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**STUDIES OF LEAD-15 WT % TIN ALLOY CORROSION
IN AN INDUSTRIAL ENVIRONMENT**

J. S. Bullock

October 1978

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OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

*prepared for the U.S. DEPARTMENT OF ENERGY under
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STUDIES OF LEAD-15 WT % TIN ALLOY CORROSION IN AN INDUSTRIAL ENVIRONMENT

J. S. Bullock
Chemicals & Plastics Department
Y-12 Development Division

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Oak Ridge Y-12 Plant

P. O. Box Y, Oak Ridge, Tennessee 37830

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ABSTRACT

The corrosion properties of a lead-15 wt % tin alloy in aqueous solutions having a pH from 2 to 6 were studied as a function of contamination by sulfur dioxide, the chloride ion, the fluoride ion, and carbon dioxide. Electrochemical methods were used. Higher acidity caused higher corrosion rates. Sulfur dioxide and carbon dioxide were found to inhibit corrosion, the chloride ion to have a mild aggressive effect, and the fluoride ion to have a noticeable aggressive effect. Semiquantitative estimates of the effects were made.

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SUMMARY

A corrosion problem in a lead-alloy-lined air compressor inspired an electrochemical study of the lead-15 wt % tin alloy in corrosion environments composed of Na_2SO_4 and H_2SO_4 solutions containing $\text{SO}_2/\text{SO}_3^{2-}$, Cl^- , F^- , and CO_2 . Potentiodynamic scans, constant potential currents, and rest potentials were observed as a function of the species addition. For the actual corrosion situation, increased SO_2 was determined to be detrimental; Cl^- mildly so, and F^- noticeably detrimental. Carbon dioxide, in certain concentrations, inhibited corrosion.

INTRODUCTION

A corrosion problem was occurring with a lead-tin-alloy-plated copper heat exchanger used in air compressor service at the Paducah Gaseous Diffusion Plant.^(a) Failure of the air compressor system was occurring through deposition of a corrosion product on the high-speed centrifugal impeller used in the subsequent stages of the multistage system. While the lead-alloy lining was intended to cope with the high-SO₂ environment of the installation, higher-than-usual atmospheric concentrations of fluoride and chloride ions existed. The question as to the effect of these species on the corrosion behavior of the lead-tin alloy needed to be answered and, therefore, a small-scale study was funded at the Oak Ridge Y 12 Plant.^(a)

(a) Operated by the Union Carbide Corporation's Nuclear Division for the Department of Energy.

CORROSION OF A LEAD-TIN ALLOY

BACKGROUND INFORMATION

Preliminary work¹ indicated that the heat exchanger, which cools the compressed air from about 135° C to about 27° C, was subject to a condensing environment wherein the condensate contained sulfate, fluoride, and chloride ions. Sulfate had been determined at up to 600 ppm and averaged about 60 ppm, fluoride had been observed up to 21 ppm, and chloride had been observed up to 12 ppm. The pH of the dewatering effluent^(b) ranged from 3.5 to 7.0. The corrosion product removed from the impeller blades analyzed, in wt %, at about 37 Pb, 37 Cu, 22 SO₄⁼, 1.7 CO₃⁼, 0.35 F⁻, 0.03 Cl⁻, and small concentrations of iron and silicon. Terne (tin-lead) alloys are commonly used as corrosion-resistant coatings in environmental service.²

Sulfur dioxide has been used³ in testing tin plates at a concentration of up to 2.5%, together with high humidity. Tin discolors above an SO₂ concentration of 0.2%. Atmospheric exposure of tin results in the formation of comparable amounts of Sn(II) and Sn(IV) oxides.⁴ The graph of Figure 1 indicates the influence of pH on the corrosion rate of tin.⁵ At a pH of 2, the corrosion rate is about five times that at pH 6. The corrosion rate of lead, as inferred from the solubility of PbO, is also highly dependent on the pH, as can be seen in Figure 2.⁶ In the more acidic area (pH < 7) of interest to this study, the solubility of lead compounds will depend on the specific anion involved; lead nitrate having a solubility of about 0.2 M at about 30° C.⁷ The corrosion rate will then depend on the presence and concentration of species which can cause precipitation of lead ions and on the presence and concentration of depolarizing species. Below a pH of about 5.2, the hydrogen ion is a possible depolarizer; although, due to the low exchange current for H⁺/H₂ on lead⁸ ($i_0 = 5 \times 10^{-12}$ A cm⁻²), it should not be significant unless the lead is contaminated with low-hydrogen-overvoltage material. Oxygen should be the most significant depolarizer in the system of interest, and it should be able to accelerate the corrosion at any pH. Of the common anions, only carbonate (and sulfate, depending on the form of lead oxide compared) forms lead(II) compounds less soluble than lead oxide.⁷ Therefore, carbonate is the most likely candidate for corrosion inhibition of lead by the precipitation mechanism.

