrations of these two species begin to decrease with the concomitant increase in the concentration of the FeOPbOH complex. The fact that there was no evidence for the formation of lead (hydr)oxide precipitates in any of our experiments provides additional confidence for our contention that lead is adsorbed on the surface of the iron oxides.

Recently, Roe et al. (20) measured X-ray absorption spectra (XAS) of lead adsorbed on the surface of goethite. The authors concluded that at the lower lead concentrations that were studied (< 400 ppm), monomeric lead complexes were formed, while polymeric species were formed when higher lead concentrations were used. In neither case did the XAS evidence suggest that lead hydroxide precipitation had occurred on the surface.

Our preliminary studies of lead corrosion under static aerated and deaerated conditions also point to the formation of mixed oxide films, but in addition, soluble lead has also been measured. Given the sorptive properties of the three iron oxides that were studied in this investigation, it follows that a significant fraction of the soluble lead that is generated from the corrosion of metallic lead or lead alloys will adsorb on oxide surfaces at the feedwater pH.

Adsorption of lead onto the surface of suspended particulate appears to be a certain, and perhaps ubiquitous process, in light of recent X-ray fluorescence measurements that detected lead on filtered feedwater samples (14). Corrosion products are transported to the steam generators where they accumulate and form deposits on tubing, support structures and the tubesheet. The most critical location for deposits is in the regions adjacent to the tubing. Once the corrosion products are immobilized in the steam generators, oxidized lead species will be reduced to metallic lead by the action of hydrazine. Since the outside temperature of the hot-leg section of the tubes is on the order of 50°C below the melting point of lead, diffusion towards the tube surface is expected to occur relatively rapidly. In light water reactors, the temperatures can be slightly higher, increasing the probability of lead diffusion to the tube surface.

Another important consideration in lead transport mechanisms is the carbon steel feedwater piping which will be covered with iron oxide phases and hence may function as a sink for the lead that is generated in the low temperature regions. As long as the pH of the feedwater remains above 9, it is expected that the lead will remain immobilized on the wall surfaces. If a chemical excursion occurred in which the system pH began to fall, it is expected that some release of lead would occur once the pH reached approximately 7.5. It should be noted that following a dry lay-up, the system pH can be significantly lower than the operating pH while the feedtrain is being refilled and chemistry control is being reestablished.

Figure 5 outlines the steps that are proposed to occur during the processes of lead corrosion and transport to the steam generators.

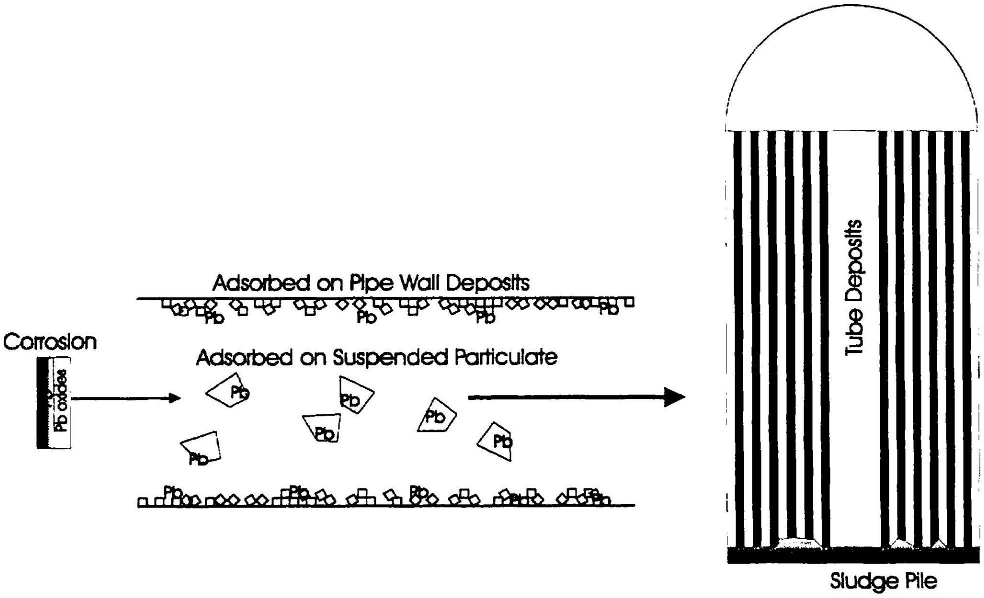

Figure 5: A schematic representation of the events involved in the transport of lead from the feedtrain to the steam generators.

CONCLUSIONS

Under laboratory conditions, the adsorption of aqueous lead onto hematite, magnetite and lepidocrocite increased to a maximum uptake level as the pH of the solution was increased and remained at that maximum level as the pH was increased further. The plateau associated with the maximum adsorption occurred at pH's which are lower than those used in the secondary feedwater systems of CANDU reactors. This implies that Pb^{2+} generated from the corrosion of lead-bearing materials can be adsorbed onto iron oxide surfaces under typical operating conditions. Lead desorption from iron oxide surfaces occurs if there is a decrease in the pH of the process fluid. There is a marked difference in the behaviour if the system is heated to high temperature; a fraction of the lead appears to be immobilized and much more resistant to the influence of lowering the pH.

These results support a lead transport mechanism to the steam generator with the lead adsorbed on iron oxide particulate. Each of the steps has experimental or field evidence to corroborate the proposed mechanism and the implication of this mechanism is that any lead entering the feedwater will find its way to the steam generator where the probability of limiting plant life increases markedly.

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