

Electrochemical Evaluation of Lead Species Under Pressurized Water Reactor Secondary Chemistry Conditions



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REPORT SUMMARY/PRODUCT DESCRIPTION

Recent examinations of degraded pulled tubes from several plants suggest possible lead (Pb) involvement in intergranular attack/stress corrosion cracking (IGA/SCC), although the morphology of attack resembles that observed in the laboratory produced by caustic and acid sulfate conditions. This program was undertaken to examine the electrochemical kinetics and thermodynamics of Pb in conditions approaching those of secondary water. Such an approach will help utilities understand the factors that activate Pb and why it apparently causes PbSCC in some steam generators and not in others.

Background

Increases in water purity and reductions in oxygen ingress have been generally successful in controlling most corrosion processes, but these measures have not prevented IGA/SCC. This type of damage continues to result in steam generator tubing degradation, plugging of large numbers of tubes, and eventual replacement of steam generators. The present strategy for mitigating IGA/SCC is based on the premise that crack initiation and propagation rates depend on pH and the electrochemical potential (ECP). Accordingly, plants have adopted the practices of injecting hydrazine to maintain reducing conditions and of adding amines to the feedwater to maintain the pH within the range of 5 to 9 at temperature. These measures have been successful in reducing the rate of degradation in tubes affected by IGA/SCC in some plants; however, other plants using the same measures have continued to experience IGA/SCC. The reason for this variability is not well understood, but there is mounting evidence that Pb is the cause.

High magnification analytical transmission electron microscopy (ATEM) performed on pulled steam generator tubing (documented in EPRI reports TR-114980, 1003587, 1009346, and 1011683) has revealed a narrow band of Pb on crack walls and at the crack tip adjacent to the substrate of oxidized, degraded grain boundaries. Other impurities found included Al, Si, Ca, K, and Mg. Although Pb is pervasive on the secondary side of steam generators, its involvement in IGA/SCC has generally been ignored because the concentration of Pb in deposits has been small in comparison to other contaminants. In the past, other causes of IGA/SCC, such as acid sulfate and caustic conditions, have been dominant and Pb involvement, if any, has been considered a secondary cause. An international group of experts performed a comprehensive review of PbSCC in the 2005 EPRI/ANL/NRC Workshop on Effects of Lead (Pb) and Sulfur (S) on the Performance of Secondary Side Tubing of Steam Generators in PWRs (documented in EPRI report 1012780). They concluded that Pb could be potentially the most aggressive of the environmental species that can occur in steam generators. A major question addressed in the workshop was why PbSCC is not more ubiquitous since Pb is in all steam generators.

Objectives

- To determine the electrochemical kinetics of Pb in steam generator secondary water conditions.
- To determine which Pourbaix diagram best describes the thermodynamics of Pb in steam generator secondary water conditions.

Approach

To eliminate possible formation of Pb complexes and pH shifts during testing, investigators used 1500 ppm boric acid solutions with sodium hydroxide. Potentiodynamic polarization curves were measured at 280°C for pure Ni and Pb electrodes. The test solutions had $1.0\text{e-}3$ m Pb and $1.0\text{e-}4$ m Pb at pH_T of 6.15, 8.31, and 9.95. Electrochemical potential was measured against an Ag/AgCl reference electrode. A Cu/CuO electrode was used for pH measurements.

Results

The polarization curves from Pb clearly did not have a passive region, meaning no film was formed under the test conditions. The results for Ni are significantly different from those for Pb. The polarization curve had a plateau region, suggesting the formation of a passive film. However, since the current density in the plateau region (passive range) is several times higher than that usually observed for a highly protective passive film, the film does not have good protective properties. This is in accordance with the observation, mainly during stress corrosion tests, that the presence of Pb causes thick scaling on Alloy 600 and Alloy 690. The electrochemical results provide bases for making predictions about the thermodynamic stability of Pb species in secondary steam generator water. These results and a comparison of Pb and Ni Pourbaix diagrams suggest that Pb in solution will oxidize Ni.

EPRI Perspective

Increases in water purity and reductions in oxygen ingress have been generally successful in controlling most corrosion processes, but these measures have not prevented IGA/SCC. Recent examinations of degraded pulled tubes from several plants have found a narrow band of Pb on crack walls and at the crack tip adjacent to the substrate of oxidized grain boundaries, suggesting possible Pb involvement in IGA/SCC. This project aids in better understanding Pb thermodynamics in steam generator secondary water conditions. Such information will aid utilities in developing strategies for reducing PbSCC in steam generator tubes.

Keywords

Steam Generators
Corrosion Potential
Lead Cracking
Lead Pourbaix Diagram
Lead Electrochemistry
PbSCC

ABSTRACT

Secondary side steam generator tubing degradation, particularly of mill annealed and sensitized Alloy 600 tubing, continues in both recirculation and once through steam generators even with plant operation having reduced impurity ingress (ALARA chemistry), boric acid additions, and molar ratio control. Recent pulled tube analysis has found Pb at crack tips suggesting PbSCC. However, since Pb is present in all steam generators and not all plants have experienced cracking, it is not clear what activates Pb. The improved understanding of the electrochemical kinetics and thermodynamics of Pb gained from this program, has the potential benefits to

- Better define plant operating conditions to prevent PbSCC
- Better understanding of approaches needed for developing remedial action for PbSCC

This report describes electrochemical investigations performed to determine which Pourbaix diagram best describes the behavior of Pb at steam generator temperatures. Potentiodynamic polarization curves were measured with Pb exposed to pH 9.95, 8.31, and 6.15 solutions at 280 °C. The solutions had 1500 ppm B as boric acid for a supporting electrolyte with the pH adjusted by the addition of NaOH. Two concentrations of Pb, 1.0e-3 m and 1.0e-4 m added as PbO, were evaluated at each pH. The polarization curves were compared with the thermodynamic predictions of Pourbaix diagrams.

