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ABSTRACT

Stress corrosion of carbon steel storage tanks containing
alkaline nitrate radioactive waste, at the Savannah River Plant
is controlled by specification of limits on waste composition
and temperature. Actual cases of cracking have occurred in the
primary steel shell of tanks designed and built before 1960 and
were attributed to a combination of high residual stresses from
fabrication welding and aggressiveness of fresh wastes from the
reactor fuel reprocessing plants. The fresh wastes have the
highest concentration of nitrate, which has been shown to be
the cracking agent. Also as the waste solutions age and are
reduced in volume by evaporation of water, nitrite and hydroxide
ions become more concentrated and inhibit stress corrosion. Thus,
by providing a heel of aged evaporated waste in tanks that receive

fresh waste, concentrations of the inhibitor ions are maintained within specified ranges to protect against nitrate cracking. Tanks designed and built since 1960 have been made of steels with greater resistance to stress corrosion; these tanks have also been heat treated after fabrication to relieve residual stresses from construction operations. Temperature limits are also specified to protect against stress corrosion at elevated temperatures.

INTRODUCTION

High-heat radioactive wastes from the Savannah River Plant (SRP) separations processes are stored in large, underground carbon steel tanks. Decay heat, due to the radioactivity of the wastes, is removed by corrosion-inhibited water pumped through carbon steel cooling coils. The primary steel containers are contained within secondary steel pans; these secondary containers are in turn supported by a concrete outer shell. A 2.5-ft-wide annulus separates the primary and secondary containers.[1]

Most of the high-level wastes at SRP are byproducts of the Purex and enriched uranium processes. In the Purex process, plutonium and uranium are recovered from irradiated natural or depleted uranium. In the enriched uranium process, uranium enriched in ^{235}U and ^{236}U is recovered from irradiated uranium fuel for reuse. Other recovery processes have also been used from time-to-time in both areas for the separation of other isotopes.[2] Each recovery process produces a characteristic waste. However, generalization of waste compositions in storage tanks based on

flowsheet or process analyses is impossible because wastes are mixed and evaporated, salts and insolubles precipitate, and radiation induces changes in composition.

Wastes are present in SRP tanks in three forms: supernate (an aqueous solution), sludge (a gel containing the insoluble components of the wastes that settle to the tank bottom with some trapped supernate), and salt cake (salt crystals formed by evaporation of water from the supernate).

The carbon steel in the tanks is susceptible to stress corrosion cracking in nitrate and caustic solutions, and stress corrosion cracks have been observed in the primary steel shells of some tanks.

This paper reviews the performance of tanks used for interim storage of high-heat waste (HHW) at SRP with respect to nitrate stress corrosion cracking. The technical investigations to identify the cause of cracking are summarized, and modifications in the construction of the tanks and in waste management that resulted from these studies are described. These modifications helped to maintain the integrity of the tanks, providing more secure containment.

DISCUSSION

Waste Storage Operations

Radioactive high-heat waste from the reprocessing plant is transferred to a tank containing cooling coils that remove decay heat (Figure 1). Fresh waste is aged from one to two years to permit solid material to settle and short-lived fission products

to decay. During this aging period insoluble materials form a layer of sludge at the bottom of the tank. The sludge consists of oxides and hydroxides of manganese, iron, and aluminum, small amounts of uranium, plutonium, and mercury, and most of the longer-lived fission products originally in the irradiated fuel except cesium. The aged supernate solution containing dissolved salts, including radioactive cesium, is transferred to a continuous evaporator. The concentrate from the evaporator is transferred to a waste tank that is equipped with cooling coils. In the tank the salts crystallize and settle as the liquid cools. The remaining supernate is returned to the evaporator for further concentration. This process continues until the liquid has been converted to a damp salt cake. Aging and processing causes changes in the chemical and radionuclide composition. The major changes are 1) radiolytic conversion of nitrate to nitrite, 2) absorption of CO_2 from air, converting NaOH to Na_2CO_3, 3) separation of radionuclides into soluble and insoluble fractions, and 4) decay of the radionuclides. The composition of the wastes in individual tanks varies widely depending on the detailed history of its contents. For this reason, the composition of the waste contained in the tanks is analyzed periodically. Concentration ranges of the major components in the high heat storage tanks are given in Table 1.[3] Nitrate is the major anion, but nitrite from radiolysis of nitrate is a major component after aging and evaporation. The relative amount of hydroxide has increased because of the difficulty in crystallizing sodium hydroxide.

