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on

CORROSIVITY OF SYNTHETIC SALT CAKE

to

ATLANTIC-RICHFIELD-HANFORD CORPORATION

July 18, 1975

by

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and Walter K. Boyd

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INTRODUCTION

As part of a waste management program, the Atlantic-Richfield-Hanford Corporation will convert high-level nuclear wastes into salt cake by using an evaporator crystallizer. This salt cake is produced by evaporating moisture from liquid nuclear fuel reprocessing waste. The major constituents of the salt cake are nitrate, hydroxide, aluminate, and nitrite. Repeated evaporation cycles will reduce the moisture content to about 5 percent, after which the cake will be stored for a minimum of 100 years in underground tanks consisting of open topped, mild steel liners in concrete vessels. Failure of several present tanks, defined as through penetration allowing leakage, has been experienced. These failures have been ascribed to stress-corrosion cracking (SCC) and possibly pitting of the mild steel liners.

Battelle's Columbus Laboratories conducted an experimental research program to determine the corrosion behavior of mild steel over a broad range of simulated salt-cake compositions. The objectives of the investigation were twofold: (1) to identify probable failure modes; for example, SCC, pitting, or general corrosion, under simulated storage conditions, and (2) to provide information which will help enable salt cake to be stored safely for a period of 100 years.

EXPERIMENTAL PROCEDURES

Synthetic Salt-Cake Compositions

Two series of synthetic salt-cake solutions were used. The first consisted of six solutions containing sodium hydroxide, nitrate,

nitrite, and aluminate at concentrations covering compositional ranges experienced in storage tanks. The compositions of these solutions were carefully chosen to study the effects of high and low ratios of $\text{OH}^-/\text{NO}_3^-$, $\text{NO}_3^-/\text{NO}_2^-$, and the effect of aluminate, AlO_2^- . After experiments with these six solutions had been completed, a base composition (Solution No. 5) was chosen with which to study the effects of other additions likely to be encountered in practice.

All of the solutions used are presented in Table 1. Solutions 1 through 6 represent the first series, and 5A through 5J represent the second series. Note that the base composition used for this second series was 5.75 M NaOH, 2.9 M NaNO_3 , 1.5 M NaNO_2 , and 1.3 M NaAlO_2 . Variables investigated with this second series included the effects of NO_3^- , NO_2^- , and AlO_2^- (Solutions 5A, 5B, 5I, and 5J, in conjunction with 5 and 6) not completely defined by results from the first series. Metal hydroxides were studied with Solutions 5C and 5D, chloride ion was investigated with Solutions 5E and 5F, and carbonate was characterized with Solutions 5G and 5H.

Certain of the hydroxides used in Solutions 5C and 5H were not readily commercially available. In those cases they were prepared by precipitation with NaOH solution from aqueous solutions of the nitrate salts of the desired metals. Each precipitate was thoroughly washed with distilled water and then added in excess to the base solution. In every instance the metal hydroxides were present at saturation concentration.

In general, all solutions were prepared from reagent grade chemicals (exception: sodium aluminate, purified) and distilled water. They were stored in air-tight, polyethylene bottles until used.

Alloy Specimen

The steel selected for this investigation was ASTM A-283, Grade B, in the form of 1/4-inch plate. This is the steel specification used to construct the oldest storage tanks. Chemical composition of the steel is presented in Table 2.

TABLE 1. SYNTHETIC SALT CAKE COMPOSITIONS

Solution	NaOH (M)	NaNO ₃ (M)	NaNO ₂ (M)	NaA/O ₂ (M)	Notes
1	10	1.6	.65	1.3	
2	10	1.6	2.4	1.3	
3	1.5	4.2	.65	1.3	
4	1.5	4.2	2.4	1.3	
5	5.75	2.9	1.53	1.3	
6	5.75	2.9	1.53	--	
5A	5.75	--	--	1.3	
5B	5.75	--	1.53	--	
5C	5.75	2.9	1.53	1.3	Fe, Mn, Ca, Mg hydroxides
5D	5.75	2.9	1.53	1.3	Uranium and misch metal hydroxides
5E	5.75	2.9	1.53	1.3	30 ppm Cl
5F	5.75	2.9	1.53	1.3	3000 ppm Cl
5G	5.75	2.9	1.53	1.3	Saturated with Na ₂ CO ₃
5H	1	2.9	1.53	1.3	Saturated with Na ₂ CO ₃
5I	5.75	2.9	--	--	
5J	5.75	--	--	--	