Figure 1. CORROSION RATE OF TIN AS A FUNCTION OF pH. (After Chatalov⁵)

(b) Effluent from the water-droplet-removal stage following the heat-exchange stage.

The ternary compound PbSnO_3 is known to exist,⁹ although its existence in the corrosion films on lead-tin alloys is unproven. The stability and reactions of lead carbonate and sulfite are reported in several documents.¹⁰⁻¹³

EXPERIMENTAL WORK

Fifty grams of an alloy of composition lead-15.1 wt % (23.7 at %) tin were melted and cast into a rod under a pressure ≤ 1 Pa. (The rod was 0.470 cm in diameter.) A 2.5-cm length of this rod was soldered to a short copper wire (carefully!) and mounted axially in a 3-cm-high standard cylindrical epoxy metallographic mount. Once mounted, the end surface was ground to 600 grit, which exposed 0.173 cm^2 of alloy surface for experimentation.

A Princeton Applied Research Model 173 potentiostat was used to measure and control the sample potential. A double-junction Ag/AgCl electrode with an Na_2SO_4 intermediary electrolyte was used as a reference. Polarization and rest-potential experiments were carried out in a cell with separate sample, counter electrode, and reference electrode compartments. A Luggin-type capillary extended from the reference electrode compartment to within 1 mm of the sample surface. The effective volume of the sample compartment was 2.5 liters. Stirring at a constant rate was provided. Two bubblers were used to allow charging the solution with O_2 and CO_2 .

An aqueous solution of Na_2SO_4 (6.25 mM), containing 600 ppm $\text{SO}_4^{=}$, was used as one electrolyte; the other was a H_2SO_4 solution of the same concentration. These solutions had initial pH values of 5.90 and 2.20, respectively. In the course of the experiment, the solutions were dosed with, respectively, 4.09 mM Na_2SO_3 and 4.09 mM SO_2 . The SO_2 was added by filling an evacuated 250-ml gas sample bottle with 1 atm SO_2 , draining 250 ml of the H_2SO_4 solution from the cell, then immersing one end of the bottle and opening the valve (injecting a small amount of solution into the bottle to more rapidly initiate the takeup of SO_2). Since the required concentration was about 0.5% of the saturation concentration of SO_2 in water, bubbling was obviously not acceptable. This dosed solution was then returned to the cell. The Na_2SO_3 was added to the Na_2SO_4 solution by adding a 10-ml aliquot of a 1.022 M Na_2SO_3 solution to the cell, resulting in the same molar concentration as the SO_2 -in- H_2SO_4 solution. Dosing of the F^- and Cl^- was done similarly, adding 10-ml aliquots of 0.276 and 0.085 M NaF and NaCl, respectively. These concentrations gave final solutions of 1.105 mM (21 ppm) in F^- and 0.339 mM (12 ppm) in Cl^- .

Polarization experiments were run by filling the cell with the H_2SO_4 (Na_2SO_4) solution, inserting the mounted specimen in its holder, initiating stirring and O_2 bubbling, then

Figure 2. INFLUENCE OF pH ON THE SOLUBILITY OF RED AND YELLOW LEAD MONOXIDE AND HYDROXIDE [$\text{Pb}(\text{OH})_2$] at 25° C. [After Pourbaix⁶; a - Red PbO , b - Yellow PbO , c - $\text{Pb}(\text{OH})_2$]

spiking the cell with SO_2 (Na_2SO_3), Cl^- , and F^- , followed by bubbling CO_2 . After setting up each new condition, at least two polarization sweeps in succession between certain potential limits were performed at a rate of potential change of about 5 mV/sec. Other experiments were conducted to examine the effect on the rest (no current) potential (and on the current at constant potential) of spiking the cell solution with aliquots of the previously mentioned solutions.

