Corrosion of Mild Steel Tank Liners Exposed to Simulated Solidified Alkaline High -Level Waste

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CORROSION OF MILD STEEL TANK LINERS EXPOSED TO
SIMULATED SOLIDIFIED ALKALINE HIGH-LEVEL WASTE

by

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Corrosion Research and Engineering Section
FUELS AND MATERIALS DEPARTMENT

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R. F. Maness

INTRODUCTION

At Hanford, liquid radioactive wastes are currently being solidified and stored in underground steel-lined concrete tanks. Of interest is the corrosion of the mild steel tank liners, including stress corrosion or caustic cracking, caused by the solidified waste. The corrosiveness of solidified waste is largely unknown but probably will be primarily dependent upon residual water content, caustic content and temperature. This study was initiated to determine the corrosiveness of high-level waste solution by exposing coupons for weight loss determinations and pit depth measurements and by exposing C-rings to determine stress corrosion cracking propensity.

SUMMARY AND CONCLUSIONS

Mild steel coupons and stressed C-rings exposed to simulated solidified waste for 7, 12, and 22 months exhibited both general and pitting corrosion but no stress corrosion cracking. Weight loss measurements indicated corrosion rates ranging from 0.7 to 4.7 mils/year after 22 months exposure. Corrosion rates were nearly the same for specimens exposed at 60 and 80°C. Corrosion rates at 95°C were about one-half those found at 60 and 80°C. Increasing the water content from 5 to 15% increased general corrosion by a factor of about two. Pitting attack occurred on all specimens exposed to high-alkali waste. The pitting rate appeared to be approximately linear with respect to time during the 22-month exposure period. A maximum pit depth

of 20 mils was observed. Corrosion of specimens exposed to waste prepared from solutions in which the caustic content had been largely neutralized with phosphoric, sulfuric or nitric acid was very light, <.01 to 0.6 mils/year with no pitting.

EXPERIMENTAL AND DISCUSSION

Wastes of varying composition were prepared by evaporating solutions of appropriate compositions followed by drying at 200°C. Water was then added to give a waste containing either 5 or 15% free water, i.e., water in excess of the amount required to form $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (The specie existing at test temperatures.) The compositions of the wastes evaluated are given in Table I. The wastes were held in containers fabricated by welding bottoms on 6-inch lengths of 2 1/4-inch diameter 1020 Schedule 40 pipe. The tops were threaded and then capped after addition of aliquots of waste and corrosion specimens. Corrosion specimens consisted of coupons (ASTM A-283, grade C) for weight loss determination and for determining pitting intensity and notched and pre-cracked C-rings to evaluate stress corrosion cracking propensity. The C-rings (see Figure 1) were fabricated from 0.5-inch lengths of 1 1/4-inch diameter Schedule 80 pipe (ASTM A-106, grade B). A starter crack was produced in each specimen prior to use by tightening the stressing bolt until cracking occurred. The containers also served as corrosion specimens, primarily to evaluate interface and weld metal attack. The closed containers were placed in ovens held at 60, 80, and 95°C and were vented at one to two-month intervals.

At high pH iron will usually react to form ferrite ion as given in Equation (1).

However, in the presence of nitrate or nitrite the reaction would be expected to proceed as given in Equation (2).

A strong odor of ammonia was detected when containers which held high-alkali waste were opened; no pressurization was noted in any case.

Specimens were removed from test and evaluated after 7, 12, and 22 months exposure. Corrosion rates obtained by weight loss determinations and pit depths obtained by microscopic measurements are given in Tables II and III. Corrosion rates in high-alkali waste ranged from 0.7 to 4.7 mils/year as determined by weight loss, whereas corrosion rates in low-alkali waste were

very low, .01 to .06 mils/year. Pitting attack occurred on all specimens exposed to high-alkali waste but on none of the specimens exposed to low-alkali waste. Photographs of exposed specimens are shown in Figure 2. The pitting frequency is seen to be quite high on specimens exposed to high-alkali waste. Maximum pit depths observed after 22 exposure months ranged from 8 to 20 mils. The pitting rate appeared to be approximately linear with respect to time. Inspection of the mild steel containers indicated preferential attack at the waste-vapor interface did not occur in any case. Eight containers (six high-alkali, two low-alkali waste) were sectioned and examined in more detail. Pitting attack closely approximated that which occurred on the exposed coupons and no preferential attack associated with weld metal areas was noted. Stress corrosion cracking (SCC) of C-ring specimens did not occur in any waste composition after 22 months exposure. The notched, pre-cracked stressed C-ring specimens of the type used in these tests had been previously used in a SCC study of nitrate systems.⁽¹⁾ Cracking occurred in hours to a few days in most systems.

A few of the tests that were made in closed systems were duplicated in open systems employing water-cooled condensers (see Table II). The results obtained in open systems were similar to those obtained in closed systems.