TABLE 2. CHEMICAL COMPOSITION OF ASTM A-283
STEEL (WEIGHT PERCENT)

C	Mn	Si	P	S	Al	Cu	Ni	Cr	Mo
0.26	0.51	0.05	0.012	0.035	< 0.002	0.01	0.05	0.02	0.01

Mechanical properties specified for A-283 Grade B steel are 50,000 - 60,000 psi tensile strength, 24,000 psi minimum yield strength, and 30 percent minimum elongation in 2 inches.

Potentiodynamic polarization and linear polarization specimens were 1/4-inch diameter by 1/2-inch long. These cylindrical specimens were drilled and tapped in one end for connection to Teflon compression gasket specimen holders.

Constant strain rate specimens were 3/16-inch diameter by 7-inches long with the length taken parallel to the rolling direction of the steel plate. A reduced gage length 0.100-inch diameter by 0.5-inch long was machined into each specimen.

Experimental Techniques

Three types of experimental techniques were used to evaluate corrosion behavior. General attack and pitting were studied by potentiodynamic and linear polarization, whereas susceptibility to SCC was determined by the constant strain rate technique. These procedures are described below.

Potentiodynamic Polarization. Potentiodynamic polarization provides a measure of reaction kinetics, both oxidation and reduction, as a function of oxidizing conditions (i.e., electrochemical potential). Analysis of current-potential relationships can indicate electrolyte-potential-temperature combinations which promote general corrosion, passivity, pitting, or SCC.

In practice a drilled and tapped cylindrical specimen was abraded on 600 grit silicon carbide paper and then inserted onto the Teflon holder. The specimen-holder combination was next placed into a Teflon electrochemical cell containing the preheated electrolyte. The electrolyte was deaerated with nitrogen and its temperature was maintained at either 50 C or 93 C until a nearly steady state open circuit potential (measured versus a saturated calomel half cell) was attained.

The potential scan was then begun from this potential, usually in the anodic direction at a rate of 3 volts per hour until evolution of oxygen was observed, after which it was returned to the starting value. Current was monitored as the voltage drop across a precision resistor in the counter electrode circuit.

Linear polarization. Linear polarization measurements indicate the instantaneous corrosion rate and also provide a measure of pitting tendency. In practice, a potential of a few millivolts was applied between two identical electrodes in the corrodent, and the resulting current flow was converted through appropriate equations to the corrosion rate.

Cylindrical steel specimens were abraded and mounted as explained above, and then inserted into Teflon bottles of 16-ounce capacity containing the preheated solutions. The specimens were positioned, two to a bottle, such that they were submerged by about 2 inches and separated by the same distance. The bottles were then placed in a stirred isothermperature bath maintained at 50 C or 93 C. Linear-polarization measurements were made periodically on these pairs of specimens.

The measurements were made by applying a 5 mV potential between the electrode pairs and recording the resultant current flow. Next, the polarity was reversed and the current again measured. This alternating procedure was performed for each electrode pair, in succession, until a steady-state current reading was obtained. The current readings obtained were subsequently converted into instantaneous corrosion rates.

Also included in each bottle were four coupons 1-inch by 1-inch by 0.34-inch. They were abraded, weighed, and then suspended in the solutions by black iron wires through a hole in one corner of each coupon. They were periodically removed, defilmed, and their weight losses determined. In this way the accuracy of the corrosion rates calculated from the linear-polarization measurements was verified.

