FINAL REPORT

on

CORROSIVITY OF SOLUTIONS FROM
EVAPORATION OF RADIOACTIVE
LIQUID WASTES

to

ATLANTIC RICHFIELD-HANFORD
CORPORATION

May 4, 1977

by

J. H. Payer, E. S. Kolic, and W. K. Boyd

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EXECUTIVE SUMMARY

As part of a waste management program, high-level nuclear liquid wastes will be treated in an evaporator to decrease volume and the residual liquor then stored underground in double-shell tanks for further processing. Typical solutions consist primarily of hydroxide, nitrate, nitrite, aluminate with minor amounts of several other anions and cations. A variety of evaporation, neutralization, and boiling combinations and heterogeneity of nuclear waste feed liquor results in a broad compositional range of residual liquors and slurries to be stored. It is necessary to determine the corrosivity of these processed wastes, broadly termed terminal solutions, to evaluate the reliability of double-shell tank storage.

A previous study by Battelle's Columbus Laboratories for ARHCO investigated the corrosion behavior of ASTM A-283 steel in synthetic salt-cake compositions and found stress-corrosion cracking to be the most likely failure mode. General corrosion rates were extremely low and pitting was not detected under any conditions investigated.

New double-shell storage tanks are constructed with ASTM A-516 Grade 65 steel. This study had two main objectives:

- (1) To characterize the corrosivity of synthetic nonradioactive terminal waste solutions to ASTM A-516 Grade 65 steel
- (2) To determine the severity of stress-corrosion cracking of carbon steel in terminal waste solutions.

The information developed provides guidance in the characterization of the aggressiveness of actual terminal liquors and in the design and operation of fail-safe tanks.

The approach was to conduct a laboratory program to investigate the corrosivity of synthetic terminal waste solutions over the expected composition range. In addition, a series of less complex solutions was investigated to determine the effects of major constituents of stored nuclear wastes namely; hydroxide, nitrate, nitrite, and aluminate.

Two experimental techniques were used extensively. First, corrosion behavior was measured over a range of oxidizing conditions by the potentiodynamic polarization technique. Using this technique, oxidizing conditions in a solution likely to promote general corrosion, pitting or stress-corrosion cracking (SCC) were identified. Secondly, absolute stress-corrosion cracking susceptibility was determined by constant strain rate procedure for ASTM A-516 Grade 65 steel for conditions identified by polarization experiments as likely to promote SCC.

Based on the results of this study, terminal waste storage tanks are safe from stress-corrosion cracking under freely corroding conditions. Corrosion potential of steel in solutions within anticipated compositions is at the positive end of the critical range for stress-corrosion cracking, and no conditions were observed which would lower the potential to more negative values within the cracking range under freely corroding conditions. Measurement of corrosion potential and hydroxide concentration provides a means to extend these results to compositions outside of the composition range studied.

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INTRODUCTION

As part of a waste management program, high-level nuclear liquid wastes will be treated in an evaporator to decrease volume and the residual liquor then stored underground in double-shell tanks for further processing. Typical solutions consist primarily of hydroxide, nitrate, nitrite, aluminate with minor amounts of several other anions and cations. The residual liquors can be further boiled down for more volume reduction to form a slurry. Alternatively, evaporator residual liquor can be partially neutralized with nitric acid followed by boiling down. The variety of evaporation, neutralization, and boiling combinations and heterogeneity of nuclear waste feed liquor result in a broad compositional range of residual liquors and slurries to be stored. It is necessary to determine the corrosivity of these processed wastes, broadly termed terminal solutions, to evaluate the reliability of double shell tank storage.

A previous study by Battelle's Columbus Laboratories for Atlantic Richfield-Hanford Corporation* investigated the corrosion behavior of ASTM A-283 steel in synthetic salt-cake compositions. An objective of that program was to identify probable modes of failure for salt-cake storage tanks built over the past 30 years. Stress-corrosion cracking was found to be the most likely failure mode. General corrosion rates were extremely low and pitting was not detected under any conditions investigated.

New double-shell storage tanks are constructed with ASTM A-516 Grade 65 steel. The double-shell tanks are fabricated by welding steel plate. All welds are stress relieved. It is the corrosivity of terminal high-level waste solutions to these tanks which is of interest in this study. Emphasis is placed on stress-corrosion cracking resistance as it remains the most probable failure mode.

The study had two main objectives:

- (1) To characterize the corrosivity of synthetic nonradioactive terminal waste solutions to ASTM A-516 Grade 65 steel
- (2) To determine the severity of stress-corrosion cracking of carbon steel in terminal waste solutions.

The information developed provides guidance in the characterization of the aggressiveness of actual terminal liquors and in the design and operation of fail-safe tanks.

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* "Corrosivity of Synthetic Salt Cake", Battelle Columbus Laboratory Report to Atlantic Richfield-Hanford Corporation, J. H. Payer, R. B. Diegle, and W. K. Boyd, July 18, 1975.

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EXPERIMENTAL PROCEDURE

Synthetic Terminal Waste Compositions

Six groups of synthetic waste solutions presented in Table 1 were investigated. The first two groups comprise solutions to investigate the effect of major constituents in slurry solutions. The remainder of solutions cover the range of compositions anticipated for storage in double-shell tanks.

All solutions were prepared from reagent grade chemicals (exception: sodium aluminate, purified) and distilled water. Solutions were stored in Teflon bottles at 93 C for a minimum of 1 week prior to testing.