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INTRODUCTION

Lead (Pb) has long been observed to accelerate intergranular attack/stress corrosion cracking (IGA/SCC) in laboratory testing and has been suspected to be involved in steam generator service degradation of operating nuclear plants. Based on relatively recent data, it is clear that lead has caused increased rates of IGA/SCC in laboratory tests and has the potential for doing so in plants. Lead is a common component in steam generator sludge deposits, yet in the past, SCC degradation has seldom been attributed to these Pb deposits, except in the cases such as Bruce B and Doel 4 where Pb blankets were inadvertently left in a steam generator. Recently, ATEM examinations of cracked steam generator tubing have definitively linked Pb to the cracking in both OTSGs such as Oconee (EPRI TR-114980), and RSGs such as Tihange 1 & 3 and Farley 1 (EPRI 1003587), and more recently at Seabrook (EPRI 1009346), Diablo Canyon 2 and Watts Bar 1 (EPRI 1011683). The high magnification ATEM results have revealed Pb within porous nanocrystalline, degraded grain boundary oxides that were several nanometers wide. Such small amounts of Pb in cracks are difficult to detect. Thus, the fraction of the extensive IGA/SCC that has occurred in many other operating steam generators with mill annealed Alloy 600 (Alloy 600MA) tubes that is attributable to, or has been significantly aggravated by, the presence of lead species has not been so clear [1-11].

Increases in water purity and reductions in oxygen ingress have been generally successful in controlling most corrosion processes, but these measures have not prevented IGA/SCC. The present strategy for mitigating IGA/SCC is based on the premise that crack initiation and propagation rates depend on pH and the electrochemical potential. Accordingly, plants have adopted the practices of injecting hydrazine to maintain reducing conditions, and of adding amines to the feedwater to maintain the pH within the range of 5 to 9. These measures have been successful in reducing the rate of degradation in tubes affected by IGA/SCC in some plants; however, other plants using the same measures have continued to experience IGA/SCC. The reason for this variability is not well understood, but there is mounting evidence that Pb is the cause.

Laboratory testing has demonstrated that lead is detrimental with respect to SCC of steam generator tubing alloys including Alloys 600MA, 600TT, 690TT, and 800NG. Although it is known that Pb concentrates in crevices, but the role of Pb is complicated by its interaction with other species. It forms insoluble compounds with many other species and is known to adsorb on iron oxide and other corrosion product deposits. Thus, the soluble Pb in the crevice may be orders of magnitude less than the available Pb. The threshold concentration of Pb in solution required for cracking is not known and no direct relationship between Pb deposits and cracking has been determined. In addition, Pb can be in several soluble forms. It has been hypothesized that the reason for variability in cracking due to Pb among plants is crevice conditions can make Pb either active or inactive with respect to its role in producing SCC. Thus, an important element

Introduction

in interpreting ongoing SCC tests and in identifying corrective measures will be the knowledge of the potential/pH conditions (Pourbaix Diagram) where Pb is soluble.

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EXPERIMENTAL PROCEDURES

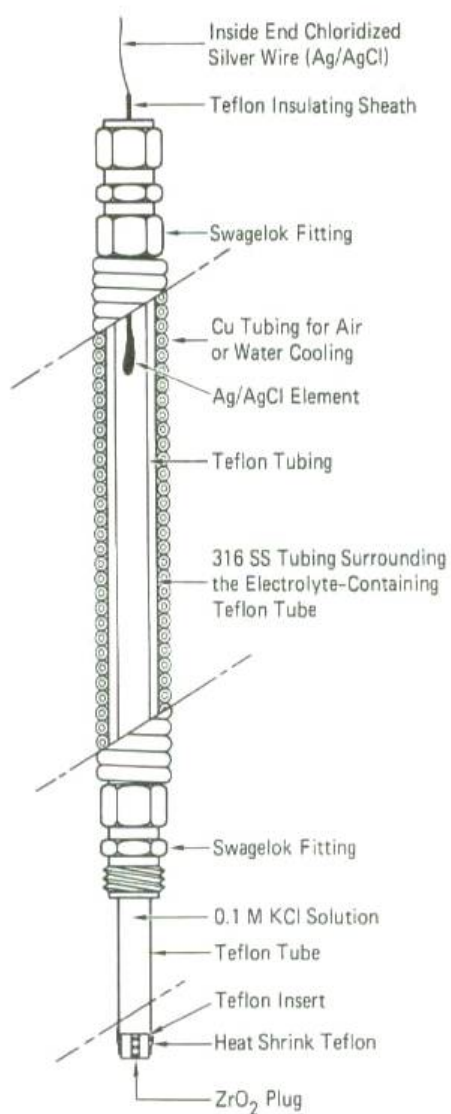
Electrochemical measurements were performed in an Alloy 718 autoclave designed and constructed for this program. The body of the two liter autoclave was sealed at both ends. It was operated in a horizontal position. The lid on one end had five symmetrically spaced ports for commercial Conax fittings to accommodate 3.2mm diameter Ni feedthrough rods. A high pressure gas introduction line with a safety pressure relief valve was welded into the center of the lid. The other lid had two ports for Conax fittings used for attaching a reference electrode and a pH electrode. The autoclave was surrounded by a thermally insulated electric heating blanket with an electronic PID temperature controller.

The working electrodes were cut from 3.2mm diameter 99.99% pure Pb rods, obtained from ABM Lead Corp. They were cut to form cylindrical specimens 1cm in length and tapped at one end to permit mounting on a 3.2mm diameter threaded Ni rod inserted in one of the ports. Before the specimens were attached to the rod they were activated by immersing in a 10% HCl solution. The Ni rod and 0.2mm length of the cylindrical Pb electrode were sleeved in heat shrink TFE tubing. A cylindrical Ni foil counter electrode, which completely surrounded the test samples, was spot welded to one of the Ni rods.