Constant Strain Rate. The constant strain rate technique was used to determine susceptibility to SCC. Typically, a specimen was strained in the environment of interest until complete fracture occurred. The presence of SCC was then detected by metallographic examination for cracks, and also by degradation of the mechanical properties, e.g., reduction in area of the test specimen compared to baseline data generated in air.

Specimens were strained at a constant rate of 2.5×10^{-6} ^{inch} per second, based on an original 0.5-inch gage length. A Teflon cell to contain the solution was equipped with a platinum counter electrode and string bridge to an external saturated calomel reference electrode. The potential was held constant throughout each experiment. The temperature was controlled and monitored by a thermocouple located inside the cell. Load on the specimens was recorded throughout the experiment.

Time to failure was measured by timers which shut off automatically when the specimen failed. The fracture surfaces and specimen gage length were examined metallographically and by scanning electron microscopy to verify the presence or absence of stress-corrosion cracks.

RESULTS AND DISCUSSION

Potentiodynamic Polarization

Anodic polarization curves for synthetic salt-cake Solutions 1 through 6 at 50 C are presented in Figure 1. (More positive potential corresponds to more oxidizing conditions.) Mild steel exhibited an extensive passive range in all solutions. Anodic peaks were observed in Solutions 1, 2, 3, 4, and 6, while spontaneous passivity with no active peak was observed in Solution 5. The rapid increase of current with rising potential in all solutions at approximately + 0.3 V(SCE) is due to oxygen evolution.

FIGURE 1. ANODIC POLARIZATION CURVES FOR SYNTHETIC SALT CAKE SOLUTIONS 1-6

Currents over the active and passive regions in all solutions ranged from 0.001 to slightly less than 0.1 milliamps, corresponding to low rates of steel dissolution.

Dissolution behavior was influenced considerably by composition of the synthetic salt-cake solutions. For example, decreasing the hydroxide concentration and increasing the nitrate concentration resulted in decreased corrosion based on lower dissolution rates in active ranges, greater tendency for passivation, and lower dissolution rates in passive ranges. Comparison of Curve 1 with Curve 2 and Curve 3 with Curve 4 indicates that dissolution in the active region is increased by higher nitrite concentrations, while passive currents are essentially unaffected. In solutions with lower nitrite to nitrate ratios, free corrosion potentials were made more positive and passivity occurred more readily. The inhibiting effect of aluminate is apparent from comparison of curves for Solutions 5 and 6. An anodic peak was observed in the absence of aluminate, Solution 6, in contrast to no anodic peak observed in the presence of aluminate, Solution 5. Aluminate had no effect on passive current.

The set of curves presented in Figure 2 are from a series of experiments designed to determine the effect of nitrate, nitrite, and aluminate on corrosion of steel in 5.75 M sodium hydroxide. Polarization curves were determined at 93 C in hydroxide solution (5 - J); hydroxide with nitrate (5 - I), nitrite (5 - B), or aluminate (5 - A); hydroxide with nitrate and nitrite (6); and hydroxide with nitrate, nitrite, and aluminate (5). Large differences in corrosion rate were observed for potentials more negative than approximately - 0.4 V (SCE), whereas at more positive potentials additions to the hydroxide solution had little affect on corrosion.

Specific observations from these data based on comparison of individual curves with Curve 5-J for pure hydroxide solution are

FIGURE 2. ANODIC POLARIZATION CURVES FOR SYNTHETIC SALT
CAKE SOLUTIONS 5, 6, 5A, 5B, 5I, and 5J

- (1) Nitrate (5 - I) increases the corrosion rate as potential is increased from the free corrosion potential to - 0.94 V (SCE). A distinct anodic peak is observed in this potential range.
- (2) Nitrite (5 - B) behaved much the same as nitrate, but the anodic peak was not as large.
- (3) Aluminate (5 - A) also increased corrosion rate below - 0.94 V (SCE), but it eliminated the anodic peak for pure hydroxide at - 0.90 V (SCE).
- (4) Nitrate and nitrite (6) produced spontaneous passivity and no anodic peak was observed.
- (5) Nitrate, nitrite, and aluminate (5) produced identical behavior to that of Solution 6.