The only radionuclides present at high concentration in the supernate (Table 2) are the isotopes of Cs which were relatively minor originally. Some Ru is also present.[3] Uranium, and plutonium are expected to remain in the sludge; their presence in the supernate probably indicates a colloidal suspension.

Waste tanks,[4] designated types I, II, and III, are used for storing HHW at SRP.

Twelve Type I waste tanks (Figure 2) were originally built in 1951-1953. The tanks are freestanding, right circular cylinders, with primary and secondary containers made of ASTM A 285-B steel. The secondaries are encased in reinforced concrete. Volume is 3/4 million gallons and radioactive decay heat is removed with water that circulates through cooling coils. Air in the annular space is dried and heated to limit corrosion of the exterior of the primary tank and the interior of the secondary.

Four Type II waste tanks (Figure 3) were built from 1955-1956. The design is similar to that of Type I except a single central support column is used (compared to 12 in Type I tanks) and the volume was increased to one million gallons.

At present (and since 1967), a series of new tanks, Type III (Figure 4), are being built for transfer of wastes from some of the older tanks. Nine Type III tanks are in service. Eighteen additional tanks of this type are in various stages of construction or planning. Each primary tank holds 1.3 million gallons and has a secondary liner the full height of the primary tank wall.

A waste tank inspection program was initiated in 1954 and
has gradually become more comprehensive. At present, periscopic
examination and direct photography are performed routinely in the
annular spaces. Wall thickness measurements of the primary tanks
and temperature profiles of the waste are also measured routinely.
The results of these inspections for the cracked tanks are shown
in Table 3.

Nine of the original 16 high-heat waste tanks contain one or
more leak sites on the primary tank wall. The largest number of
cracks were observed in Tank 16. This tank has been emptied ex-
cept for sludge, and the annular space is presently being cleaned
out. Seven of the original tanks, some of which have been in
service for about 23 years, show no evidence of leakage through
the primary. None of the Type III tanks have leaked.

Nitrate Stress Corrosion Cracking

Investigation of the cause of leakage has continued since the
first leak was observed. The first major conclusion drawn from the
investigation was that the tanks cracked from nitrate stress cor-
rosion.

Mild steels are susceptible to stress corrosion cracking in a
number of environments,[5] including nitrate and caustic solutions.
Measurements indicated that the corrosion potential, the emf at
zero current, for several waste tanks was in the range of -0.44
to -0.064 V vs. a saturated calomel electrode (SCE). This emf was

within the range for nitrate stress corrosion (-0.3 to 1.1 V vs. SCE), but outside that required for caustic cracking (-0.8 to -1.0 V vs. SCE).

For stress corrosion cracking to occur, both stress and a corrosive environment are required.

Stresses

In waste tanks, stress corrosion cracks have been predominantly associated with welds. Cracks form at right angles to the weld bead and propagate a short distance into the base metal, then stop. The largest observed crack in a waste tank was six inches long. Crack propagation decreases with distance from the weld. Figure 5 shows the residual stresses associated with a butt weld, the most common type of weld made in fabricating the tanks.[6] A weld with the properties shown in Figure 5 might be expected to generate a crack 1 to 2 inches long.

Residual stresses can be relieved by uniformly heating a structure to a sufficiently high temperature (approximately 1100°F in mild steels) for annealing to take place. Such heat treatment should eliminate SCC by removing the stress. This effect was demonstrated in the laboratory[7,8] by welding large, 3-foot square plates and exposing as-welded and stress-relieved plates to synthetic waste solutions or to 50% $NaNO_3$, which is a particularly aggressive solution in causing SCC. Plates that were fully stress relieved by heat treatment did not crack in 167 days; as-welded plates consistently cracked after a short exposure (about 3 to 10

days). "Flame-washed" plates gave inconsistent results because
of the difficulty in controlling the temperature in this procedure.