An external Ag/AgCl, pressure balanced, high temperature reference electrode was assembled using a design that was a modification of designs published previously [12, 13]. This was constructed using a 10cm long, 3mm O.D., 0.8mm wall Ti tubing to form the support for the active Ag/AgCl portion of the reference electrode. The reference compartment of the electrode contained a silver-plated 5 cm Ti rod. The plated Ag was chloridized anodically in 1 M HCl by passing $2\text{mV}/\text{cm}^2$ for two hours. The Ag plated Ti rod was then inserted into a 60cm long heat shrink TFE tube with approximately 2.5 cm protruding outside of the tube. The TFE/Ag/AgCl assembly was sealed in a Conax, ceramic insulated pressure fitting. A Swagelok fitting was attached to the other end of the Ag/AgCl coated Ti rod. The TFE tube was filled with ZrO powder and the end was sealed with a porous zirconia plug, 3mm by 1.3cm long. A reservoir of 0.1M KCl was attached to the Swagelok fitting on the Ti rod and solution was allowed to flow into and saturate the ZrO powder, forming a salt bridge between the Ag/AgCl and the porous zirconia plug. The reference electrode was checked for continuity and the potential was compared to a standard calomel reference electrode at room temperature (SCE). The potential difference was approximately 44 mV. The electrode was completed by attaching the Conax fitting into a copper tubing wrapped, stainless steel tube water jacketed for cooling the external compartment of the reference electrode assembly. A schematic and photograph of the Ag/AgCl electrode are shown in Figure 2-1.

Experimental Procedures

The pH measurements were made using a yttria-stabilized zirconia pH sensor. The assembly was obtained from GE. A schematic and picture of the pH electrode are shown in Figure 2-2.



(a)



(b)

Figure 2-1
Schematic (a) and Photograph (b) of External Pressure Balanced Ag/AgCl Reference Electrode

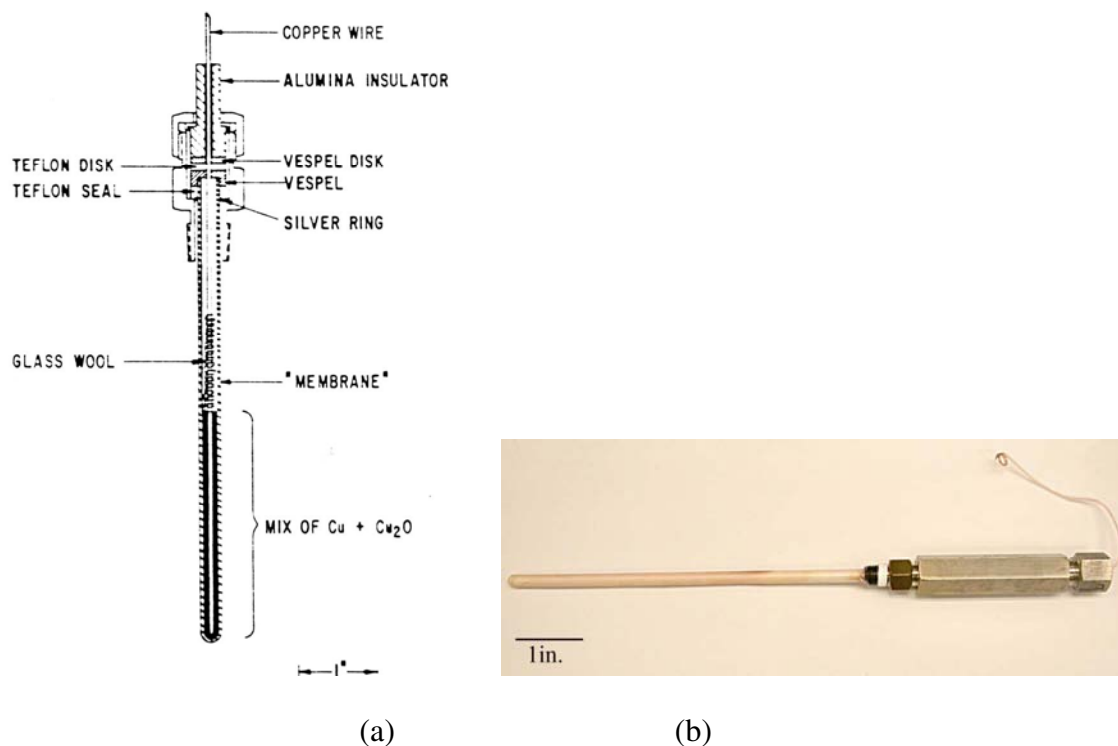


Figure 2-2
Schematic (a) and Photograph (b) of Yttria-Stabilized Zirconia pH Sensor

Figure 2-3 shows the autoclave with the attached electrodes. Figure 2-4 shows the autoclave surrounded by the thermal blanket and seated in the bottom section of the Al “blast shield” with the Ag/AgCl reference electrode to the right and the pH electrode to the left. The gas introduction and return lines are located above the autoclave.