Interaction between additions to the hydroxide solution resulted in a less corrosive environment that promoted spontaneous passivity.

The effect of metal hydroxides on corrosion in a salt-cake solution is shown in Figure 3. Curve 5 is for a base salt-cake solution; Curves 5-C and 5-D are for the base solution containing iron, manganese, calcium, and magnesium hydroxides, or uranium and misch metal hydroxides, respectively. The former group of additions increased the free corrosion potential from that observed in the base solution, approximately 0.3 volts, while the latter group had no appreciable effect on corrosion.

As shown in Figure 4, addition of 30 ppm chloride (5 - E) did not change the corrosion in the base solution (5). Addition of 3000 ppm chloride (5 - F) slightly increased corrosion over the entire passive range.

FIGURE 3. ANODIC POLARIZATION CURVES SHOWING EFFECT OF METAL OXIDE ADDITIONS

FIGURE 4. ANODIC POLARIZATION CURVES SHOWING EFFECT OF CHLORIDE ADDITION

The effect of carbonate addition is shown in Figure 5. Saturating Base Solution 5 with sodium carbonate, yielding Solutions 5-G, slightly increased corrosion. At a lower hydroxide concentration, IM (Solution 5-H) as opposed to 5.75M (Solution 5-G), the free corrosion potential increased to -0.7V (SCE) and the passive current decreased by approximately an order of magnitude. Based on behavior observed in solution 4, also of low hydroxide concentration, the decreased corrosion rate in solution 5-H can be mainly attributed to the decrease in hydroxide concentration and not to the presence of carbonate.

Linear Polarization

A comparison of corrosion rate, expressed as mils per year (mpy), determined L.P. and weight loss is presented in Table 3. The rate of corrosion, i_{corr} as measured by linear polarization was calculated from the Stern-Geary equation:

$$i_{\text{corr}} = \frac{1}{2.3} \frac{B_a B_c}{B_a + B_c} \times \frac{\Delta I \text{ applied}}{A \times \Delta E}$$

in which B_a and B_c are anodic and cathodic tafel slopes, ΔI applied is the current flow resulting from application of a potential difference ΔE , and A is the area of one electrode. This equation simplifies, for $B_a = 0.06$, $B_c = 0.08$ (experimentally determined), $A = 3.0\text{cm}^2$, and $\Delta E = 5\text{mV}$, to

$$i_{\text{corr}} = 1.00\text{cm}^{-2} \times \Delta I \text{ applied.}$$

Using the fact that i_{corr} of $1\text{A}/\text{cm}^2$ corresponds to a corrosion rate of 4.54×10^5 mpy, one derives that the corrosion rate (CR) in mils per year is given by

$$\text{CR(mpy)} = 1.00 \times \Delta I \text{ applied} \times 4.54 \times 10^5$$

Corrosion rates obtained by weight loss techniques represent fairly constant, or steady state, rates. They were calculated by measuring the weight losses which occurred during the period of transient decrease

FIGURE 5. ANODIC POLARIZATION CURVES SHOWING EFFECT OF CARBONATE ADDITION

TABLE 3. CORROSION RATES DETERMINED BY LINEAR
POLARIZATION AND WEIGHT LOSS TECHNIQUES

Solution No.	Corrosion Rate (Linear Polar) (mpy)	Corrosion Rate (Weight Loss) (mpy)
1	0.7	0.6, 0.7
2	0.8	0.9, 1.1
3	0.2	0.1, 0.2
4	0.02	0.1, 0.07
5	0.03	0.2, 0.1
6	0.03	0.4, 0.4
5-A	9	7
5-E	14	9
5-I	0.1	0.6

in corrosion rate during the early period of exposure, and those on a comparison set of coupons after a much longer period of time had elapsed. The difference in weight loss divided by the time elapsed between the two measurements yielded a fairly steady state set of corrosion rate data with which to verify that obtained by linear polarization.