In several cases, loss of potentiostatic control occurred and limited the range over which the potential could be varied during the polarization-curve studies. Loss of control also entirely prohibited potential control in one case. This effect is judged to be due to excessive impedance in the specimen/counter electrode circuit, a result of the low conductivity of these dilute solutions and also partly a result of the specific cell geometry used. A more compact cell with a lower cell constant would probably permit more flexibility in studies of systems of this type.

Temperature was kept at $33.4 \pm 1.9^\circ \text{C}$ ($92.1 \pm 3.4^\circ \text{F}$) to a confidence of 95%. Final pH values after all polarization and other studies were 2.06 and 4.74.

RESULTS AND DISCUSSION

Polarization Experiments

Sample results of polarization experiments are illustrated for the Na_2SO_4 solution in Figures 3 and 4 and for the H_2SO_4 solution in Figures 5 and 6. Initial pH of the Na_2SO_4 solution was 5.90; but, after the series of aliquot additions and polarization curves, the value decreased to 4.74. Initial pH of the H_2SO_4 solution was 2.20; after addition of the SO_2 it was 2.17; after the entire series of aliquot additions and polarization curves the value was 2.06. The values of some pertinent features on the polarization curves are summarized in Table 1.

Not listed in Table 1 is the change in the value of the potential at which the (-)-to-(+)(c) anodic current peak occurs. This is a peak characteristic of an active/passive transition, and its potential as well as amplitude is a clue to the relative corrosion resistance of the alloy. In general, lower potentials and lower amplitudes for this peak both indicate better corrosion resistance.¹⁴ For the Na_2SO_4 solution, the amplitude of this peak and other currents in its vicinity drop as SO_3^{2-} , Cl^- , and F^- are added; however, its potential does not change. When CO_2 is added, although the amplitude increases, the potential moves from about - 0.335 to - 0.415 V vs Ag/AgCl. Additionally, the (-)-to-(+) current crossover potential becomes more positive when CO_2 is added—enough so that passivation is reached soon after the first positive current flows. Finally, another criterion of corrosion rate is the current level at which the extrapolated anodic and cathodic curves meet around the zero current potential—the lower this value, the lower the corrosion rate. Notice, from Figures 3 and 4, that before adding CO_2 , this value is just above 0.1 mA/cm²; after adding CO_2 , the value

(c) This expression signifies a potential sweep in the direction from (-) to (+) values.

Figure 3. POLARIZATION BEHAVIOR OF LEAD-15 Wt % TIN ALLOY IN AN OXYGENATED SODIUM SULFATE SOLUTION. [Pb-15 Sn in 6.25 mM Na_2SO_4 (O_2)]

becomes more on the order of 0.01 mA/cm^2 . After lengthy CO_2 exposure, this value seems to increase again, about which more will be said later. The rest potentials do not agree with the zero-current potentials, but this relationship is common with potentiodynamic voltammetric studies.

For the H_2SO_4 solution, the anodic passivation peak occurs with a higher amplitude than for Na_2SO_4 , particularly after the addition of SO_2 , Cl^- , and F^- . However, passivation again occurs almost immediately after onset of the positive current, and the hysteresis between the (+)-to-(-) and (-)-to-(+) zero current potentials is greater than for Na_2SO_4 . There is no detectable effect of CO_2 in this case; due, most likely, to the instability of lead carbonates in acid solution. The overload region indicated on Figure 5 is an area which, for the system used in this study, was inaccessible due to the onset of oscillation. This situation was also responsible for contracting the anodic-region studies with Na_2SO_4 .

Differences seen between the $\text{SO}_3^{=}/\text{SO}_2$, Cl^- , F^- , and CO_2 species for the polarization studies in the two solutions are summarized as follows:

1. For $\text{SO}_3^{=}/\text{SO}_2$ - In the Na_2SO_4 solution, the crossover and rest potentials drop, as well as the anodic and cathodic peaks. Since $\text{SO}_3^{=}$ is a reductant, a drop in potential is not surprising, although the drop in the anodic peak value indicates that its effect in improving the metal passivation exceeds the effect of its own oxidation at these potentials. In the H_2SO_4 solution, SO_2 actually increases both the potential and level of the anodic (and cathodic) peaks. This result suggests improved passivation from the potential's point of view and oxidation of the SO_2 from the current's point of view. Apparently, the surface oxides at the two pH values are significantly different.
2. For Cl^- - These changes are not strong and somewhat contradictory in the case of the rest potential compared to the anodic current peak for H_2SO_4 . On balance, little change is indicated by either parameter.
3. For F^- - The indications are again contradictory, with the final rest potentials and anodic peak currents changing in "opposite" directions for both solutions. The effect would seem to be subtle; and, possibly, in opposite directions for H_2SO_4 compared to Na_2SO_4 .
4. For CO_2 - There is essentially no effect in H_2SO_4 ; due, probably, to carbonate instability. There is some increase in the anodic current which is not explained at this time. In Na_2SO_4 , all potential changes indicate improved passivity, although the anodic current peak level actually rises considerably. This rise is not understood at this time.

This information is summarized in Table 1, which also shows averages taken over all the H_2SO_4 and Na_2SO_4 conditions, with differences. This information gives an idea as to the overall pH factor effect. The difference in pH between the two solutions was 3.70, initially,

Figure 4. POLARIZATION BEHAVIOR OF LEAD-15 Wt % TIN ALLOY IN AN OXYGENATED SODIUM SULFATE SOLUTION CONTAINING $\text{SO}_3^{=}$, Cl^- , AND F^- . [Pb-15 Sn in 6.25 mM Na_2SO_4 (O_2)]

Figure 5. POLARIZATION BEHAVIOR OF LEAD-15 Wt % TIN ALLOY IN AN OXYGENATED SULFURIC ACID SOLUTION. [Pb-15 Sn in 6.25 mM H_2SO_4 (O_2)]

Figure 6. POLARIZATION BEHAVIOR OF LEAD-15 Wt % TIN ALLOY IN AN OXYGENATED SULFURIC ACID SOLUTION CONTAINING SO_2 , Cl^- , AND F^- . [Pb-15 Sn in 6.25 mM H_2SO_4 (O_2)]

Table 1
PERTINENT POLARIZATION PARAMETERS FOR LEAD-15 Wt % TIN IN OXYGENATED
SULFATE SOLUTIONS WITH NOTED ADDITIONS

Species Added	Initial Rest Potential, Before Polarization Cycles(1,2) (V)	Final Rest Potential, After Polarization Cycles(1,2) (V)	Negative-to-Positive (-)-(+) Values		Positive-to-Negative (+)-(-) Values	
			Current Peak Level, Anodic (log i)	Crossover Potential(2) (V)	Current Peak Level, Cathodic (log /i/)	Crossover Potential(2) (V)
<u>H₂SO₄</u>						
Only	-0.222	-0.340	-3.00	-0.450	-2.85	-0.285
and SO ₂	-0.270	-0.415	-2.80	-0.420	-2.60	-0.235
and Cl ⁻	+0.030	-0.360	-2.95	-0.420	-2.50	-0.300
and F ⁻	-0.250	-0.350	-2.80	-0.420	-2.50	-0.335
and CO ₂	-0.320	-0.360	-2.75	-0.435	-2.55	-0.350
Only	-0.194	-0.230	-3.05	-0.470	-2.50	-0.420
<u>Na₂SO₄</u>						
Only	-0.380	-0.235	-3.10	-0.500	-2.80	-0.460
and SO ₃ ⁼	-0.240	-0.205	-3.47	-0.505	-3.01	-0.490
and Cl ⁻	-	-0.235	-3.62	-0.470	-2.98	-0.490
and F ⁻	-0.150	-0.255	-3.77	-0.480	-3.09	-0.480
and CO ₂	-0.120	-0.195	-3.28	-0.440	-3.10	-0.470
Average H ₂ SO ₄	-0.206	-0.365	-2.860	-0.429	-2.600	-0.301
Average Na ₂ SO ₄	-0.223	-0.225	-3.448	-0.479	-2.996	-0.478
Δ Value	-0.017	+0.140	-0.588	-0.050	-0.396	-0.177
[Na ₂ SO ₄] - [H ₂ SO ₄]			(x0.258)		(x0.402)	

(1) Not generally true steady-state values.