Experimental Procedures



Figure 2-3
Autoclave Immediately After Sealing with Test Solution

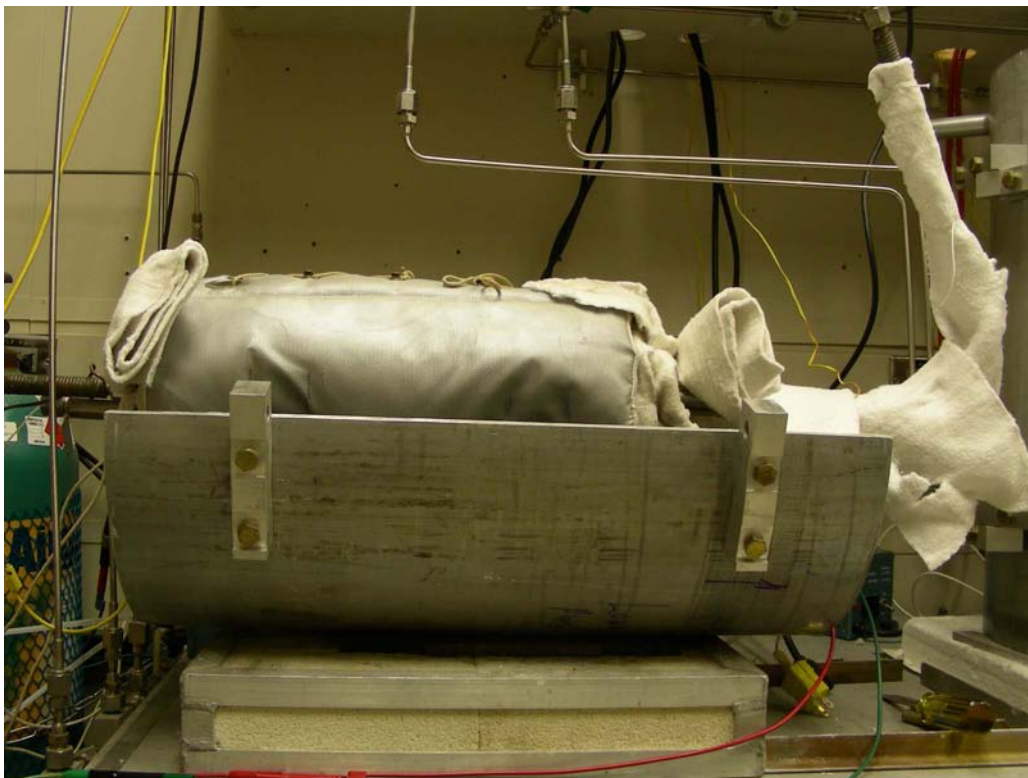


Figure 2-4
Autoclave Enclosed in Thermal Blanket and Seated in the Bottom Section of Clam Shell Blast Shield

The test solutions require an electrolyte which does not form insoluble compounds or soluble complexes with Pb and is not electrochemically active. The boric acid/sodium borate buffer system, using sodium hydroxide to adjust the pH, meets the requirements. The following test solutions were used with the MULTEQ pH calculations at 280°C and percent of soluble Pb species as shown:

pH 9.95:	1500 ppm B + 11,500 ppm Na + 1.0e-4m and 1.0e-3m Pb as PbO		
	PbOH ⁺	Pb(OH) ₂	Pb(OH) ₃ ⁻
	0.01%	2.1%	97.89%
pH 8.31:	1500 ppm B + 500 ppm Na + 1.0e-4m and 1.0e-3 m Pb as PbO		
	PbOH ⁺	Pb(OH) ₂	Pb(OH) ₃ ⁻
	15.2%	68.94%	15.9%
pH 6.15:	1500 ppm B + 0 ppm Na + 1.0e-4 m and 1.0e-3 m Pb as PbO		
	PbOH ⁺	Pb(OH) ₂	Pb(OH) ₃ ⁻
	96.9%	3.1%	

In each test, the quantity of electrolyte added was adjusted so that the electrolyte level was at least 5 mm above the top of the specimens at the 280°C test temperature. The cover gas was 5% hydrogen/95% argon. Before heating, the solution was deoxygenated in the autoclave by three pressurizing/aspirating cycles from 1.4 to 13.6 MPa (200 psia to 2000 psia). Each pressurization was held for 30 minutes followed by a slow release of the gas. Following the last aspiration, heating was begun with a 1.4 MPa (200 psia) overpressure to maintain a stable immersion level. The pH measurements were made before initiating the tests and at the end of the each test.

The test environment has a room temperature concentration of hydrogen of approximately 6 ppm. This is considerably higher than the 1 ppb hydrogen concentration in the secondary water of an operating steam generator. However, it is more relevant to consider the 3 ppm STP hydrogen concentration of the primary water than that of the secondary water. Since hydrogen diffuses through a steam generator tube at operating temperature, the hydrogen partial pressure at the OD of the tube and at a crack tip will closely approximate that in the primary water. The 5% hydrogen cover gas has a long history in autoclave SCC testing. It originated at B&W in caustic testing [14, 15] and has been used by Westinghouse [16, 17], Brookhaven [18], and French investigators [19]. These tests effectively benchmark the test results for the PbSCC work reported here.

Experimental Procedures

An EG&G Princeton Applied Research Model VersaStat II Potentiostat/Interface connected to a computer was used to obtain the polarization curves. The software used was EG&G SoftCorr™ Corrosion Measurement Software. Curves were taken using a scan rate of 0.3 mV/s.

3

RESULTS

Table 3-1 provides the results for the pH measurements and compares the measured results with the pH values calculated using MULTEQ. The agreement is excellent and provides credibility for both the lead and borate models used in MULTEQ.

Table 3-1
Measured pH Values for Test Solutions and MULTEQ Values

B, ppm	Na, ppm	pH			
		Pb, 1e-4 m MULTEQ	Pb, 1e-4 m Measured	Pb, 1e-3 m MULTEQ	Pb, 1e-3 m Measured
1500	0	6.1	6.1	7	6.8
1500	25	7.2	6.9	—	—
1500	500	8.3	8.2	8.3	8.2
1500	11500	10	9.9	10	9.9

Figures 3-1 through 3-6 show the polarization curves obtained for Pb and in some cases Ni. The curves show how the absolute value of the current density changes as the potential increases. The sweeps were initiated at 150 mV below the open circuit potential and scanned in a positive direction. The initial current is negative and decreases in absolute magnitude as the potential increases. It continues to decrease until it reaches a minimum value, at which potential (the corrosion potential) there is a polarity change and the current density begins to increase with increase in potential.

The results for Ni and Pb in the pH 7 solution with 1e-3 m Pb are shown in Figure 3-1. The abrupt increase in current density observed on a Pb electrode at approximately -0.520 V is an experimental artifact, otherwise the polarization curves for the two Pb electrodes almost superimpose. The corrosion potentials for the two Pb electrodes are -0.731 V and -0.740 V. This is only a 9mV difference and well within experimental error. The corrosion potential for Ni is -0.755 V. The current density from the Pb electrodes and Ni initially increases rapidly as the potential is scanned through the corrosion potential to more positive values. Then, at approximately -0.7 V the current density from Ni reaches a plateau while that from Pb continues to increase, but at a slower rate.

Results

The results for Pb in the pH 6.15 solution with $1\text{e-}4$ m Pb, in the pH 8.31 solutions with $1\text{e-}3$ m Pb and with $1\text{e-}4$ m Pb, and in the pH 9.95 solutions with $1\text{e-}3$ m Pb and with $1\text{e-}4$ m Pb are shown in Figures 3-2 thru 3-6, respectively. These curves are similar to those obtained for the pH 7 solution with $1\text{e-}3$ m Pb. The two polarization curves from Pb at each condition almost superimpose. The corrosion potentials for Pb obtained from the curves are as follows: the value at pH 6.15 is -0.730 V for the solution with $1\text{e-}4$ m Pb, the values at pH 8.31 are -0.811 V for the solution with $1\text{e-}3$ m Pb and -0.931 V in the solution with $1\text{e-}4$ m Pb, the values at pH 9.95 are -1.10 V for the solution with $1\text{e-}3$ m Pb and -1.14 V for the solution with $1\text{e-}4$ m Pb.