Excellent correlation was observed when corrosion rates were of the order of 1 mpy and greater. Correlation was not quite so good for solutions exhibiting corrosion rates of less than 0.1 mpy. This less than perfect agreement is attributed in part to the inaccuracies inherent in measuring very small weight changes, such as those produced by corrosion rates of less than 0.1 mpy.

Corrosion rates of mild steel in solutions 1-6 at 50 C are presented in Table 4. After 222 hours exposure the corrosion rates were extremely low in all solutions (0.04 to 0.01 mpy). Initial corrosion rates in solution 1, 2, and 3 were higher but decreased steadily to low values. The highest corrosion rates were observed with highest hydroxide concentrations. No evidence of pitting or other localized attack was observed on any specimen.

Linear polarization results in salt cake solution 5A-5J at 93 C are presented in Table 5. Aluminate (5A) greatly increased the corrosion rate, and dissolution rate remained high over the entire 1000 hour exposure period. Nitrite (5B) decreased the corrosion rate slightly, whereas nitrate (5I) produced an initial increase in corrosion rate followed by a slight decrease after several hundreds of hours exposure.

The addition of metal hydroxides had no appreciable influence on corrosion rate. Chloride greatly increased corrosion at a concentration of 30 ppm (5E), but it had no effect at a higher concentration of 3000 ppm (5F). (This reversal of detrimental behavior at higher chloride concentration is anomalous and subject to question.) Note that although 30 ppm Cl^- had no effect on potentiodynamic polarization behavior, it greatly increased the open circuit corrosion rate as measured by extended time L.P. tests. Corrosion rate increased slightly with addition of carbonate (5G) and decreased markedly with addition of carbonate at the lower hydroxide level (5H). The latter decrease is probably due to lower hydroxide rather than to lower carbonate.

TABLE 4. CORROSION RATES OF A-283 MILD STEEL IN SALT
CAKE SOLUTIONS 1-6 AT 50 C

Solution No.	Time After Immersion (Hr)	i_{corr} (A/cm ²)	Corrosion Rate (mpy)
1	29	6.10^{-6}	2.7
	76	7.10^{-7}	0.3
	150	3.10^{-7}	0.14
	222	8.10^{-8}	0.04
2	29	6.10^{-6}	2.7
	76	1.10^{-6}	0.6
	150	2.10^{-7}	0.09
	222	7.10^{-8}	0.03
3	29	2.10^{-6}	0.7
	76	3.10^{-7}	0.14
	150	3.10^{-8}	0.01
	222	2.10^{-8}	0.01
4	29	4.10^{-8}	0.02
	76	3.10^{-7}	0.14
	150	3.10^{-8}	0.01
	222	2.10^{-8}	0.01
5	29	1.10^{-7}	0.04
	76	1.10^{-7}	0.04
	150	5.10^{-8}	0.02
	222	3.10^{-8}	0.01
6	29	7.10^{-8}	0.03
	76	1.10^{-7}	0.04
	150	7.10^{-8}	0.03
	222	6.10^{-8}	0.02