(2) vs Ag/AgCl.

and 2.68, finally. If a potential change of -0.0591 V/unit (due to metastable film formation) is appropriate as a model, then potential differences from -0.219 to -0.158 V could be expected in comparing Na₂SO₄ to H₂SO₄. Such difference values were not seen; in fact, in general, changes of the opposite sign were seen, indicating that protection of the alloy by film formation is very poor in the H₂SO₄ solution compared to the Na₂SO₄ solution. Such a conclusion is also supported by the higher anodic current peak for the acid. For the two solutions prior to addition of other species, the mode of approach of the rest potential to a final value is somewhat different, as can be seen in Figure 7, the final values approached having a difference of 0.163 V. This relationship may, again, indicate worsening of the corrosion performance of the alloy in the H₂SO₄ solution, compared to the Na₂SO₄ solution.

Constant-Potential Spiking Tests

Studies just described indicated reasonably strong effects due to SO₃⁼/SO₂ and CO₂ (in Na₂SO₄) on the corrosion behavior of the Pb-15 Sn alloy. The effects of Cl⁻ and F⁻,

Figure 7. REST POTENTIAL OF LEAD-15 Wt % TIN ALLOY AS A FUNCTION OF TIME AFTER IMMERSION IN OXYGENATED SOLUTIONS.

however, were too subtle to be revealed by studies over such broad potential scan ranges. A second method, used to obtain a better "signal-to-noise ratio" for the effect, consisted of holding at a specific potential vs the Ag/AgCl reference and observing the anodic current as a function of time, as the solution was spiked with the species of interest.

The Na_2SO_4 solution used in prior polarization studies (already containing 600 ppm SO_3^- , less whatever had been consumed in oxidation to SO_4^-), 12 ppm Cl^- , 21 ppm F^- , and whatever concentration of CO_2 was obtained by continuous bubbling (CO_2 solubility in water at $33.4^\circ\text{C} = 1150$ ppm)⁷ was used for the first spiking test. Results of this test are illustrated in Figure 8. A shot of CO_2 was added first. This injection initially caused a drop in current on the alloy; but, as bubbling was continued, the current increased to beyond the level obtained previously (the currents for this study were all in the 0.01 to 0.1 mA/cm² range). This effect is similar to that of Figure 4, where the polarization curve continued to change with time after the addition of CO_2 , and may be due to production of a somewhat more soluble bicarbonate similar to those of the alkaline earths. An addition of 600 ppm SO_3^- caused a dramatic drop in the current, over a 3-minute period, to a level 0.45 of that which existed before the SO_3^- addition. This behavior is consistent with either an improvement in the protective film produced by removing oxygen as a depolarizing species (similar to the effect observed for SO_3^- in reducing the corrosion rate of tin in an alkaline solution¹⁵), or production of a less-soluble film of a lead sulfite. The only reference found to the

Figure 8. RESPONSE OF CURRENT DENSITY AT CONSTANT POTENTIAL OF CERTAIN ADDITIONS TO AN Na_2SO_4 SOLUTION. (Solution already Contained some CO_3^- , SO_3^- , Cl^- , and F^-)

relative solubilities of lead sulfate and lead sulfite¹⁰ indicates a solubility ratio of 400:1 for the respective compounds (but a heat of formation, for PbSO_4 , that is 62 kcal more negative than for PbSO_3). An addition of 12 ppm Cl^- caused no detectable change in the current level, while an addition of 21 ppm F^- caused a transient increase in the current to a level 1.08 times that of the original value.

An H_2SO_4 solution, initially without an added species, was used for the next spiking test. Results of this test are reported in Figure 9. Spiking with SO_2 in this case was done by adding 25 ml of a 6.3% solution of SO_2 in water to the 2.5-liter sample chamber, which produced 630 ppm SO_2 in the solution. The result of this spike was a drop to 0.74 of the original current. As with the Na_2SO_4 solution, addition of 12 ppm Cl^- had no detectable effect on the current level; addition of 21 ppm F^- , however, increased the current level to 1.14 times the original value. Addition of CO_2 had no effect, as has been indicated previously.

Rest-Potential Spiking Tests

A final test was done by spiking an Na_2SO_4 solution. This solution was diluted somewhat (to about 480 ppm SO_4^{2-}) from the original. Apparently, this slight dilution was enough to increase the resistance in the control circuit to the point of instability, because attempts to control the potential at any useful value resulted in oscillation. Therefore, this test was done by observing changes in the rest potential due to the addition of species. Results are given in Figure 10.