Steel

Mild steel for the study was supplied by Atlantic Richfield-Hanford Corporation (ARHCO) from plate used in construction of the SV double-shell storage tanks. A section of 1/2-inch thick, mill-normalized ASTM 516 grade 65 steel plate from Heat Number T83361 was sent to Battelle. Chemical composition and mechanical properties of the as-received steel are presented in Table 2.

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

TABLE 1. SYNTHETIC WASTE COMPOSITIONS

Solution Identification	OH ⁻	Composition			Other
		NO ₃ ⁻	NO ₂ ⁻	AlO ₂ ⁻	
MAJOR CONSTITUENTS SOLUTIONS					
M-1	2.0	--	--	--	
B-7	5.75	--	--	--	
M-2	8.0	--	--	--	
B-8	5.75	2.9	--	--	
B-9	5.75	--	2.9	--	
B-10	5.75	--	--	2.9	
E-4	5.75	2.9	--	2.9	
NITRATE-NITRITE MATRIX SOLUTIONS					
D-1	5.75	--	1.5	--	
D-2	5.75	--	0.5	--	
D-3	5.75	--	0.1	--	
D-4	5.75	1.5	--	--	
D-5	5.75	0.5	--	--	
D-6	5.75	0.1	--	--	
D-7	5.75	1.5	1.5	--	
D-8	5.57	0.5	0.5	--	
D-9	5.75	2.9	0.5	--	
D-10	5.75	2.9	1.5	--	
B-11	5.75	2.9	2.9	--	
TERMINAL WASTE SOLUTIONS					
B-1	5.5	2.7	2.2	1.7	Residual Liquors
B-2	4.0	2.4	2.9	2.5	
B-4	2.5	2.7	3.2	3.2	
B-1A	7.3	3.6	2.9	2.3	Double-Shell Slurries
B-2A	6.0	3.2	4.4	3.8	
B-4A	3.8	4.1	4.8	4.8	
MINOR CONSTITUENTS SOLUTIONS					
B-7M	5.75	--	--	--	(1)
B-2M	4.0	2.4	2.9	2.5	(1)
LOW NITRITE SOLUTION SERIES					
E-1	7.3	3.6	--	3.8	
E-3	7.3	3.6	0.1	3.8	
E-2	7.3	3.6	1.0	3.8	
E-5	6.0	3.2	--	3.8	
E-6	1.0	3.4	--	0.5	
COMPLEXANT SOLUTION SERIES					
1-C	7.3	3.6	2.9	2.3	Citrate, EDTA, HEDTA
2-C	7.3	3.6	2.9	2.3	Citrate
3-C	7.3	--	--	--	Citrate, EDTA, HEDTA

(1) Minor constituents consisted of 0.1M CO₃, 0.01M PO₄, 0.05M SO₄, 0.003M SiO₃, 0.005M F, and 0.1M Cl.

TABLE 2. PROPERTIES OF NORMALIZED ASTM 516
GRADE 65 STEEL

<u>Chemical Composition (w/o)</u>									
C	Mn	P	S	Cr	Ni	Mo	S	Al	Cu
0.18	1.04	0.020	0.24	0.03	0.05	<0.01	0.024	0.03	0.10
<u>Mechanical Properties</u>									
<u>Yield Strength, psi</u>		<u>Ultimate Strength, psi</u>				<u>% Reduction In Area</u>		<u>% Elongation (2 inches)</u>	
49,800		72,400				57		39	

Constant strain rate specimens were 3/16-inch diameter by 7-inches long with a reduced gage length of 0.100-inch diameter by 0.5-inch long. All specimens were prepared with their length parallel to the steel plate rolling direction.

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 a Teflon holder. The specimen-holder combination was next placed into a Teflon electrochemical cell containing the preheated electrolyte maintained at 93 C. Fast-scan polarization curves were determined by pre-polarizing the specimen at -1.3 V-SCE for several minutes, followed by potentiodynamic scanning to 0.0 V-SCE at a rate of 1 V/min. Slow-scan polarization curves were determined by first prepolarizing the specimens at -1.3 V-SCE for several minutes; secondly, allowing the specimen to freely corrode for 5 minutes; and finally, potentiodynamically scanning from the corrosion potential to 0.0 V-SCE at a rate of 20 mV/min.

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. Severity of SCC was expressed as apparent stress-corrosion crack velocity. Velocity was calculated by dividing the length of longest secondary crack observed metallographically by time-to-failure. Qualitative expressions for severity used in the report were defined as severe for $v > 0.7 \mu\text{m/sec}$, moderate for $0.2 \leq v \leq 0.7$, and slight for $v < 0.2 \mu\text{m/sec}$.

Specimens were strained at a constant rate of 2.5×10^{-6} 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 OF MAJOR CONSTITUENT SOLUTIONS STUDY

Hydroxide Solutions

A 5.75 M NaOH solution was selected as the basis for the composition study for two reasons. First, hydroxide is the major constituent of nuclear terminal waste solutions, and the selected concentration is in the mid-range of reported slurry compositions. Secondly, this solution provides a link between the study of synthetic terminal waste solutions and the extensive studies of stress-corrosion cracking of carbon steel in caustic solutions⁽¹⁻¹¹⁾.

Potentiodynamic polarization curves for all solutions given in Table 1 are presented in Appendix A along with results of all constant strain rate tests. These results are summarized in this section.