TABLE 5. L.P. CORROSION RATE OF A-283 MILD STEEL IN
SALT CAKE SOLUTIONS AT 93 C

Solution No.	Time After Immersion (Hr)	i_{corr} (A/cm ²)	Corrosion Rate (mpy)
5-A	26	21.10^{-5}	10
	138	$1.6.10^{-5}$	7
	218	$3.5.10^{-5}$	16
	1,171	$3.2.10^{-5}$	15
5-B	26	$1.6.10^{-7}$	0.07
	138	$2.2.10^{-7}$	0.10
	218	$3.0.10^{-7}$	0.14
	403	$4.0.10^{-7}$	0.18
	1,171	$3.0.10^{-7}$	0.14
5-C	26	$1.8.10^{-7}$	0.08
	138	$3.0.10^{-7}$	0.14
	218	$3.2.10^{-7}$	0.15
	403	$2.8.10^{-7}$	0.13
	668	$4.0.10^{-7}$	0.18
	1,171	$8.0.10^{-7}$	0.36
5-D	26	$1.4.10^{-7}$	0.06
	138	$4.0.10^{-7}$	0.18
	218	$2.5.10^{-7}$	0.11
	403	$1.7.10^{-7}$	0.08
	668	$2.1.10^{-7}$	0.10
	1,171	$4.0.10^{-7}$	0.18
5-E	26	$2.0.10^{-5}$	9
	138	$2.7.10^{-5}$	11
	218	$2.3.10^{-5}$	10
	403	$3.1.10^{-5}$	14
	668	$2.8.10^{-5}$	13
	1,171	$0.6.10^{-5}$	3
5-F	26	$2.2.10^{-7}$	0.32
	138	$4.0.10^{-7}$	0.18
	218	$2.6.10^{-7}$	0.12
	403	$2.2.10^{-7}$	0.10
	668	$1.5.10^{-7}$	0.07
	1,171	$3.0.10^{-7}$	0.14

TABLE 5. (CONTINUED)

Solution No.	Time After Immersion (Hr)	i_{corr} (A/cm ²)	Corrosion Rate (mpy)
5-G	26	$2.2 \cdot 10^{-7}$	0.10
	138	$2.0 \cdot 10^{-7}$	0.09
	218	$1.2 \cdot 10^{-7}$	0.05
	403	$1.5 \cdot 10^{-7}$	0.07
	668	$1.0 \cdot 10^{-7}$	0.04
	1,171	$3.0 \cdot 10^{-7}$	0.14
5-H	26	$7.0 \cdot 10^{-8}$	0.03
	138	$5.0 \cdot 10^{-8}$	0.02
	218	$5.0 \cdot 10^{-8}$	0.02
	403	$4.6 \cdot 10^{-8}$	0.02
	668	$3.0 \cdot 10^{-8}$	0.01
	1,171	$3.5 \cdot 10^{-8}$	0.02
5-I	65	$8.0 \cdot 10^{-6}$	3.6
	186	$6.0 \cdot 10^{-6}$	2.7
	426	$0.25 \cdot 10^{-6}$	0.11
	689	$0.30 \cdot 10^{-6}$	0.14
5-J	65	$6.0 \cdot 10^{-7}$	0.27
	186	$3.0 \cdot 10^{-7}$	0.14
	426	$6.0 \cdot 10^{-7}$	0.27
	689	$4.5 \cdot 10^{-7}$	0.20

In general, corrosion rates in salt cake solutions were small, and no pitting or localized attack was observed.

Constant Strain Rate

Since SCC of mild steel occurs over a finite potential range in caustic solutions, and the number of solutions studied precluded testing over a broad potential range in each solution, anodic polarization curves were used to select potential ranges likely to promote cracking. In caustic solutions SCC is most likely in the potential range from that corresponding to the maximum anodic current of an active peak to that for onset of passivity. In most cases a potential between these two values was selected. If no active peak was observed, i.e. spontaneous passivity occurred, the experiment was run at the corrosion potential. In a few solutions, experiments were conducted at more than one potential; these instances will be discussed individually.

The occurrence of SCC was determined by visual examination at a magnification of 10 times, by scanning electron microscopy, and by metallography. Photomacrographs of a specimen exhibiting SCC and one not exhibiting SCC are presented in Figure 6. Fine secondary cracks near the fracture surface indicate SCC, in contrast to the fibrous surface observed when SCC does not occur. A photomicrograph of secondary cracks near the primary fracture is shown in Figure 7. These shallow cracks are predominantly intergranular.

A scanning electron micrograph of secondary cracks is shown in Figure 8. The transition from a faceted SCC region to a fibrous ductile, mechanical fracture region is shown in Figure 9, which is a scanning electron micrograph of a primary fracture surface. Rating of SCC severity by SEM examination was necessary in this study because times-to-failure and reductions of area were not sufficiently sensitive. Results are presented in Table 6.