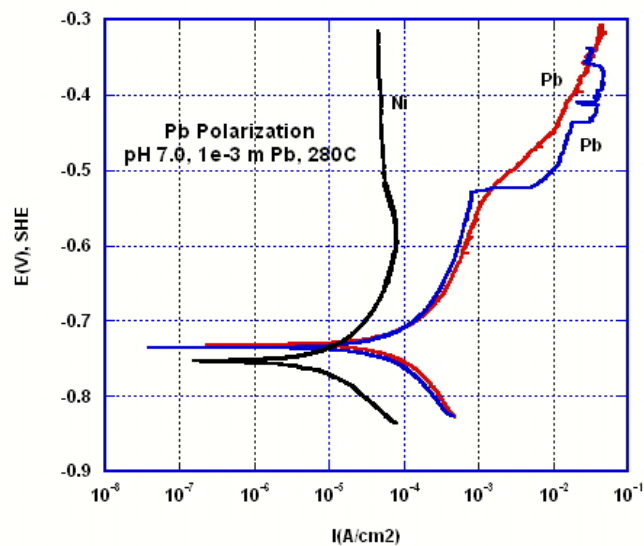


Figure 3-1
Polarization Curves for Pb and Ni in pH 7 Solution with $1\text{e-}3$ m Pb (Scan Rate 0.3 mV/s)

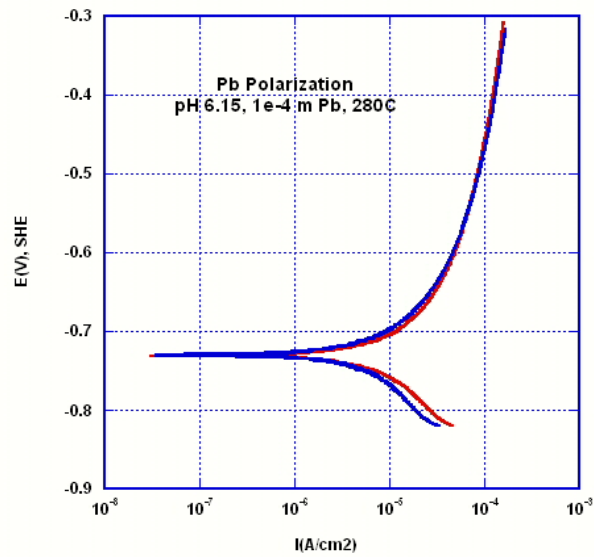


Figure 3-2
Polarization Curves for Pb in pH 6.15 Solution with 1×10^{-4} m Pb (Scan Rate 0.3 mV/s)

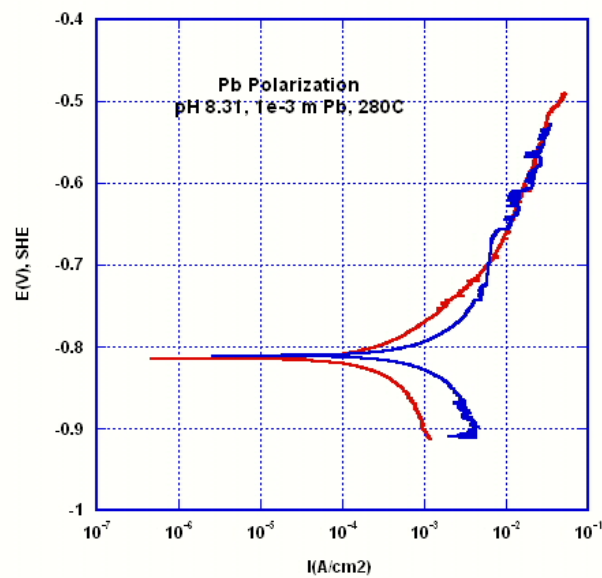


Figure 3-3
Polarization Curves for Pb in pH 8.31 Solution with 1×10^{-3} m Pb (Scan Rate 0.3 mV/s)

Results

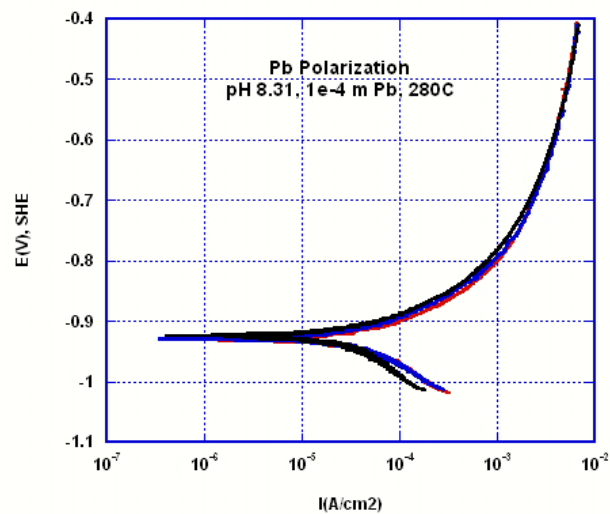


Figure 3-4
Polarization Curves for Pb in pH 8.31 Solution with 1e-4 m Pb (Scan Rate 0.3 mV/s)