The general approach was to screen solutions to determine potential ranges likely to promote SCC using fast and slow scan rate potentiodynamic polarization techniques, followed by constant strain rate tests to determine absolute SCC susceptibility. This procedure was successfully applied to the investigation of SCC of carbon steel in caustic and carbonate-bicarbonate solutions⁽⁹⁻¹¹⁾.

Results for 5.75 M NaOH at 93 C are shown in Figure 1. At the fast scan rate (IV/min), mild steel exhibited active-passive behavior.

FIGURE 1. FAST AND SLOW SCAN RATE POLARIZATION CURVES OF ASTM 516 STEEL IN 5.75 M NaOH AND CONSTANT STRAIN RATE SCC RESULTS

A primary anodic peak was observed at -1.0 V-SCE and a secondary anodic peak at -0.77 V-SCE. Current densities (c.d.) at the primary and secondary peaks were 8 and 2 mA/cm², respectively. At the slow scan rate (20 mV/min), the entire polarization curve was shifted to the left, and anodic peak c.d.s. were reduced by more than an order of magnitude to 0.4 and 0.02 mA/cm².

For carbon steel in caustic solutions, potential ranges likely to promote SCC are those where (1) reductions in current density of greater than an order of magnitude are observed between fast and slow scans and (2) anodic current densities for the fast scan exceed approximately 1 mA/cm². Based on these criteria, constant strain rate tests in 5.75 M NaOH were run at intervals from -1.05 to -0.77 V-SCE. This range extends from just below the primary anodic peak to the maximum of the secondary anodic peak.

Stress-corrosion crack velocities are presented in Figure 1 as a function of potential. Velocities were calculated by dividing length of the deepest crack determined metallographically by the time-to-failure in the constant strain rate test. Severity of SCC corresponded directly to anodic c.d. and was greatest (1.3 μ m/sec) at -1.0 V-SCE, the maximum in the primary anodic peak.

Many secondary stress-corrosion cracks were observed along the gage length of constant strain rate specimens tested in the critical range for SCC. A photomicrograph of a specimen pulled to failure at a strain rate of 2.5×10^{-6} per second in 5.75 M NaOH, -1.0 V-SCE applied potential, and 93 C is presented in Figure 2. Secondary cracks are more numerous and open near the primary fracture in the "necked" portion of the specimen. Stress-corrosion cracks propagated in an intergranular mode until the remaining cross section failed by ductile, mechanical failure. The transition between brittle, intergranular SCC and ductile, mechanical region is shown in a scanning electron micrograph of the primary fracture surface in Figure 3a. Secondary cracks along the side of the specimen are also shown in the right side of Figure 3a. The intergranular appearance of the SCC region is clearly shown in Figure 3b.

FIGURE 2. PHOTOMACROGRAPH OF STRESS-CORROSION CRACKS
IN STEEL AFTER CONSTANT STRAIN RATE TEST
(5.75 M NaOH, -1.0 V-SCE, 93 C)

FIGURE 3. SCANNING ELECTRON MICROGRAPH OF PRIMARY FRACTURE SURFACE OF STEEL AFTER CONSTANT STRAIN RATE TEST SHOWING INTERGRANULAR STRESS-CORROSION CRACKING

Multiple, secondary cracks are shown in cross section in Figure 4. The etched specimen confirms intergranular SCC through the ferrite-pearlite microstructure of ASTM A-516 steel.

Hydroxide concentrations in waste solutions range from approximately 2 M to 8 M. Anodic polarization curves at these levels indicated that corrosivity increases with increasing hydroxide concentration. First, maximum anodic c.d. which remained at -1.0 V-SCE increased from 1 mA/cm² for 2 M to 8 mA/cm² for 5.75 M and to 9 mA/cm² for 8 M NaOH. Secondly, corrosion potential became more active (negative) and the secondary anodic peak more pronounced as hydroxide concentration increased. Increased SCC susceptibility is reflected by both increased crack velocity at a potential and a broader potential range over which SCC is observed.

Single Addition of Nitrate, Nitrite, and Aluminate

Single additions of nitrate, nitrite, and aluminate were made to a 5.75 M NaOH solution and the effect on SCC investigated. Each constituent was added at 2.9 M, a concentration within the range expected in terminal waste solutions. Both, oxidation-reduction kinetics and SCC susceptibility were evaluated.

Nitrate greatly suppressed the anodic peak at -1.0 V-SCE and resulted in a complex anodic polarization curve. At potentials more positive than -0.9 V-SCE little effect of nitrate was observed. Corrosion potential was more noble with nitrate than without, -1.03 and -1.14 V-SCE respectively. Constant strain rate tests at constant potential over the range of -1.0 to -0.75 V-SCE revealed that the severity of SCC followed the same pattern as observed in pure caustic solution, i.e., SCC was most severe at -1.0 V-SCE. At -1.0 V-SCE, SCC was more severe with nitrate than without.

Nitrite suppressed the anodic peak at -1.0 V-SCE further than nitrate. The complex polarization behavior is presented in Figure 5. Corrosion potential was -0.86 V-SCE and the steel was spontaneously passive.

