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CORROSION OF CARBON STEEL IN WASTE SOLUTIONS CONTAINING MERCURY

by

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Pile Materials Division

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ABSTRACT

The corrosion behavior of A-285, A-135, A-106, and A-53 carbon steel was studied in multicomponent simulated waste solutions containing mercury. In the liquid phase, the carbon steels corroded at a very low rate; mercury did not increase the corrosion rate in any of the solutions tested. In the vapor phase and at the vapor-liquid interface, pitting occurred; the pitting was independent of solution composition, and was caused mainly by the condensation of oxygenated water from the aqueous wastes.

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CORROSION OF CARBON STEEL
IN WASTE SOLUTIONS CONTAINING MERCURY

INTRODUCTION

Waste solutions from the separations process are stored in large underground carbon steel tanks. Since these wastes are highly radioactive and must be stored indefinitely, it is essential that the corrosion rate of carbon steel be low in the waste solutions. It is therefore necessary to investigate the corrosion problems that may be introduced by any proposed changes in the separations processes. Two process changes, one involving the addition of mercurous nitrate to waste evaporator feed, and the other involving the addition of mercuric nitrate to fuel element dissolver solutions, have been proposed.

Radio-iodine presents a problem in the operation of the "Purex" waste evaporators, because 1 to 10% of the fission product iodine appears in the condensate, probably as hydrogen iodide. When this condensate is processed in the acid recovery unit, annoying health and operating problems can arise. The addition of 0.001 to 0.1M mercurous nitrate to the waste evaporator feed could possibly reduce the volatilization of iodine by a factor of 10 to 1000. The effectiveness of the mercurous ion in reducing iodine volatility appears to involve the formation of mercurous iodide, the very low ionization of which allows virtually no iodide ion to exist for the formation of volatile hydrogen iodide or iodine.

In the "25" process for dissolving aluminum-clad, aluminum-uranium alloy fuel elements in nitric acid, mercuric nitrate catalyzes the aluminum dissolution. The mercury destroys the protective oxide film and activates the aluminum surface, so that rapid dissolution rates can be obtained.

This report summarizes laboratory studies of the corrosion behavior of carbon steels in simulated waste solutions from these two processes.

SUMMARY

The addition of either mercurous or mercuric nitrates does not increase the corrosion of carbon steel in simulated waste storage solutions.

In "Purex" and "25" process waste solutions containing mercury, the average corrosion rates of Type A-53, A-135, and A-285 carbon steel are below 4 mils per year. For Type A-106 the average corrosion rate is below 8 mils per year. At the boiling point of the liquid, the vapor phase is usually more corrosive than the liquid phase.

After testing 3 months in "25" process wastes from the nitric acid dissolution of aluminum-uranium elements, A-285 coupons show low liquid phase corrosion rates, but develop pits up to 8 mils deep in the vapor phase.

DISCUSSION

PROCEDURE

Conventional test procedures were used. The carbon steel samples were wet-ground to 120-grit finish just prior to testing to prevent rusting. After the wet-grinding operation, the samples were measured and the surface areas were calculated. Then the samples were degreased and weighed. Corrosion tests at room temperature, 40°C, and 60°C were conducted in polyethylene beakers or "Saran" pipe sections using "Teflon" sample holders. Boiling temperature tests were conducted in 1000-ml wide-mouthed Erlenmeyer flasks equipped with cold-finger condensers. Glass cradles were used to support the coupons.

In all tests about 40 ml of solution was used per square inch of surface area of the sample. Corrosion rates were calculated from the weight losses of the coupons by the following equation.

$$\begin{array}{c}\text{Corrosion Rate}\\ \text{(mils per year)}\end{array} = \frac{527{,}000 \times \text{weight loss (grams)}}{\text{Area (in}^2\text{)} \times \text{density(g/cm}^3\text{)} \times \text{time (hr)}}$$

Scale that deposited or formed on the mild steel coupons was removed by pickling the samples in inhibited 5% H_2SO_4 for five to fifteen minutes prior to weighing.

Since carbon steel forms relatively adherent corrosion products, short-time corrosion rates cannot be accurately extrapolated to long times. Corrosion product film formation can result in either a decrease or an increase in corrosion rate, depending on the protective or nonprotective nature of the film. Therefore, the term "corrosion rate" applied to carbon steel corrosion in this report should be interpreted as a corrosion rate only for the test period of time.