The principle^{al} observation made from these constant strain rate experiments is that SCC can occur in salt cake compositions simulating those found in storage tanks. Critical controlling parameters are solution composition, electrochemical potential, and temperature.

C-4717

10X

b. No SCC [5C, -.500 V(SCE)]

C-4716

10X

2. SCC [5J, -.900 V(SCE)]

250X

C-4718

FIGURE 7. PHOTOMICROGRAPH OF SECONDARY STRESS CORROSION
CRACKS FOR SOLUTION 5-A at -1.0 V(SCE)

115X

C-4719

FIGURE 8. SCANNING ELECTRON MICROGRAPH OF SECONDARY
CRACKS FOR SOLUTION 5I at -0.942 V(SCE)

FIGURE 9. SCANNING ELECTRON MICROGRAPH OF TRANSITION
FROM RELATIVELY FACETED (SCC) TO CUP AND
CONE (DUCTILE MECHANICAL) FRACTURE REGIONS
[51, -0.942 V(SCE)]

TABLE 6. CONSTANT STRAIN RATE RESULTS FOR MILD STEEL IN SYNTHETIC SALT CAKE SOLUTIONS

Solution	Potential V(SCE)	Temperature C	t _{tf} hrs	RoA %	Notes
1	7 → -6.780	50	31.3	57.8	No SCC
1	-0.780	93	24.1	54.4	Moderate SCC
2	-0.860	93	--	57.75	Minor SCC
2	-0.700	93	23.8	61.0	Moderate SCC
2	-0.750	93	24.1	54.4	SCC
2	-0.685	93	66.6*	57.8	SCC, *1.0 x 10 ⁻⁶ in/in-sec
3	-0.400	93	27.8	59	No SCC
4	-0.690	93	25.0	54.4	No SCC
5	-0.685	93	23.3	57.8	No SCC
5	-0.685	115	24.0	54.4	Minor SCC
6	-0.685	93	19.3	52.4	Minor SCC
5A	-0.920	93	23.8	54.4	Minor SCC
5A	-1.000	93	22.5	54.4	SCC
5A	-0.590	93	23.2	57.8	Moderate SCC
5B	-0.990	93	23.3	54.4	SCC
5C	-0.500	93	--	57.8	No SCC
5D	-0.800	93	25.2	59.0	No SCC
5D	-0.470	93	24.1	57.8	No SCC
5E	-0.850	93	25.7	54.4	No SCC
5F	-0.850	93	26.7	54.4	Minor SCC
5F	-0.585	93	26.3	57.8	Minor SCC
5G	-0.800	93	25.2	54.4	Minor SCC
5G	-0.550	93	26.1	54.4	Minor SCC
5H	-0.460	93	23.1	52.4	No SCC
5H	-0.650	93	25.4	57.8	No SCC
5H	-0.600	93	24.9	57.8	Minor SCC
5I	-0.940	93	22.1	52.4	SCC
5J	-0.900	93	26.7	60.9	Moderate SCC
5J	-0.960	93	25.6	54.4	SCC

Volts - Standard calomel electrode

t_{tf} = time to failure

RoA = reduction of area

The effect of temperature was demonstrated with solutions 1 and 5. As temperature increased, SCC became more severe. With all other variables maintained constant, SCC occurred upon increasing the temperature from 50 to 93 C and from 93 to 115 C in solutions 1 and 5, respectively.

The effect of potential was demonstrated with solution 2. The most severe SCC was observed at -0.750 V(SCE), and severity decreased at potentials more active, -0.800 V(SCE), and more noble, -0.700 V(SCE). The potential range for SCC corresponds approximately to that for the active-passive transition during potentiodynamic polarization.

Regarding the effect of strain rate, it was noted that SCC became worse if the applied strain rate decreased. For instance, reducing the rate from 2.5×10^{-6} per second to 1.0×10^{-6} per second markedly increased the severity of SCC.