An anodic loop was observed in the potential range from -0.94 to -0.99 V-SCE, i.e., instead of the cathodic current increasing mono-

a. Unetched Micrograph 600x

b. Nital Etched Micrograph 600x

FIGURE 4. METALLOGRAPHIC CROSS SECTIONS OF SECONDARY SCC
IN STEEL AFTER CONSTANT STRAIN RATE TEST IN
5.75 M NaOH

FIGURE 5. COMPLEX POLARIZATION BEHAVIOR OF STEEL IN
5.75 M NaOH - 2.9 M NaNO₂

tonically with more negative potential from the corrosion potential, a current reversal was observed and anodic currents were measured over a small potential range, further decrease in potential resulted in return of cathodic currents. This current reversal results from the suppressed anodic peak at -1.0 V-SCE and will be discussed in more detail in a later section of this report. A constant strain rate test at the maximum current in the anodic loop resulted in severe SCC. This is an important result in that SCC was observed at a potential more active (negative) than the corrosion potential; therefore, cathodic polarization in this situation can promote SCC.

Aluminate increased the anodic peak at -1.0 V-SCE and suppressed the secondary anodic peak at -0.77 V-SCE. Maximum c.d.'s for these two peaks changed from 8 to 15 mA/cm² and from 2 to 0.2 mA/cm² respectively with the addition of 2.9 M NaAlO₂ to 5.75 M NaOH. Constant strain rate results found severity of SCC to correlate directly with anodic c.d. Maximum severity was observed at -1.0 V-SCE where SCC was more severe with aluminate than without. No SCC was observed in the potential range of the secondary anodic peak in the presence of aluminate.

Aluminate (2.9 M) had no major effect on polarization behavior when added to a solution of 5.75 M NaOH - 2.9 M NaNO₃. While aluminate and nitrate alone increased SCC severity at -1.0 V-SCE, addition of both to 5.75 M NaOH reduced SCC severity.

Nitrate-Nitrite Additions to Hydroxide Solutions

A matrix of solutions was designed to further study the effects of nitrate and nitrite additions. Single and combined additions of up to 2.9 M NaNO₃ and NaNO₂ were made to 5.75 M NaOH at 93 C, and polarization behavior was determined.

Anodic polarization curves over the composition range studied are presented in Figure 6. The curves are consolidated to show the overall trends observed with addition of nitrate and nitrite. Shown, also, are corrosion potentials over the composition range.

Both nitrate and nitrite increased reduction kinetics as indicated by a shift in corrosion potential to more noble (positive) values.

FIGURE 6. ANODIC POLARIZATION CURVES OF STEEL AS FUNCTION OF NITRATE AND NITRITE ADDITIONS TO 5.75 M NaOH

The effect of nitrite was much greater than nitrate. Increasing nitrate concentration through 2.9 M resulted in steadily more positive corrosion potential, -1.14 V-SCE with no nitrate to -1.03 V-SCE with 2.9 M NaNO_3 . As corrosion potential became more positive, the anodic peak at -1.0 V-SCE became less prominent until it was barely discernible at the highest nitrate concentration.

Even the smallest addition of nitrite, resulted in a large positive shift in corrosion potential from -1.14 V-SCE with no nitrite to -0.91 V-SCE with 0.1 M NaNO_2 . Steel was spontaneously passive with any nitrite addition and no anodic peaks were observed. In 5.75 M NaOH - 0.1 M NaNO_2 , evidence of an anodic peak observed in 5.75 M NaOH was manifested by an anodic loop in the cathodic polarization curve. Increasing nitrite to 2.9 M resulted in a steady increase in cathodic reaction rates. All solutions containing both nitrate and nitrite were spontaneously passive. The most noble corrosion potential observed was -0.84 V-SCE for 5.75 M NaOH - 2.9 M NaNO_3 - 2.9 M NaNO_2 .

Severe SCC was observed in constant strain rate tests for specimens maintained at -0.95 and -1.0 V-SCE in 5.75 M NaOH - 2.9 M NaNO_3 - 2.9 M NaNO_2 . These potentials are more than 0.1 V more active (negative) than the free corrosion potential.

Discussion of Major Constituent Effects

In general, the roles of major constituents in terminal waste solutions can be summarized as follows. The dissolution behavior of steel in these solutions is dominated by hydroxide concentration, since the anodic kinetics are not affected greatly by other constituents. Nitrate and nitrite additions increase the reduction kinetics and consequently affect the corrosion potential. This in turn influences the corrosion behavior of steel under freely corroding conditions. Aluminate has only a secondary effect and is generally beneficial.

Steel exhibits active-passive behavior over the range of caustic concentrations observed for terminal waste solutions (2-8 M). These concentrations are not particularly corrosive to steel, and general corrosion

or pitting is not considered a problem. This view was supported by direct weight loss measurements and linear polarization experiments in synthetic salt cake solutions in a previous study. Stress-corrosion cracking does occur, however, at potentials within a critical range more noble (positive) than the free corrosion potential in caustic solutions^(4,9). This, SCC is the most likely mode of environmentally-related failure which can be operative in storage of terminal waste solutions. The primary issue is whether compositions within the range observed in storage can maintain the potential of steel within the critical range for SCC under freely corroding conditions.

Results for ASTM A-516 Grade 65 steel agree with those reported for mild and carbon steels in the literature. Stress corrosion was observed over the potential range of -1.05 to -0.77 V-SCE, with SCC most severe at -1.0 V-SCE. At potentials more negative than this range, anodic currents are not great enough to support SCC and cathodic protection occurs. At potentials more positive than the critical range, steel is passive and no SCC is observed.