Figure 9. RESPONSE OF CURRENT DENSITY AT CONSTANT POTENTIAL TO CERTAIN ADDITIONS TO AN H_2SO_4 SOLUTION.

Addition of 12 ppm Cl^- caused a transient 5-mV negative shift in the alloy potential—only a mild response. Addition of 21 ppm F^- caused a negative shift of long duration, which peaked at 15 mV. Addition of 600 ppm SO_3^{2-} caused a strong negative shift of 27 mV, which seemed to occur in two stages. Addition of CO_2 produced a dramatic positive shift in potential of 83 mV. Stopping the flow of CO_2 was followed by a decay of the potential back toward the original value. In environments where it is stable, PbCO_3 may be a more effective passivating species than PbSO_3 , as its heat of formation is 10 kcal more negative.⁸ Turning the gas on then off again produced a similar response. Leaving the CO_2 on for a long period of time caused a positive shift, then a drift to more negative values. This trend

could be evidence of de-passivation at high CO_2 concentrations due to bicarbonate formation. Figure 11 shows the effect of the corrosion behavior of lead after introducing CO_2 to the lead/water system.⁶ Since saturated CO_2 in water only reaches a pH value of 6.38,¹⁶ and the "corrosion" zone for the system with CO_2 only begins

at a value of about 5.0, bicarbonate formation may not be the cause of the apparent de-passivation. However, the lines of Figure 11 are drawn for equilibrium at Pb^{++}

Figure 10. RESPONSE OF THE LEAD-15 Wt % TIN ALLOY POTENTIAL IN AN Na_2SO_4 SOLUTION TO CERTAIN ADDITIONS OF SELECTED SPECIES.

Figure 11. THEORETICAL CONDITIONS OF CORROSION, IMMUNITY, AND PASSIVATION OF LEAD AT 25° C. (After Pourbaix⁶)

concentrations of $1 \mu\text{M}$. Another complication is that surface films do not necessarily reach a composition in agreement with the Pourbaix diagrams.¹⁷

Comments on Reduced Data

Relative to the equilibrium phases and species in the tin/water and lead/water systems, 18-20 shown in Figures 12-14, the initial rest potentials for the two solutions are shown both before and after addition of the $\text{SO}_3^{2-}/\text{SO}_2$, Cl^- , F^- , and CO_2 species. In addition, the potential at which the anodic current peak occurs is indicated for the lead/water system

Figure 12. POTENTIAL/pH EQUILIBRIUM DIAGRAM FOR THE SYSTEM TIN/WATER AT 25°C. (Considering the Anhydrous Oxides, SnO and SnO_2 ; After Pourbaix⁶)

Figure 13. POTENTIAL/pH EQUILIBRIUM DIAGRAM FOR THE SYSTEM TIN/WATER AT 25°C. [Considering the Hydroxides, Sn(OH)_2 and Sn(OH)_4 ; After Pourbaix^{6]}

(Figure 14). The general picture for the actual exposure situation with respect to the tin component is that, in the less acidic environment, there is formation of tin(IV) oxide or hydroxide whether or not chlorides and fluorides are present; while, in the more acid environment, addition of chloride and fluoride may change the dissolution characteristics such that tin(II) hydroxide is formed under some conditions. This film is likely to be less protective than the tin(IV) film. The general picture for the lead component is that the only protective oxide that can be formed would be a metastable film, similar to that responsible

potential. This phenomenon would result from a decrease in the $\text{Pb} \rightarrow \text{Pb}^{++}$ reaction rate, causing the $\text{Pb} \rightarrow \text{Pb}^{++}/\text{O}_2 \rightarrow \text{OH}^-$ mixed potential to shift upward. Conversely, the lower rest potential in the more acidic solution would be caused by increased $\text{Pb} \rightarrow \text{Pb}^{++}$ rates, although part of the shift could also be due to a drop in the $\text{O}_2 \rightarrow \text{OH}^-$ rate due to a change in the catalytic surface.