Both wrought and welded coupons were tested. The compositions of the wrought carbon steels are given in the following table.

Carbon Steels

	Composition, %						
Steel	C	Si	S	P	Mn	Cu	Fe
A-53	0.15	0.16	0.033	0.017	0.55	-	Balance
A-106	0.22	0.20	0.030	0.016	0.60	-	Balance
A-135	0.318	-	0.021	0.015	0.41	-	Balance
A-285	0.107	-	0.037	0.011	0.28	0.305	Balance

Welded A-106 and A-285 samples were "Heliarc" welded without filler rod.

CARBON STEEL IN SIMULATED "PUREX" WASTE SOLUTIONS

To study the effect on the corrosion rate of mercury addition to prevent iodine volatilization, various types of carbon steels used in the construction of the waste storage tanks were exposed to simulated "Purex" waste solutions listed in the following table. Both solutions represent neutralized composite waste solutions. "Solution 1" contained mercuric nitrate, and "Solution 2" contained mercurous nitrate.

Simulated "Purex" Waste Solutions

Solution 1		Solution 2	
Component	Molarity	Component	Molarity
$NaNO_3$	0.80	$NaNO_3$	6.31
$Fe_2(SO_3)_2$	0.017	KNO_3	0.760
Na_2SO_4	0.010	NaOH	0.382
NaOH	0.310	$HgNO_3$	0.014
$Mn(NO_3)_2$	0.675		
MnO_2	0.004		
$NaAlO_2$	0.021		
Gluconic Acid	0.072		
$Hg(NO_3)_2$	0.008		

Corrosion results were as follows.

Corrosion of Carbon Steel
in Simulated "Purex" Waste Solutions

	Corrosion Rate, mils per year			
	Solution 1			Solution 2
	Boiling(115°C)		40°C	Boiling(107°C)
Steel	Vapor	Liquid	Liquid	Liquid
A-285, welded	3.6	0.7(a)	0.5	2.4
A-285	0.6	1.6(b)	0.4	-
A-106, welded	6.4	1.6(a)	0.6	5.1
A-106	3.6	4.0(b)	0.5	-
A-53	3.9	0.9(c)	0.6	3.6
A-135	3.1	0.7(c)	0.6	4.4
Total test time (hours)	221	145(a) 256(b) 131(c)	404	240

No controls without mercury were run since Hanford data for the corrosion of SAE 1010 carbon steel in a simulated "Purex" solution was available.(1,2) For exposure periods up to 10 months, Hanford found that steel exposed to the liquid waste solution was not subject to corrosion damage, but that steel exposed to the vapors over the solution was attacked. These tests indicated (1) that SAE 1010 steel exposed to the vapors over neutralized "Purex" waste solution was subject to rather severe initial pitting, but that the rate of pitting attack decreases rapidly with time, to a value of 4.8 mpy after ten months of exposure, (2) that there was so significant difference between polished steel surfaces and fine sandblasted steel surfaces in their resistance to pitting during exposure in the vapor, and (3) that general corrosion rates in the liquid are of the order of 1.2 mpy or less.

The addition of mercury to "Purex" waste solutions did not accelerate the corrosion rate of carbon steel. Of the steels tested, A-106 was the least corrosion resistant. The corrosion resistances of A-285, A-135, and A-53 were approximately equal.

At the boiling point, corrosion rates in the vapor phase of Solution 1 were generally higher than in the liquid phase. Increasing the temperature from 40°C to boiling increased the corrosion rates slightly in the liquid phase. No preferential weld attack was observed in either of the solutions.

At boiling temperatures in the liquid phase, corrosion rates in Solution 2 were higher than corrosion rates in Solution 1. This slight increase in corrosion rate was probably due to the difference in solution composition, rather than to the valence state of mercury.

CARBON STEEL IN "25" PROCESS WASTE SOLUTIONS

The corrosion of carbon steel in "25" process wastes from the dissolution of aluminum-uranium alloys was studied initially in the following two simulated solutions.

"25" Process Waste Solutions

Solution 3		Solution 4	
Component	Molarity	Component	Molarity
$NaNO_3$	3.27	$NaNO_3$	2.83
NaOH	1.35	NaOH	0.256
$NaAlO_2$	0.855	$NaAlO_2$	0.795
$Hg(NO_3)_2$	0.009	$Hg(NO_3)_2$	0.006
		$Fe(NH_2SO_3)_2$	0.002

Results of the corrosion tests are summarized in the following table.