Aluminate did not affect the reduction kinetics and had little affect on the corrosion potential. The primary effects of aluminate were the essential elimination of a secondary anodic peak observed in 5.75 M NaOH at -0.77 V-SCE and an increase in the maximum current density of the peak at -1.0 V-SCE. This combination decreases the likelihood for SCC under freely corroding conditions for two reasons. First, the critical range for SCC is reduced to approximately 100 millivolts (-1.05 to -0.95 V-SCE) from approximately 300 mV. Secondly, increased height of the anodic peak over a narrower potential range decreases the likelihood of the reduction curve intersecting the anodic curve in the critical range, i.e., a potential either more negative (cathodic protection) than the critical range or more positive (passivation) is favored.

Both nitrate and nitrite, since they are reducible species, stimulate the reduction kinetics by the following reactions⁽¹²⁾:

Nitrate can be reduced to nitrite and nitrite can be reduced to ammonia. At the potential of steel in terminal waste solutions, ammonia is the thermodynamically stable species and reduction is favored. In fact, ammonia was detected upon opening sealed steel capsules containing synthetic solidified waste after long term exposures carried out by ARHCO. The reduction of nitrite is relatively fast since additions greatly affect the cathodic polarization, whereas reduction of nitrate proceeds relatively slowly and affects cathodic reduction much less.

All of the complex polarization curves observed for solutions with nitrate and nitrite can be rationalized on the basis of invariant dissolution behavior for steel with increased cathodic reaction rate from reduction of nitrate or nitrite. This is shown schematically in Figure 7. The net current (algebraic sum of anodic and cathodic current) is measured experimentally⁽¹³⁻¹⁶⁾. As cathodic reactions proceed more rapidly, the cathodic polarization curve shifts up and to the right - (1) through (4). At each condition one of the four curves indicated is measured experimentally. Solutions investigated here corresponding to these four are (1) 5.75 M NaOH; (2) 5.75 M NaOH, 0.5 M NaNO₃; (3) 5.75 M NaOH, 2.9 M NaNO₃; and (4) 5.75 M NaOH, 2.9 M NaNO₃, 2.9 M NaNO₂.

Free corrosion potential becomes more positive as the reaction rate increases. For (2), the height of the first anodic peak is decreased. For (3), the first anodic peak is submerged and an anodic loop is observed in the cathodic polarization curve. For (4), the first anodic peak is completely submerged and the only evidence of its existence is an inflection in the cathodic curve. With further increase in reduction kinetics no indication of the submerged anodic peak would be observed. SCC is promoted under freely corroding conditions when the cathodic curve intersects the anodic curve at a potential in the critical range for SCC.

RESULTS OF TERMINAL WASTE SOLUTIONS STUDY

Anticipated Composition Range

Six synthetic terminal waste compositions designated by ARHCO were studied to cover the anticipated compositional range of solutions to be

FIGURE 7. SCHEMATIC POLARIZATION CURVES FOR INCREASING CATHODIC REACTION RATE

stored. All solutions contained hydroxide (2.5-7.3 M), nitrate (2.4-4.1 M), nitrite (2.2-4.8 M), and aluminate (1.7-4.8 M); complete compositions are listed in Table 1. Only the four major constituents of waste solutions were added here with the effect of minor constituents studied in another series of solutions.

Mild steel was spontaneously passive in all six solutions. Free corrosion potentials ranged from -0.83 to -0.94 V-SCE. In general, corrosion potential became more negative with increasing hydroxide concentration. A fast-scan polarization curve for 5.5 M hydroxide, 2.7 M nitrate, 2.2 M nitrite, and 1.7 M aluminate solution is shown in Figure 8. An anodic loop was observed in the cathodic polarization curve at approximately -1.0 V-SCE. These results are consistent with predictions from investigation of major constituents discussed in the previous section.

Constant strain rate SCC results are also shown in Figure 8. Under freely corroding conditions, no stress-corrosion cracking was observed; however, when potential was maintained at -1.0 V-SCE, greater than 100 mV negative of the corrosion potential, stress-corrosion cracking was observed. As shown in Figure 9, multiple secondary cracks were observed along the steel surface. These metallographic cross sections through the failed specimen indicated the cracks were branched and intergranular. Scanning electron microscopic examination of the primary fracture surface confirmed the intergranular mode of crack propagation. Two SEM photomicrographs are shown in Figure 10. The transition from brittle, stress corrosion in the upper-right of Figure 10 to ductile, mechanical response is apparent. Figure 10 shows the intergranular, stress corrosion region at higher magnification. Stress-corrosion cracking observed here was identical in every respect to that observed in pure hydroxide solutions.

Thus, in synthetic terminal waste solutions as in the solutions discussed in the previous section there is a critical potential range for stress-corrosion cracking. In the anticipated composition range for terminal waste solutions the critical range is more negative than the corrosion potential and cathodic polarization is necessary to shift steel into the critical potential range. Synthetic terminal waste solutions resulting in more active corrosion potentials (more negative) maintain

FIGURE 8. POLARIZATION CURVE AND CONSTANT STRAIN RATE SCC RESULTS FOR MILD STEEL IN SYNTHETIC WASTE SOLUTION

23

a

150x

b

600x

FIGURE 9. PHOTOMICROGRAPHS OF SECONDARY STRESS-CORROSION
CRACKS IN STEEL WITH APPLIED CATHODIC CURRENT
IN SYNTHETIC SLURRY SOLUTION

FIGURE 10. SCANNING ELECTRON MICROGRAPHS OF PRIMARY FRACTURE SURFACE OF CONSTANT STRAIN RATE SPECIMEN EXPOSED WITH APPLIED CATHODIC CURRENT TO MAINTAIN POTENTIAL IN CRITICAL SCC RANGE

steel near the upper end of the critical potential range. In two of these solutions, steel exhibited free corrosion potentials of -0.92 and -0.94 V-SCE and slight severity stress-corrosion cracking was observed under freely corroding conditions, i.e., crack velocities were less than 0.2 $\mu\text{m}/\text{sec}$.