The high resistance of lead to strong sulfuric acid solutions is apparently due to formation of the bisulfate $[\text{Pb}(\text{HSO}_4)_2 \cdot \text{H}_2\text{O}]$, which has only about 0.01 as much solubility as PbSO_4 , as is indicated by the data in Table 2. However, HSO_4^- does not exist in equilibrium with

Table 2
SOLUBILITIES IN WATER FOR SELECTED COMPOUNDS OF INTEREST
TO LEAD-15 TIN ALLOY CORROSION
(From CRC Handbook)

Compound	Temperature (° C)	Solubility (g/100 ml)	Solubility (Pb equivalents/liter)	Comments(1)
SnO_2	RT	-	-	i
$\text{Sn}(\text{OH})_2$	RT	-	-	i
$\text{Sn}(\text{OH})_4$	RT	-	-	i
SnSO_4	25	33	1.54	-
$\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$	RT	-	-	vs
SnCl_2	15	269.8(2)	12.56	-
SnCl_4	RT	-	-	s
SnF_2	RT	-	-	s
SnF_4	RT	-	-	vs
PbO	20	0.0017	7.6×10^{-5}	-
$\text{Pb}(\text{OH})_2$	20	0.0155	6.43×10^{-4}	-
PbSO_3	RT	-	-	i
PbSO_4	25	0.00425	1.40×10^{-4}	-
$\text{PbSO}_4 \cdot \text{PbO}$	0	0.0044	1.67×10^{-5}	-
$\text{Pb}(\text{HSO}_4)_2 \cdot \text{H}_2\text{O}$	18	0.0001(2)	2.39×10^{-6}	-
PbCl_2	20	0.99	3.56×10^{-2}	-
PbF_2	20	0.064	2.61×10^{-3}	-
PbCO_3	20	0.00011	4.12×10^{-6}	-
$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$	RT	-	-	i(3)
PbC_2O_4	25	0.0000058	1.80×10^{-7}	-
PbC_2O_4	18	0.00016	5.42×10^{-6}	-
$\text{PbCl}_2 \cdot \text{Pb}(\text{OH})_2$	18	0.0095	3.66×10^{-4}	-
PbS	18	0.000086	3.59×10^{-6}	-
CO_2	25	0.145	$3.29 \times 10^{-2(4)}$	-
SO_2	22	7.6	1.19(4)	-
O_2	25	0.0045	$1.41 \times 10^{-3(4)}$	-

(1) i - insoluble, s - soluble, vs - very soluble.

(2) Decomposes.

(3) Slightly soluble in aqueous CO_2 .

(4) In moles/liter.

an equal concentration of $\text{SO}_4^{=}$ until the pH is lowered to a value of 1.91.²² Since a solution of about 350 ppm of SO_2 in water produces a pH of 2.4 (by actual test), it is uncertain if sufficient HSO_4^- exists to be significant (as SO_2 dissolution is the only available acidification mechanism). The comparable equimolar pH for $\text{HSO}_3^-/\text{SO}_3^{=}$ is 7.26,²² however, so consideration should only be given, in all cases, to the bisulfite ion.

This species does not reach equimolar equilibrium with H_2SO_3 until the pH drops to 1.97.²²

While it is not possible to unequivocally equate current values on potentiokinetic polarization curves to corrosion rates, due to the possibility of current contributions from other reactions, such current values are another form of evidence to consider in evaluating a corrosion situation. Table 3 lists rest potentials found for the alloy in the various solutions

Table 3
COMPARISONS OF POLARIZATION CURRENTS OF LEAD-15 TIN ALLOY
IN DIFFERENT ENVIRONMENTS

Solution Composition (1)	Rest Potential After the Polarization Curve (2) (V)	Current Density from the Polarization Curve at Rest Potential (mA/cm ²)
H_2SO_4	-0.235	0.912
$\text{H}_2\text{SO}_4, \text{SO}_2$	-0.205	1.82
$\text{H}_2\text{SO}_4, \text{SO}_2, \text{Cl}^-$	-0.235	3.63
$\text{H}_2\text{SO}_4, \text{SO}_2, \text{Cl}^-, \text{F}^-$	-0.255	5.13
$\text{H}_2\text{SO}_4, \text{SO}_2, \text{Cl}^-, \text{F}^-, \text{CO}_2$	-0.195	10.2
Na_2SO_4	-0.340	0.447
$\text{Na}_2\text{SO}_4, \text{SO}_3^-$	-0.415	0.692
$\text{Na}_2\text{SO}_4, \text{SO}_3^-, \text{Cl}^-$	-0.360	0.661
$\text{Na}_2\text{SO}_4, \text{SO}_3^-, \text{Cl}^-, \text{F}^-$	-0.350	0.513
$\text{Na}_2\text{SO}_4, \text{SO}_3^-, \text{Cl}^-, \text{F}^-, \text{CO}_2$	-0.360	1.12

(1) Oxygenated.