Corrosion of Carbon Steel in "25" Process Waste Solutions

Steel	Corrosion Rate, mils per year				
	Solution 3			Solution 4	
	Boiling		40°C	Boiling	40°C
	Vapor	Liquid	Liquid	Liquid	Liquid
A-285, welded	3.4	1.8	2.3	-	-
A-285	0.3	1.8	2.3	1.6	0.1
A-106, welded	5.0	3.0	3.2	-	-
A-106	7.7	4.3	2.2	1.1	0.2
A-53	1.8	2.5	1.6	-	-
A-135	2.8	2.0	1.1	-	-
Total test time (hours)	96	240	404	1188	

Solution 4, which was less concentrated than Solution 3, appeared to corrode the carbon steel at a lower rate. However, the difference in testing time may account for the difference in the corrosion rates of the two solutions.

As noted in "Purex" waste solutions, A-106 was the least resistant steel. Excluding A-106, the maximum corrosion rate in both solutions was less than 4 mpy. Generally, the corrosion rate was higher in the vapor than in the liquid. Slight pitting at the areas of contact between the coupon and the "Teflon" holder occurred in Solution 4. No preferential weld attack was observed in either solution.

To investigate further the corrosion behavior of carbon steel in "25" process waste solutions, a 3-month test of A-285, Grade C, firebox quality samples was run. Two series of solutions, representing minimum and maximum predicted waste storage conditions with varying mercury concentrations, were used. Since the test was mainly to characterize the vapor phase pitting reported by Phillips,(3) tests were conducted at 60°C to approximate vapor space temperatures in the waste storage tanks. Results were as follows:

Three-Month Corrosion Test of A-285 Carbon Steel in "25" Process Waste Solutions at 60°C

Solution Composition, Molarity				50 w/o NaOH Added, ml/liter	Corrosion Rate, mpy			Max. Pit Depth, mils
$Al(NO_3)_3$	HNO_3	FeSA*	$Hg(NO_3)_2$		Liquid	Inter-face	Vapor	
1.2	0.3	0.01	-	330	0.02	0.16	1.5	4.0
1.2	0.3	0.01	0.005	330	0.15	0.44	1.9	5.4
1.2	0.3	0.01	0.025	330	0.16	0.39	1.2	7.4
1.2	0.3	0.01	0.1	330	0.18	0.53	1.3	7.0
2.5	0.7	0.02	-	690	0.01	0.02	1.0	6.6
2.5	0.7	0.02	0.005	690	0.04	0.02	0.64	3.6
2.5	0.7	0.02	0.025	690	0.01	0.03	0.60	6.6
2.5	0.7	0.02	0.1	690	0.01	0.09	1.3	4.9

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* $Fe(NH_2SO_3)_2$

Negligible corrosion was observed in the liquid phase. However, in the vapor phase preferential corrosion was observed, and pitted areas up to 8 mils deep were measured. The liquid phase samples were still shiny after testing in most cases. Samples that were partially immersed had black corrosion product on the vapor portion, but were not corroded in the liquid phase. Slight pitting was observed at the vapor-liquid interface line in most solutions.

The corrosion rates for A-285 in all the solutions tested were approximately equal. However, the solutions with lower concentrations of $Al(NO_3)_3$ and HNO_3 appeared to corrode the samples slightly more than the more highly concentrated solutions. Increasing the mercury concentration did not increase the corrosion rate of carbon steel.

MEASUREMENT OF CORROSION WITH THE "CORROSOMETER"

The "Corrosometer" determines the extent of corrosion by means of a sensitive bridge circuit which measures small changes in electrical resistance. A variety of specially designed probes are used with the instrument.

A mild steel probe, Figure 1, was used to measure the corrosion in the vapor phase of the last solution in the previous table. Readings were taken daily and plotted against time, Figure 2.