The chemical composition of salt cake was found to be a variable of major importance. In general, data from solutions 1-6 indicate that increasing the hydroxide concentration causes SCC to be more severe. Other compositional effects are discussed below.

The effects on SCC severity of individual and multiple additions to a 5.75 M sodium hydroxide solution were studied in solutions 5, 6, 5A, 5B, 5I, and 5J. Individual additions of nitrate, nitrite, and aluminate did not increase the severity of SCC over that of the pure sodium hydroxide solution. Less severe SCC was observed in multiple component solutions 5 and 6. No SCC was noted for solutions 5 (all components) until the temperature was increased to 115 C.

Additions of different species to Solution 5 produced generally minor modifications in corrosion behavior. For instance, the presence of metal hydroxides (solutions 5C and 5D) did not cause SCC. Chloride additions at a level of 3000 ppm (5F) produced SCC, although 30 ppm (5E) had no effect. Saturating Solution 5 with carbonate (5G) enhanced SCC, but no SCC was observed in a solution identical to 5G except for a lower hydroxide concentration (5H).

In general, it is concluded that the system mild steel-salt cake solution is not highly susceptible to SCC. For instance, careful potential control was usually necessary to produce cracking, and the

cracks were relatively shallow and had propagated at very low rates relative to those which have been observed in other alloy-corrodent systems. It should therefore be possible to prevent SCC by observing several precautions. First, strong oxidizing agents should be precluded from the salt cake, since these can shift the corrosion potential in the noble direction and hence into the SCC range. Second, the ratio of concentration of passivating species, i.e. nitrate, nitrite, and aluminate, to that of hydroxide should be maximized. Third, all welds should be stress relieved. And fourth, the temperature of the salt cake should be kept as low as possible.

Probable Life Expectancy and Modes of Failure

For salt cake compositions within the concentration and temperature ranges examined in this study, the general corrosion and pitting corrosion will not be expected to limit the useable life of storage tanks. On the other hand, stress corrosion cracking observed in synthetic salt cake solutions appears to be the most likely cause of premature failures.

Methods to Measure Salt Cake Corrosivity

Potentiodynamic polarization is a reliable technique for determining the corrosivity of salt cake. Although this technique can be used in the field, it is better suited for laboratory studies.

Since linear polarization correlates well with weight loss measurements of corrosion rate, it provides a useful supplement to weight loss measurements and can be applied to field studies. One advantage of L.P. is that instantaneous corrosion rates can be monitored over long exposure periods.

The constant strain rate technique provides a positive test of SCC. The minor and moderate SCC observed in this study would quite possibly not have been detected by constant load or fixed displacement techniques.

CONCLUSIONS

The results of this research program, which utilized synthetic salt cake solutions of compositions simulating those likely to be encountered in the practice, support the following conclusions.

- (1) Pitting and general corrosion are not expected to limit the life of mild steel salt cake storage vessels. This is because no solution, even with 3000 ppm Cl^- present, produced pitting, and in the majority of solutions the corrosion rate was extremely low.
- (2) SCC is the most probable mode of tank failures observed to date. The occurrence of SCC was observed in several compositional ranges.
- (3) SCC occurs only with considerable difficulty and at relatively low rates in the compositional systems investigated. To minimize the opportunity for SCC to occur, the molar ratio of nitrate plus nitrite plus aluminate to hydroxide should be maintained as high as possible, without entering a nitrate SCC region of compositions. Also, oxidizing agents such as PbO which can shift the corrosion potential into a range causing SCC should be avoided.
- (4) Compositional effects can be summarized as follows:
 - a. Increasing the hydroxide concentration increases general corrosion and SCC.
 - b. Nitrate, nitrite, and aluminate, when present together, enhance passivity and decrease corrosion.
 - c. Chloride enhances both general corrosion and SCC.
 - d. Carbonate increases the severity of SCC.
 - e. Alkaline earth, heavy metal, rare earth, and actinide metal hydroxides do not significantly affect corrosion or SCC behavior.