1) Letter Report "SCC Studies With Pre-Cracked C-Rings" R. F. Maness
to E. L. Moore, July 18, 1972

TABLE I
WASTE COMPOSITIONS PRIOR TO EVAPORATION

Constituent	g/l of Constituent for Indicated Waste							
	I-OH	II-OH	I-PO ₄	II-PO ₄	I-SO ₄	II-SO ₄	I-NO ₃	II-NO ₃
NaOH	400	200	40	20	40	20	40	20
NaAlO ₂	139	139	139	139	139	139	139	139
NaNO ₃	366	366	366	366	366	366	1131	749
NaNO ₂	90	90	90	90	90	90	90	90
Na ₂ CO ₃	170	170	170	170	170	170	170	170
NaCl	12	12	12	12	12	12	12	12
Na ₂ SiO ₃	1	1	1	1	1	1	1	1
Na ₃ PO ₄	-	-	492	246	-	-	-	-
Na ₂ SO ₄	-	-	-	-	639	320	-	-

TABLE II

CORROSION RATES OF MILD STEEL EXPOSED TO SIMULATED SOLIDIFIED WASTE

Waste ⁽¹⁾	Water Content, %	Average Corrosion Rate, Mils/Year											
		-----60°C-----				-----80°C-----				-----95°C-----			
		7 mo	12 mo	22 mo		7 mo	12 mo	22 mo		7 mo	12 mo	22 mo	
I-OH	5	1.1	-	0.7		0.8	2.9	2.0		0.5	0.4	0.7	
II-OH	5	1.8	1.3	2.0(1.5) ⁽²⁾		1.5	1.6	2.1		0.6	0.5	1.0	
I-OH	15	2.6	1.4	2.4		2.4	4.2	1.6		0.8	0.4	0.9	
II-OH	15	2.2	1.7	4.7(1.5) ⁽²⁾		2.7	2.6	1.4		1.1	0.5	1.4	
I-PO ₄	5	<0.01	-	<0.01		<0.01	0.02	0.01		0.08	0.2	0.01	
II-PO ₄	5	<0.01	0.03	<0.01		<0.01	0.01	0.01		-	0.05	-	
I-PO ₄	15	<0.01	0.01	0.01		<0.01	0.02	0.01		0.07	0.05	0.01	
II-PO ₄	15	<0.01	0.01	0.01		<0.01	-	0.01		0.09	0.06	0.01	
I-SO ₄	5	-	-	0.01 ⁽²⁾		0.02	0.02	0.01		-	-	-	
II-SO ₄	5	-	-	0.05 ⁽²⁾		0.02		-		-	-	-	
I-SO ₄	15	-	-	--		0.05	0.02	-		-	-	-	
II-SO ₄	15	-	-	0.02 ⁽²⁾		0.02	0.02	-		-	-	-	
I-NO ₃	5	-	-	-		0.02	0.01	-		-	-	-	
II-NO ₃	5	-	-	-		0.01	0.08	0.01		-	-	-	
I-NO ₃	15	-	-	-		0.02	-	-		-	-	-	
II-NO ₃ ⁽³⁾	15	-	-	-		0.06	-	-		-	-	-	
II-OH ⁽³⁾	5	-	1.7 ⁽²⁾	-		-	2.3	0.01		-	-	-	
II-OH ⁽⁴⁾	5	-	-	1.8		--	-	-		-	-	-	

Notes: ⁽¹⁾

See Table I for compositions

⁽²⁾

Open system using water-cooled condenser

⁽³⁾

1% fluoride added as NaF

⁽⁴⁾

Waste contained no nitrite

TABLE III

PITTING INTENSITY OF MILD STEEL EXPOSED TO SIMULATED SOLIDIFIED WASTE

Waste ⁽²⁾	Water Content, %	Pit Depth, mils ⁽¹⁾								
		60°C			80°C			95°C		
		7 mo.	12 mo.	22 mo.	7 mo.	12 mo.	22 mo.	7 mo.	12 mo.	22 mo.
I-OH	5	2(4)	5(7)	9(15)	4(5)	7(12)	13(20)	2(4)	3(6)	7(12)
I-OH	15	1(1)	3(4)	6(8)	4(6)	7(10)	7(10)	2(4)	3(3)	6(8)
II-OH	5	1(1)	4(4)	8(10)	0(0)	7(10)	12(17)	0(0)	3(3)	8(14)
II-OH	15	0(0)	1(2)	4(8)	0(0)	5(7)	14(20)	5(9)	1(2)	8(12)

-6-

Notes:

(1)

Values given are the average depth of ten measurements. Parenthetical values represent the maximum pit depth found.

(2)

See Table I for compositions

C-Ring with Starter Crack 2X

Starter Crack 20X

Figure 1. Unexposed Stressed C-Ring with Starter Crack

Waste I-OH
5% H₂O

Waste I-OH
15% H₂O

Waste II-OH
15% H₂O

Waste I-NO₃
15% H₂O

Figure 2. Mild Steel Coupons After 22 Months Exposure to Solidified Waste.

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