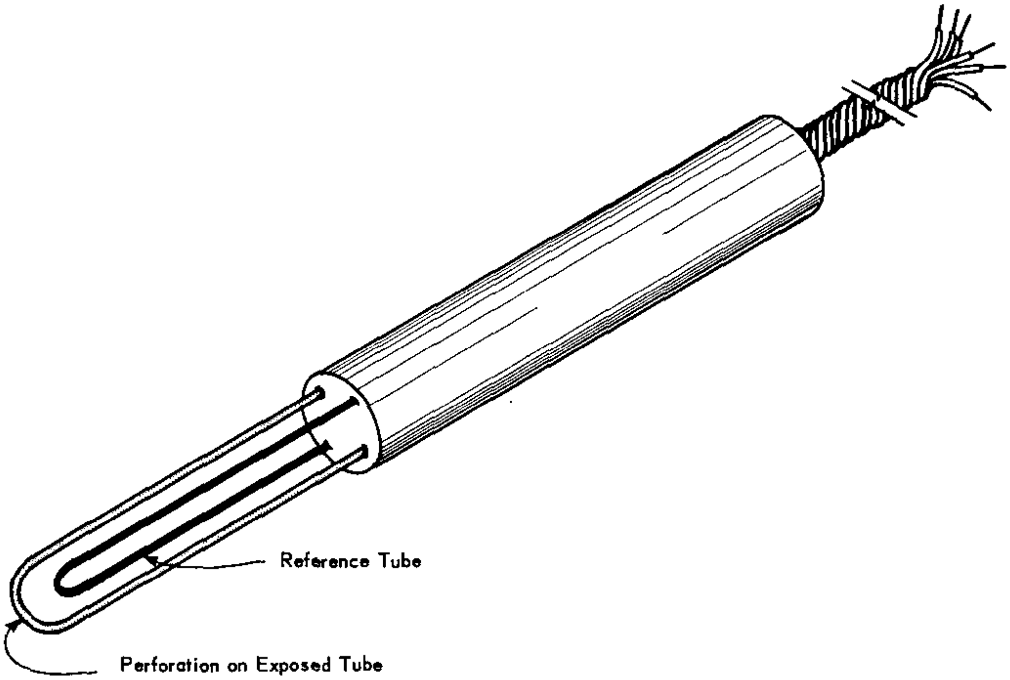


FIGURE 1 - "CORROSOMETER" PROBE

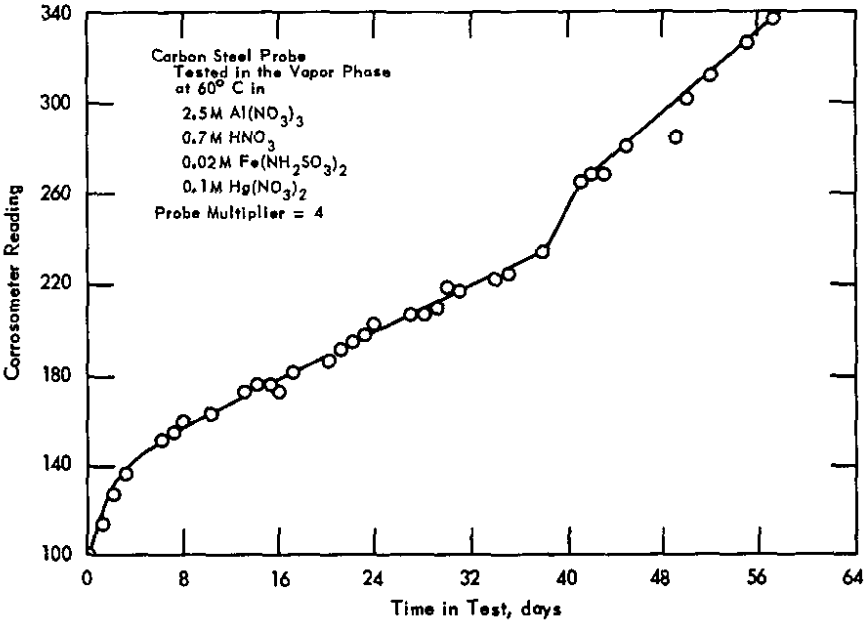


FIGURE 2 - MEASUREMENT OF THE CORROSION RATE OF CARBON STEEL WITH THE "CORROSOMETER"

Slopes were determined from the corrosion data for the first 40 days and the final 17 days.