(2) vs Ag/AgCl.

of interest, along with current density values taken from polarization curves performed in those solutions. For both the H_2SO_4 and Na_2SO_4 solutions, addition of $\text{SO}_2/\text{SO}_3^-$ causes increases in the anodic current. Since the potentials at which these currents were measured were, in each case, above the $\text{SO}_3^-/\text{SO}_4^-$ equilibrium reaction potential,²³ the current increase may, in part, be due to this reaction. Chloride addition to these solutions causes no detectable change for the Na_2SO_4 solution; but, possibly, doubles the current for H_2SO_4 . Addition of fluoride has little effect on or perhaps slightly depresses the current for Na_2SO_4 , but increases the current in H_2SO_4 by 40%. Addition of CO_2 doubles the current in both solutions. The fact that CO_2 bubbling was continuous is probably significant here.

CONCLUSIONS

Conclusions on the effect of added species to the H_2SO_4 and Na_2SO_4 solutions have been made on the basis of the information contained in Figures 8 through 10 and Table 3. While the direction of the effect determined by the spiking method is more likely to be correct than that determined by the potential-sweep method, the opposite may be true of the

magnitude of the corrosion current in any given environment since the potential-sweep-method currents were taken at the actual free corrosion potential. The response of the rest potential may be more sensitive than the current, but also more difficult to interpret quantitatively. The best judgements of the effect of the species are as follows:

$\text{SO}_2/\text{SO}_3^-$ - While the rest potential decreases (which might be taken as evidence of an increased corrosion rate), this change is probably due to the $\text{SO}_3^- \rightarrow \text{SO}_4^-$ reaction. Evidence from Figures 8 and 9 indicate a drop in current and probably improvement of passivation (but see the comment to follow).

Cl^- - Evidence is mixed. There would seem to be little effect. Only the Table 3 data argues otherwise. There is probably some increase in the corrosion rate, but it is difficult to estimate from these data.

F^- - Most data indicate an increase in the corrosion rate, but more severe in the more acid solution. This increase would be on the order of 15 to 40% from the information of Figure 9 and Table 3. The Na_2SO_4 environment may be less sensitive.

CO_2 - Data indicate that a certain lower range of concentration causes marked passivation in the Na_2SO_4 solution, where carbonates are stable. Higher concentrations may cause depassivation. No accurate estimate of an acceptable range is available. A rough estimate follows from the 30-second period before depassivation seems to start, an approximate $1 \text{ cm}^3/\text{sec}$ delivery rate, and the CO_2 solubility in water. These data suggest that up to 0.01 atmosphere, or 30 times the normal atmospheric concentration, might improve passivation.

The increase in $\text{SO}_2/\text{SO}_3^-$, which by itself possibly improves alloy passivation, is overall damaging to the corrosion situation. First, the pH drops due to acidification, which apparently makes the alloy more sensitive to F^- and Cl^- . On balance, the lower pH solution, although containing SO_2 , is more aggressive to the alloy. Second, the $\text{SO}_2/\text{SO}_3^-$ is converted on the catalytic surface of the alloy to SO_4^- . From the entrance of the compressor system inward, a gradient will exist wherein $\text{SO}_2/\text{SO}_3^-$ decreases as SO_4^- increases. The greater the total ion concentration, the higher the solution conductivity and the further dissimilar metals can couple with a damaging effect. The presence of considerable quantities of copper compounds in the corrosion product argues for the possibility of such coupling to exposed copper. Both the chloride and fluoride ions should increase the corrosion rate of copper.

The most serious problem in this system would seem to be the high concentration of $\text{SO}_2/\text{SO}_3^-/\text{SO}_4^-$ in the condensed water in the heat exchanger. This problem is further aggravated by the fluoride, and possibly the chloride ion, contamination. Removing SO_2 , F^- , and Cl^- from the input air, doping the input air with CO_2 , or injecting more water into the input which is then removed at the dewatering step (effectively scrubbing the air as well as lowering the ion concentration) may be beneficial.

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