Other Solution Variables

Several other solution variables were investigated to determine their effects on stress-corrosion cracking susceptibility. The principle objective of these tests was to determine if any conditions in operating storage tanks were likely to shift potentials more negative and consequently favor stress-corrosion cracking. Effects investigated included--minor constituents, low-nitrite concentration, temperature, and complexant additions.

In addition to the four major constituents of terminal waste solutions, many minor constituents can be present. The combined effect of carbonate (0.1 M), phosphate (0.01 M), chloride (0.1 M), sulfate (0.05 M), silicate (0.003 M), and floride (0.005 M) was studied in two solutions: (1) 5.75 hydroxide and (2) 4.0 M hydroxide, 2.4 M nitrate, 2.9 M nitrite, and 2.5 M aluminate. No significant effect upon polarization behavior was observed in either solution. In the former, active-passive behavior was observed. Minor constituents resulted in a more active corrosion potential of -1.19 from -1.14 V-SCE and a slight reduction in current density of the primary anodic peak to 5 from 8 mA/cm^2 . In the latter, both solutions were spontaneously passive with corrosion potentials of -0.85 and -0.87 V-SCE without and with minor constituents respectively. Based on the results for the two solutions studied it was concluded that minor constituents do not significantly increase the dissolution or stress-corrosion cracking susceptibility of steel in terminal waste solutions. This is consistent with results of a previous study which found no significant effect of alkaline earth, heavy metal, rare earth, and actinide metal hydroxides on steel dissolution or stress corrosion.

A series of solutions was prepared to study the effect of low nitrite concentrations. Nitrite contributed most strongly of all constituents to maintaining potentials more positive than the critical potential range, with even small additions to hydroxide solutions resulting in spontaneous passivity; however, nitrite is consumed during storage by reduction to ammonia. Therefore, extreme cases of major reduction or complete elimination of nitrite from terminal waste solutions were studied at low and high hydroxide concentrations.

Using 7.3 M hydroxide, 3.6 M nitrate, 2.9 M nitrite, and 2.3 M aluminate for comparison, nitrite was reduced to 1.0 M, 0.1 M, and 0. The steady state corrosion potential in these solutions was not significantly affected; however, for cathodic polarization curves a clearer delineation of anodic peaks was observed as nitrite concentration decreased. With no nitrite, both anodic peaks observed in pure hydroxide solutions were clearly apparent at potentials more negative than the corrosion potential. Constant strain rate stress corrosion tests under freely corroding conditions resulted in moderate stress-corrosion cracking with no nitrite and only slight stress-corrosion cracking with either 1.0 or 2.3 M nitrite.

For a solution of 6.0 M hydroxide, 3.2 M nitrate, and 3.8 M aluminate, reducing nitrite concentration from 4.4 M to 0 had no significant effect on the fast-scan polarization curves and reduced corrosion potential from -0.92 to -0.95 V-SCE. Spontaneous passivity was observed in both solutions. In the most dilute hydroxide concentration investigated 1.0 M hydroxide, 3.4 M nitrate, 0 M nitrite, and 0.5 M aluminate, steel was spontaneously passive. No SCC was observed under freely corroding conditions, while as observed in all solutions maintaining potential at -1.0 V-SCE resulted in stress corrosion.

Thus, nitrite is consistently a beneficial component of terminal waste solutions in favoring more noble (positive) potentials and maintaining steel at potentials more positive than the critical potential range for SCC. Nitrite is not necessary for spontaneous passivity of the more concentrated nitrate and aluminate solutions. Also, as hydroxide concentration decreases less nitrite and/or nitrate is required for passivation.

A brief investigation of the effect of temperature was undertaken with synthetic terminal waste solutions. Fast scan polarization curves for solutions B-1A, B-2A, and B-4A at 50 C showed no significant effect of lower temperature. Steel was spontaneously passive in all solutions, as it was at 93 C. Increasing temperature to 121 or 148 C had no significant effect on the polarization behavior of steel in synthetic solution B-2A. In general, it is expected that stress corrosion severity increases with increasing temperature over the range studied. This is likely to be a secondary effect for terminal waste solution storage; however, since temperature affected the freely corroding potential only slightly.

In the processing of nuclear wastes three complexants are used somewhat interchangeably and can consequently be found in terminal waste solutions. They are EDTA, HEDTA, and sodium citrate. Three 100 ml alliquots comprising 40 w/o EDTA, 40 w/o HEDTA, and 3 M sodium citrate were added to 1ℓ 7.3 M sodium hydroxide and to 1ℓ of synthetic waste solution B-1A, and 100 ml alliquot of 3 M sodium citrate alone was added to 1ℓ of synthetic solution B-1A. Fast-scan polarization curves in these three solutions found no major effect of complexants on the dissolution behavior of steel in solution B-1A and increase in the maximum current density of the primary anodic peak in 7.3 M sodium hydroxide solution. In solution B-1A, no stress corrosion was observed in constant strain rate tests under freely corroding conditions with either single or triple complexant additions. Maintaining potential in the critical cracking range at (-1.0 V-SCE) resulted in stress corrosion. A constant strain rate test at potential of maximum anodic c.d. for complexant addition to hydroxide solution, (-1.0 V-SCE), resulted in severe stress corrosion, which is consistent with the high value of c.d. It appears that complexants by themselves would not cause potential shifts into the critical range.