On the basis of this work and other supporting laboratory[9]
and industrial[10] experience on the role of residual stresses, the
new Type III waste tanks have been heat treated after fabrication
to relieve the welding stresses. Any long-range reaction stresses
would also be relieved. This heat treatment is a significant
advance in minimizing the probability of stress corrosion cracks
in waste tanks.

Corrosion

In addition to the studies on reducing stresses to prevent
stress corrosion cracking, corrosion studies were also performed.
The objectives of the corrosion studies were to determine what solu-
tion compositions were sufficiently aggressive to cause cracking
if stresses were present, and what steels were most resistant to
nitrate stress corrosion cracking. Two general approaches were
used, electrochemical and mechanical.

Electrochemical Studies

Initially, polarization curves were plotted for both actual
and synthetic waste solutions. The synthetic compositions
were based on analysis of the actual solutions and contained at
least 10 cations. Polarization curves are a plot of the surface
current density passing through the sample vs. potential as
measured against a reference electrode. Three such curves are

shown in Figure 6. The curves indicate that the carbon steel reacted in the same way to synthetic solutions as to actual wastes.[11] This means that a nonradioactive synthetic solution can be used for corrosion investigations and that the steel would be expected to react in the same manner as it would in the actual waste. Nonradioactive synthetics greatly simplify and expedite experimental procedures.

The low current flow in the region between 0 and 0.3 V in Figure 6 indicates a passive system with low corrosion rates; between -0.1 V and -0.2 V corrosion currents are much higher and the corrosion system is active. An active-passive transition is characteristic of systems susceptible to stress corrosion cracking.

Tensile Tests with Impressed Current

A test to evaluate the influence of waste solution composition on stress corrosion initiation was also developed.[11] The test determines the loss of ductility when a tensile specimen is strained to failure. The specimen is extended at a uniform rate while acting as the anode in a controlled-current electrochemical cell with the waste solution being tested as the electrolyte. The current level was chosen on the basis of potentiodynamic polarization curves and was the same for all tests in a given series. The effects of synthetic waste solutions of various compositions compared with tests in air are shown in Figure 7. The test data show that aged evaporated waste (Tanks 1 and 9) were less aggressive than fresh (newly generated) wastes (Tanks 8 and 14).

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Tensile strength and all of the common measures of ductility, uniform elongation, total elongation, or reduction in area, were similarly affected by the test solutions. Figure 8 shows the increase in ultimate tensile strength with increasing OH^- concentration, indicating that the presence of OH^- impedes crack initiation and allows maximum strength of the metal to be achieved if enough OH^- is present.

The electrochemical tensile test data confirmed that A 516-70 steel used in Type III waste tanks is less susceptible to cracking than the A 285-B steel used in Types I and II tanks. Results of recent unpublished work show that A 537-I steel has essentially the same corrosion behavior as A 516-70 steel.

Temperature and nitrate concentration were the two solution variables that had the greatest effect on mechanical properties of the steel in two series of statistically designed experiments. Hydroxide and nitrite ions acted as inhibitors.

An equation given in Reference 12 was derived to relate elongation of A 285-B steel in this test to the combined effect of four variables of the solution:

- Temperature from 50-100°C
- NO_3^- from 1.5 to 5.5M
- NO_2^- from 0 to 3.5M
- OH^- from 0 to 5.0M

In addition to NO_3^-, NO_2^-, and OH^-, to simulate waste solutions more closely, the test solutions also contained six ionic constituents

- 10 -

in constant concentrations. Surface cracking was observed in all specimens when total elongation in the test was less than the uniform elongation observed in air (approximately 13%). This value was used as a figure of merit to estimate whether stress corrosion cracking of A 285-B steel would be a risk if the steel were exposed to equivalent solutions and temperature in service.

Like other corrosion phenomena, the severity of stress corrosion usually increases with temperature. Tensile tests with constant applied current support this generalization, as shown in Table 4. These tests were conducted at three different temperatures[12] with A 285-B steel in synthetic 221-H waste, an aggressive solution simulating fresh waste from the fuel reprocessing building. The data indicate that if the tensile properties are an important factor in the tank performance, wastes as aggressive as fresh 221-H waste should be stored at <75°C.