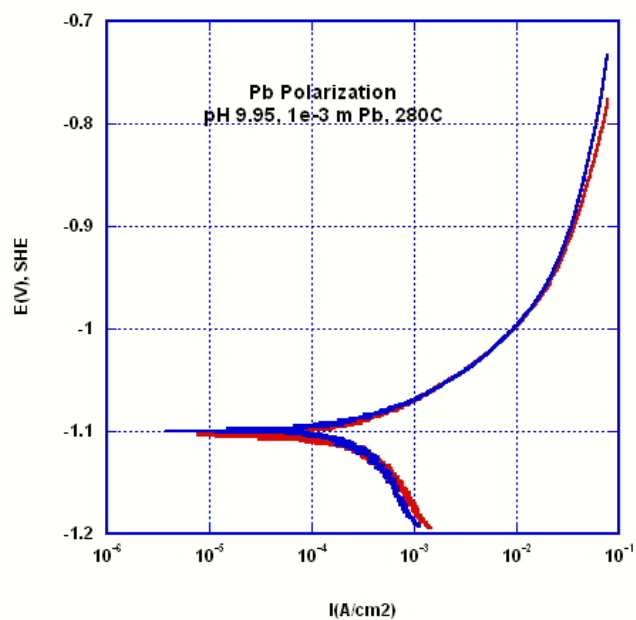


Figure 3-5
Polarization Curves for Pb in pH 9.95 Solution with 1e-3 m Pb (Scan Rate 0.3 mV/s)

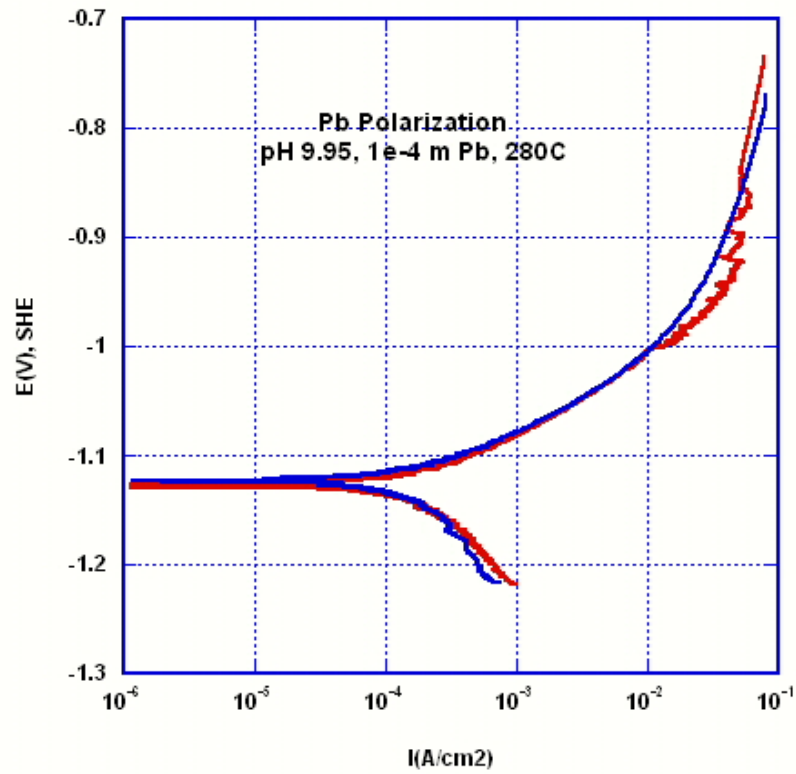


Figure 3-6
Polarization Curves for Pb in pH 9.95 Solution with 1e-4 m Pb (Scan Rate 0.3 mV/s)

4

DISCUSSION

The interpretation of these results depends upon the relating kinetic phenomena to thermodynamics. Using the potentiostatic method for applying a constant potential, it is possible to measure a reaction current. This reaction current results from oxidation reactions such as the dissolution of the metal electrode (Equation 4-1) or the formation of an oxide film (Equation 4-2).



Sweeping the potential while measuring the current can aid in understanding the behavior of film covered metals. The reaction current, following processes similar to Equations 4-1 and 4-2, is measured to obtain a characteristic polarization curve similar to the one in Figure 4-1. In this figure a schematic of a portion of a potential-pH diagram (Pourbaix diagram) is shown to the left. The relationship between these thermodynamic equilibria and kinetic processes are shown in the center schematic. The figure to the right labels important zones and transition points. Metals that have current-potential curves like those shown in Figure 4-1 are said to have active-passive-transpassive behavior. The currents shown are absolute values. At potentials below the M/M^{++} equilibrium potential, the current is negative, and positive above. The current increases rapidly as the potential is increased above the M/M^{++} equilibrium since this is the potential regime of thermodynamic stability of M^{++} ions. Rapid dissolution continues until the potential is reached that is the transition between thermodynamic stability of the metal ions and the metal oxide. This potential marks the onset of oxide film formation on the metal where a rapid decrease (usually several orders of magnitude) in current occurs. The metal then is protected by a passive film, and changes little with further increase in potential over a broad potential range. The current in this region is called the passive current, and it is typically on the order of a microampere per square centimeter or less.

The polarization curves from Pb clearly did not have a passive region. The current density continued to increase as the potential increased, reaching values in the milliampere range or higher. The only exception was the curves from the pH 6.15 solution with $1e-4$ m Pb, where the maximum current was approximately 0.3 mA.

Discussion

The results for Ni (Figure 3-1) are significantly different from those for Pb. The current density at potentials higher than -0.7 V did not change with increase in potential and remained in the 10 microampere range. This behavior suggests the formation of a passive film; however, since the current density in the passive range is several times higher than that usually observed for a highly protective passive film, the film does not have good protective properties. But still does not prevent a relatively high corrosion rate. This is in accordance with the observation, mainly during stress corrosion tests, that the presence of Pb causes thick scaling on Alloy 600 and Alloy 690. Analyses of the films show that they are oxides with Pb incorporated in them, suggesting that the incorporation of Pb causes the passive oxide films to lose some of their protective properties.

These results are in general agreement with the Pourbaix diagrams based on work by Chen [20] and Miglin [21]. The Pourbaix diagram for Pb superimposed on that for Ni at 300°C, from this work, is shown in Figure 4-2. Also shown are the potential-pH conditions that water is stable. Water decomposes to form hydrogen gas at a pressure of one atmosphere at the potential-pH values on line “a”; whereas, water decomposes to form oxygen gas at one atmosphere at the potential pH values on line “b”.