Discussion of Synthetic Terminal Waste Solution Study

All results of the study of synthetic slurry solutions are consistent with observations and conclusions from the study of major constituents. Steel in terminal waste solutions is spontaneously passive and protected from corrosion and stress corrosion by an adherent oxide layer. Under freely corroding conditions, steel potential is more noble (positive) than the critical potential range for stress-corrosion cracking. This critical potential range is narrow and extends from approximately -0.95 to -1.03 V-SCE. Prevention of stress corrosion depends upon maintaining potential outside of this range.

The primary question, therefore, is: Are there conditions over the range of composition and temperature experienced in storage of terminal waste solutions which can result in more negative potentials under freely corroding conditions? These conditions could then promote stress corrosion; however, in order for stress corrosion to occur several conditions must be met. First, a metal susceptible to SCC is required; steel is susceptible to SCC. Secondly, a specific environment to promote SCC is required; terminal waste solutions are among the group of caustic solutions which could promote SCC. Thirdly, sufficient tensile stresses are required; in this study constant strain rate was applied to the specimens to meet this requirement. In storage tanks, sources of tensile stresses are operating stresses, thermal stresses, and residual stresses from fabrication and construction. Residual stresses can be lowered by stress relief treatment during construction, which is the procedure for all double-shell tanks constructed at Hanford. Finally, oxidizing conditions must result in a potential within the critical range for SCC. If any of these criteria are not met, SCC will not occur.

No composition within the range anticipated in terminal waste solution storage was found to promote either moderate or severe SCC. Results did indicate that corrosion potential of steel was at the edge of a critical potential range for some solutions. Aggressiveness of the solutions increased with increasing hydroxide concentration. Nitrate and nitrite are beneficial and promote passivity, with nitrite being the more effective species. Small concentrations of nitrite, on the order of 0.1 M,

are sufficient to passivate steel. Aluminate is considered beneficial, because while it increases severity of SCC it also reduces the critical potential range. Other constituents likely to be contained in terminal waste solutions, i.e., carbonate, phosphate, sulfate, silicate, fluoride, chloride, and complexants, had no significant effect on SCC susceptibility. Moreover, temperature over the range of 50 to 148 C had no significant effect.

A means to protect steel from corrosion and stress corrosion is through the control of oxidizing conditions. Either, cathodic or anodic protection is possible. The former depends upon polarization to more active (negative) potentials where steel dissolution is suppressed, while the latter depends upon polarization to more noble (positive) potentials where passivation is favored. The possible danger of applying insufficient cathodic protection to polarize steel to potentials below the critical potential range for SCC and therefore to a potential within the critical range is apparent. For this reason cathodic protection of steel in terminal waste solutions is not recommended, and of the two alternatives, anodic protection to promote passivity is preferred.

The data base developed in this study provides a means to screen waste solutions for SCC aggressiveness. Measurement of hydroxide concentration and free corrosion potential of steel in a solution provides an indication of the likelihood of that solution promoting SCC. Solutions outside of the composition range studied or the effect of other constituents not included in this study can readily be screened by polarization technique with subsequent constant strain rate tests if desired. Knowledge of the free corrosion potential alone gives a good indication of SCC aggressiveness.

CONCLUSIONS

The following conclusions are drawn from the study of steel in synthetic terminal waste solutions:

- (1) No composition within the anticipated range of composition for terminal waste solution storage was found to promote

stress-corrosion cracking (SCC) under freely corroding conditions. Solutions investigated covered the composition range of 2.5-7.3 M hydroxide, 2.4-4.1 M nitrate, 2.2-4.8 M nitrite, and 1.7-4.8 M aluminate.

- (2) Steel is spontaneously passive in waste solutions with corrosion potential more noble (positive) than the critical range for SCC.
- (3) Anodic dissolution kinetics are controlled primarily by hydroxide concentration with solution aggressiveness increasing with increasing concentrations.
- (4) Nitrate and nitrite increase the rate of reduction and promote passivity with nitrite being the more effective passivating agent.
- (5) Aluminate narrows the critical potential range for stress-corrosion cracking and increases severity of stress-corrosion cracking within the critical range.
- (6) Based on results of this study and a previous study of steel corrosivity in salt cake solutions, numerous additional anions and cations that can be present in terminal waste solutions have no significant effect on steel corrosion or stress-corrosion cracking.
- (7) The combination of polarization measurement and constant strain rate SCC experiments provided a basis for determination of critical potential range for stress-corrosion cracking, severity of stress-corrosion cracking, and the effects of constituents of complex chemical solutions.
- (8) Stress-corrosion cracking of steel in synthetic terminal waste solutions propagates in a branched, intergranular mode.
- (9) Severity of stress-corrosion cracking expressed as apparent crack velocity increases directly with anodic current density.

Based on the results of this study, terminal waste storage tanks are safe from stress-corrosion cracking under freely corroding conditions. Corrosion potential of steel in solutions within the anticipated compositions is at the positive end of the critical range for stress-corrosion cracking, and no conditions were observed which would lower the potential to more negative values within the cracking range under freely corroding conditions. Measurement of corrosion potential and hydroxide concentration provides a means to extend these results to compositions outside of the composition range studied.