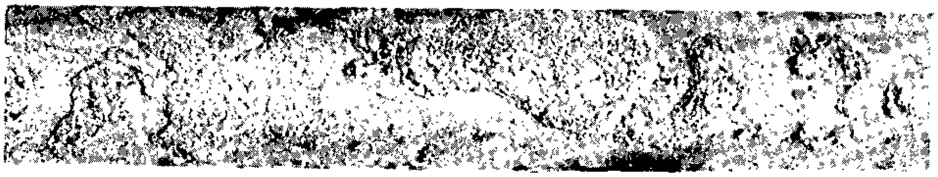
$$\text{First 40 days:} \quad \text{slope} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{234 - 150}{38 - 6} = \frac{84}{32} = 2.63$$

$$\text{Final 17 days:} \quad \text{slope} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{338 - 264}{57 - 41} = \frac{74}{16} = 4.62$$

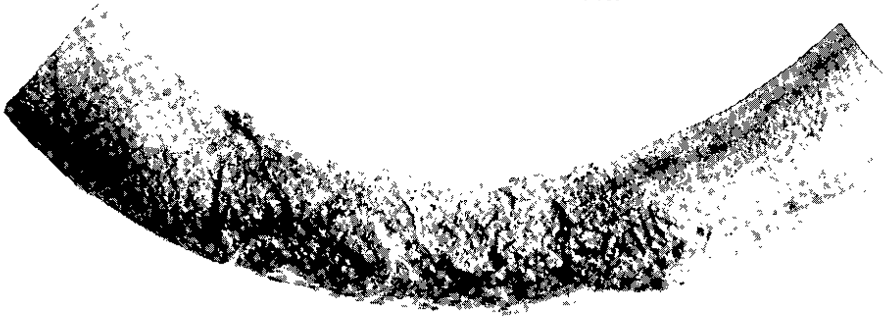
The corrosion rates were determined from the following equation.

$$\text{C.R. (mpy)} = \frac{365}{1000} \times \text{slope} \times \text{probe multiplier}$$

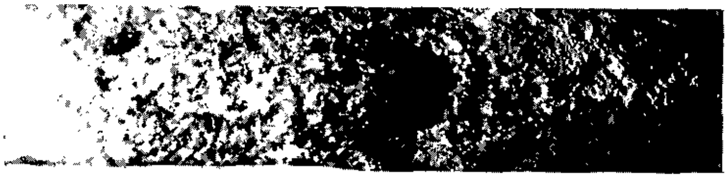
For the first 40 days the mild steel probe corroded at a rate of 3.8 mpy. At the end of 41 days the slope of the corrosion curve increased abruptly to give a corrosion rate of about 6.8 mpy. When the probe was removed from test after 57 days, the 8-mil-wall tube was found to be perforated at the bend of the probe. The other parts of the probe were preferentially corroded but were not perforated, as shown in Figure 3. Examination of the corrosion curve in Figure 2 indicates that perforation probably occurred after 41 days in test, when the slope of the corrosion curve changed.



Preferential Corrosion of Probe



Side View of Probe



Perforation of Tube Wall by Vapor Phase Pitting

FIGURE 3 - CARBON STEEL "CORROSOMETER" PROBE AFTER TEST 57 DAYS AT 60° C IN VAPOR PHASE (Mag. 13X)

The pitting of the bend section may be explained as follows. As moisture condensed on the probe, the liquid ran down the probe and, eventually, dropped off at the bend. The drop of water set up an oxygen concentration cell and initiated corrosion at the shielded point. Once the oxide deposit formed, corrosion accelerated under the deposit until the tube was perforated.

Since the "Corrosometer" measures the change in resistance as the metal probe is corroded, it is not a good tool to measure pitting or preferential attack. The data from the method would be comparable to weight loss determinations. However, in this test, the fact that the 8-mil tube probe was perforated in 41 days provides a measure of the pitting rate under conditions in which the condensate can set up oxygen concentration cells.

CONCLUSION

Carbon steel that is exposed to the liquid phase of waste solutions containing mercury corrodes at a rate less than 5 mpy. However, carbon steel is subject to pitting corrosion in the vapor phase and at the vapor-liquid interface. Test results for simulated "25" process waste solutions predict pits up to 8 mils deep in the first 3 months at 60°C. It appears that the vapor phase corrosion of carbon steel is essentially independent of solution composition, and is due mainly to condensation of oxygenated water from the aqueous waste with the subsequent initiation of oxygen concentration cells. To prevent corrosion of the tanks, the vapor section should be kept to a minimum. Increasing mercury concentrations from 0 to 0.1M does not increase the corrosion rate of carbon steel. Therefore, the mercury concentration resulting in the most favorable processing conditions can be used.

Of the steels tested, A-106 appeared to be the least corrosion resistant. No preferential attack of the welds or weld zones was observed on welded A-106 and A-285 samples.

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