The diagram for Pb suggests that only soluble species are formed in the range from pH 6.15 to pH 9.95, in accordance with the polarization curves obtained in this range. The current was not affected by changes in concentration, which is another indication that a film was not formed. This behavior suggests that the reaction expressed by Equation 4-2 did not occur as such a reaction would follow the concentration dependence given by Equation 4-3:

$$\text{Log (Pb}^{++}\text{)} = 12.65 - 2 \text{ pH}$$

Eq. 4-3

The Pourbaix diagram for Ni indicates the formation of a NiO passive film at pH 6.15 at an equilibrium potential below that of the Pb/Pb⁺⁺ equilibrium. The polarization curve for Ni followed the predictions of Figure 4-1; 1) there was no active peak, indicating that there was no film free dissolution potential regime, 2) there was a passive region, suggesting passive film formation, and 3) the corrosion potential was below that of Pb.

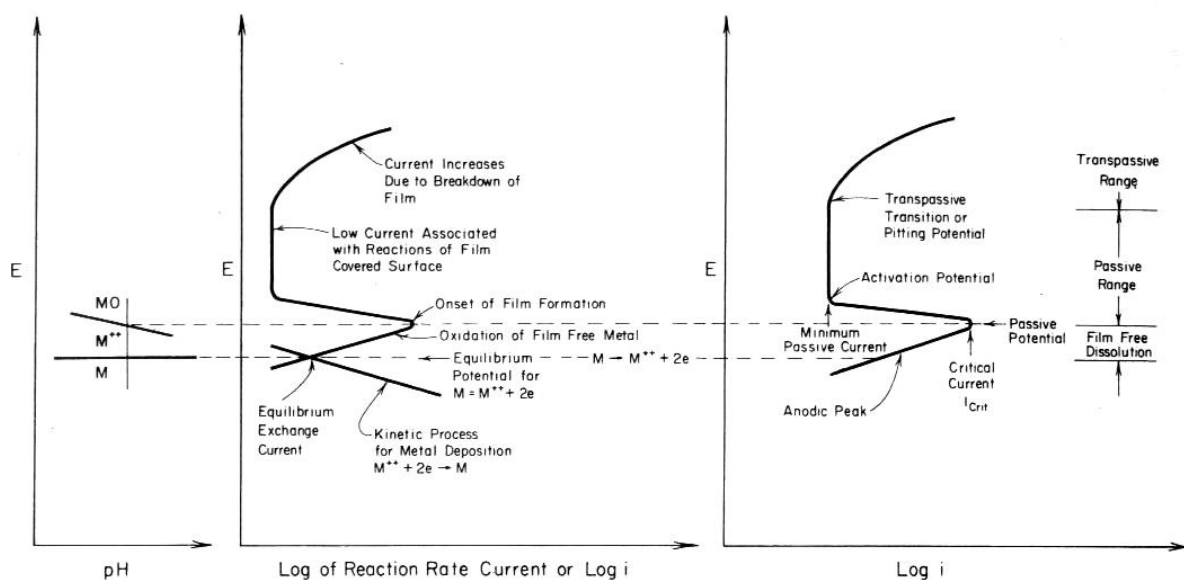


Figure 4-1
Schematic Relationship between Polarization Behavior and Thermodynamics, Showing Various Features in Polarization Curves and Defining Regions of Film Free Dissolution, Passivity and Transpassivity

Discussion

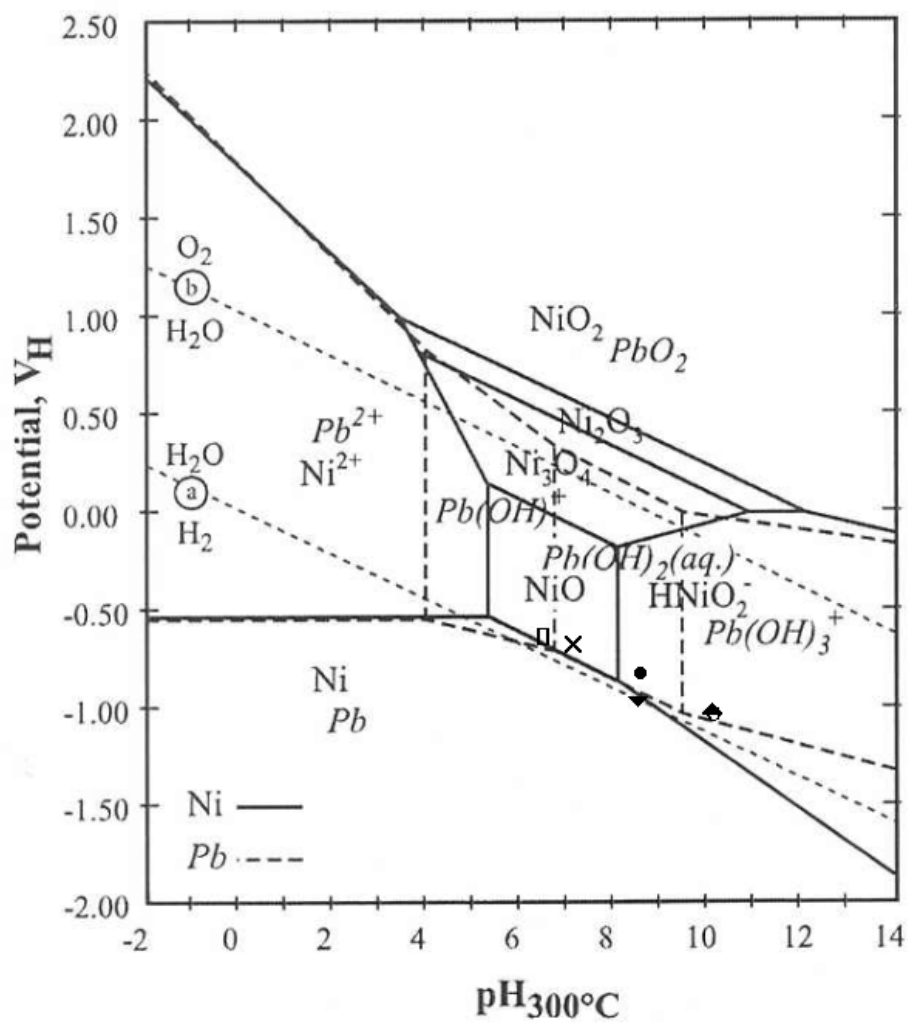


Figure 4-2
Pourbaix Diagrams for Ni (Solid Lines) and Pb (Dotted Lines) at 300°C

5

CONCLUSIONS

Potentiodynamic polarization curves were measured at 280°C for pure Ni and Pb electrodes. To eliminate possible formation of Pb complexes and pH shifts during testing, 1500 ppm boric acid solutions with pH adjusted with sodium hydroxide were used. The test solutions had 1.0e-3 m Pb and 1.0e-4 m Pb at pH_T of 6.15, 8.31, and 9.95. Electrochemical potential was measured against a Ag/AgCl reference electrode. A Cu/CuO electrode was used for pH measurements. Based on the results of this experiment, the following conclusions were made:

1. Pb does not form a passive film in the pH range of 6 to 10 in 280°C water.
2. The Pourbaix diagram given in the EPRI report NP7367 best describes the thermodynamics of Pb in secondary steam generator water.

The corrosion potential of Ni at pH 6, and likely to pH 10, is less than that of Pb. Thus Pb can oxidize and electroplate onto Ni.

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REFERENCES

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1. H.R. Copson and S.W. Dean, "IGSCC of Nickel Alloys in Lead Contaminated High Purity Water," *Corrosion Vol 21*, NACE, Houston, TX, 1965, p.1.
 2. B.P. Miglin, Investigation of Lead as a Cause of Stress Corrosion Cracking at Support Plate Intersections; NP-7367, EPRI, Palo Alto, 1991.
 3. R. Kilian, "Influence of Lead on the SCC Behavior of SG Tubing Materials," *IAEA Specialists Meeting on Steam Generator Problems and Replacement*, International Atomic Energy Agency, Madrid 1993, p137.
 4. H.R. Copson, D. van Rooyen, A.R. McIlree, "Stress Corrosion Behavior of Ni-Cr-Fe Alloys in High Temperature Aqueous Solutions," *Proceedings of the 5th International Congress on Metallic Corrosion*, N. Sato, editor, NACE, Houston, TX, 1974, p. 396.
 5. G.P. Airey, "The Effects of Carbon Content and Thermal Treatment on the SCC Behavior of Inconel Alloy 600 Steam Generator Tubing," *Corrosion Vol. 24*, NACE, Houston, TX, 1979, p129.
 6. J. Lumsden, A. McIlree, R. Eaker, "Effects of Lead on SCC of Alloy 600 and Alloy 690 in Prototypical Steam Generator Chemistries", *Proceedings of the 12th International Conference on Environmental Degradation of Materials in Nuclear Power Systems—Water Reactors*, TMS, ANS, and NACE, 14-18 August, 2005.
 7. Lumsden, J., and McIlree, A., "Factors Affecting PbSCC in Alloy 600 and Alloy 690 Steam Generator Tubing", *Proceedings of Fontevraud 6*, September 2006.
 8. McIlree, A., Fruzzetti, K., Gorman, J., Shack, W., Staehle, R., and Stevens, J., "A Case for the Major Influence of Lead and Sulfur in the Secondary Side Degradation of PWR Steam Generator Tubing", *Proceedings of Fontevraud 6*, September 2006.
 9. A. Agrawal and J.N.P. Paine "Lead Cracking of Alloy 600 – A Review" *Proceedings of the 4th International Conference on Environmental Degradation of Materials in Nuclear Power Systems—Water Reactors*, TMS, ANS, and NACE, 14-18 August, 1989.
 10. R. Staehle, "Clues and Issues in the SCC of High Nickel Alloys Associated with Dissolved Lead", *Proceedings of the 12th International Conference on Environmental Degradation of Materials in Nuclear Power Systems—Water Reactors*, TMS, ANS, and NACE, 14-18 August, 2005.
 11. *Proceedings: 2005 EPRI/ANL/NRC Workshop on Effects of Lead and Sulfur on the Performance of Secondary Side Tubing of Steam Generators in PWRs*, EPRI 1012780, December 2005.
 12. D. D. Macdonald, A. C. Scott and P. Wentrcck, "External Reference electrode for Use in High Temperature Aqueous Systems", *J. Electrochem. Soc.* 126, 908 (1979).

13. M. J. Danielson, "The Construction and Thermodynamic Performance of Ag-AgCl Reference Electrode for Use in High Temperature Aqueous Environments Containing H₂ and H₂S", Corrosion 35, 200 (1979).
14. L. Niedrach, "Use of a High Temperature pH Sensor as a Pseudo-Reference Electrode in the Monitoring of Corrosion and Redox Potentials at 285C" , J. Electrochem Soc. 129, 1221 (1982)
15. J.R. Cels, "Stress Corrosion Cracking of Stainless Steel and Nickel Alloys at Controlled Potentials in 10% Caustic Soda Solutions at 550°F", J. of the Electrochemical Society 123, 1152 (1976).
16. G.J. Theus and J. R. Cels, "Slow Strain Rate Technique: Application to Caustic Corrosion Cracking Studies", in Stress Corrosion Cracking-the Slow Strain Rate Technique, ASTM STP 665, G. M. Ugianski and J. H. Payer, eds, ASTM, pp 81-96 (1979)
17. N. Pessall, Corrosion Science 20, 225 (1980).
18. G.P Airey, " Optimization of Metallurgical Variables to Improve Corrosion resistance on Inconel Alloy 600" EPRI-NP3051, Palo Alto, CA (1983).
19. R. Bandy, R. Roberge, and D. Van Rooyen, "Intergranular Attack and Stress Corrosion Cracking of Alloy 600 in High Temperature Caustic Solutions Containing Contaminants", EPRI-NP-3137, Palo Alto, CA (1985).
20. C. M. Chen, K. Aral, and G. J. Theus, "Computer Calculated Potential pH Diagrams to 300C", NP-7367, EPRI, Palo Alto, 1983.
21. B. P. Miglin, "Investigation of Lead as a Cause of Stress Corrosion Cracking at Support Plate Intersections", NP7367, EPRI Palo Alto, 1991.

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