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APPENDIX A

CONSTANT STRAIN RATE SCC TEST RESULTS
AND POTENTIODYNAMIC POLARIZATION
CURVES FOR SYNTHETIC NUCLEAR
WASTE SOLUTIONS

A-1

FIGURE A-1. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION M-1

A-2

FIGURE A-2. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-7

A-3

FIGURE A-3. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION M-2

A-4

FIGURE A-4. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-8

A-5

FIGURE A-5. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-9

A-6

FIGURE A-6. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-10

A-7

FIGURE A-7. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION E-4

A-8

FIGURE A-8. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION D-1

A-9

FIGURE A-9. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION D-2

A-10

FIGURE A-10. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION D-3

A-11

FIGURE A-11. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION D-4

A-12

FIGURE A-12. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION D-5

A-13

FIGURE A-13. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION D-6

A-14

FIGURE A-14. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION D-7

A-15

FIGURE A-15. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION D-8

A-16

FIGURE A-16. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION D-9

A-17

FIGURE A-17. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION D-10

A-18

FIGURE A-18. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-11

A-19

FIGURE A-19. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-1

A-20

FIGURE A-20. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-2

A-21

FIGURE A-21. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-4

A-22

FIGURE A-22. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-1A

A-23

FIGURE A-23. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-2A

A-24

FIGURE A-24. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-4A

FIGURE A-25. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-7M

A-26

FIGURE A-26. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION B-2M

A-27

FIGURE A-27. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION E-1

A-28

FIGURE A-28. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION E-3

FIGURE A-29. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION E-2

A-30

FIGURE A-30. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION E-5

A-31

FIGURE A-31. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION E-6

A-32

FIGURE A-32. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION 1-6

A-33

FIGURE A-33. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION Z-6

A-34

FIGURE A-34. POTENTIODYNAMIC POLARIZATION BEHAVIOR OF ASTM 516 STEEL IN SYNTHETIC WASTE SOLUTION C-3

TABLE 1. CONSTANT STRAIN RATE RESULTS

Solution No.	Applied Potential -V(SCE)	Time To Failure Hrs.	Red. of Area %	Length mils	Velocity $\mu\text{m/sec}$	Remarks
B-7	-0.077	44.9	76.0	1.7	0.26	Shallow SCC
B-7	-0.85	42.3	51.1	1.4	0.23	Ditto
B-7	-0.90	33.8	77.0	1.0	0.21	"
B-7	-0.95	43.3	64.0	6.5	1.05	Severe SCC
B-7	-1.00	39.7	57.7	7.1	1.27	Ditto
B-7	-1.05	43.1	64.0	4.4	0.72	"
B-8	-0.75	34.2	71.9	0.7	0.14	SCC Slight
B-8	-0.80	35.4	76.0	1.0	0.20	Slight
B-8	-0.85	35.7	75.0	1.0	0.20	Slight
B-8	-0.90	33.6	73.0	1.7	0.35	Moderate
B-8	-0.95	36.2	59.0	6.5	1.26	Severe
B-8	-1.00	33.3	49.6	10.9	2.30	Ditto
B-9	-0.98	40.7	65.2	4.1	0.70	"
B-10	-0.85	32.5	75.0	--	--	No
B-10	-0.95	32.8	73.0	3.4	0.73	Severe
B-10	-1.00	32.4	67.5	9.5	2.07	Severe
B-10	-1.05	38.0	70.8	--	--	No
B-10	-1.10	31.9	66.4	--	--	No
E-4	-1.00	46.0	73.0	2.0	0.31	Moderate
B-11	-0.95	34.1	53.8	11.9	2.46	Severe
B-11	-1.00	35.7	48.2	10.9	2.15	Severe
B-1	FCP (-0.670)*	42.5	74.0	--	--	No
E-1	-1.00	45.6	67.5	2.7	0.42	Moderate
B-1	-1.00	45.6	67.5	0.7	0.42	Moderate
B-2	FCP (-0.70)	45.3	75.0	--	--	No
B-1A	FCP (-0.91)	35.9	75.0	0.7	0.13	Slight
B-2A	FCP (-0.90)	45.4	74.0	1.0	0.16	Slight
B-2M	-1.00	35.0	56.4	3.7	0.75	Severe
E-1	FCP (-0.95)	44.0	70.8	4.1	0.65	Moderate
E-1	-0.90	45.2	71.9	1.4	0.21	Ditto
E-1	-0.95	42.2	67.5	3.4	0.57	"
E-1	-1.00	32.8	71.9	2.4	0.51	"
E-2	FCP (-0.73)	34.4	75.0	0.3	0.05	Borderline
E-6	FCP (-0.35)	45.0	71.9	--	--	No
E-6	-1.00	45.8	62.8	2.7	0.41	Moderate
1-C	FCP (-0.72)	46.8	77.0	0.7	0.10	Borderline
1-C	-1.00	43.8	71.9	3.7	0.60	Moderate
2-C	FCP (-0.79)	33.3	70.8	--	--	No
3-C	-1.00	29.2	49.6	6.8	1.64	Severe

* FCP = Test Run at Free Corrosion Potential with No Applied Current.

Value in Parenthesis is Corrosion Potential at start of test.