Mechanical Studies

Modified wedge opening load (WOL) specimens[13] with a fatigue crack (Figure 9) were used for this laboratory study to determine the influence of waste composition on crack growth. Specimens were stressed by tightening the bolt, and, by relating the load to crack opening and crack length, the state of stress can be calculated. Specimens were immersed in the test solution and the crack length measured as a function of time. For this type of specimen, stress intensity K, a parameter that characterizes the state of stress in the crack tip region, decreases with crack length. Therefore, the threshold stress intensity, K_{SCC} (the minimum intensity necessary

to cause stress corrosion cracking), is the K value at which the crack ceases to propagate.

In solutions that caused crack growth, the rate of growth and K_{SCC} were independent of solution composition. This observation is evidence of the independence of crack tip chemistry from bulk solution chemistry. The initiation time, however, was related to the composition of the bulk solution.

From these data, a map dividing the compositional variables into cracking vs. noncracking regions was drawn[14] as shown in Figure 10. To approximate actual waste, all solutions contained 5M $NaNO_3$ and various amounts of OH^- and NO_2^-. The map shows that sufficient amounts of either OH^- or NO_2^- can inhibit crack growth and that they are more effective (less of either is required) if both are present.

Data from the precracked specimens was compared to the calculated data from the equation developed in the tensile tests with impressed currents. The precracked specimen data were limited to 5M NO_3^- at 97°C with variable nitrite and hydroxide; the electrochemical test results included variations in nitrate and temperature in addition to nitrite and hydroxide.

The comparison is good for sodium hydroxide concentrations to about 0.3M. The difference between the two may be due to the six anionic constituents added to the electrochemical tensile test to more closely simulate the waste. In waste management, the NaOH concentration is maintained above 0.3M when nitrate is at its maximum of 5.5M (Table 5).

As the nitrate concentration decreases, the amount of inhibitor required also decreases. In SRP wastes these values, chosen as conservative ones, are shown in Table 5. At low nitrate concentrations hydroxide is not added to prevent stress corrosion, but rather to avoid general corrosion and pitting attack.

Stress Corrosion Control Methods

These laboratory studies have led to a better understanding of the conditions required for stress corrosion cracking in carbon steel waste tanks. Appropriate fabrication procedures and process controls have been applied to minimize the probability of stress corrosion cracking. Stress relief of the tanks during construction is now specified to relax the high welding stresses that caused stress corrosion cracks associated with the welds.

Various steels have been evaluated for resistance to nitrate stress corrosion. Early tanks were built of ASTM A 285-B. Later tanks were built of more stress corrosion resistant A 516-70. Tanks are now being built of A 516-70 normalized or A 537 Class I. These last two alloys were chosen to improve mechanical performance but are equivalent to A 516-70 (as rolled) in stress corrosion resistance.

During waste storage operations, technical standards require waste composition to be controlled. A maximum NO_3^- concentration is specified to limit the aggressiveness of the supernate. The concentration of inhibitors, OH^- and NO_2^-, is maintained at specific minimum levels depending on the NO_3^- concentration. These levels

of OH^- and NO_2^- have been shown to prevent crack initiation in highly stressed specimens.

Temperature of fresh supernate is maintained at less than 70°C. Since stress corrosion is a thermally activated process, the lower temperature will also inhibit the initiation and growth of cracks. Because aged and evaporated waste contain sufficient OH^- and NO_2^- to inhibit SCC by themselves, the above temperature limit specifically applies only to fresh waste.

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TABLE 1

Concentration Range of Major
Constituents in Aged HHW Supernates

Constituent	Concentration, M
Na^+	4.0 - 12.5
NO_3^-	⌐1.6 - 6.4
NO_2^-	0.2 - 3.2
$Al(OH)_4^-$	0.4 - 1.6
OH^-	0.8 - 6.3

TABLE 2

Concentration Range of Major Radioactive
Constituents of Aged HHW Supernates

Constituent	Concentration Range, Ci/gal	
^{134}Cs	0.2	- 4.6
^{137}Cs	1.7	- 44
^{103}Ru	ND^a	- 0.2
^{89}Sr	$<10^{-6}$	- 3×10^{-5}
^{90}Sr	2×10^{-4}	- 4×10^{-3}

_a._ Not detected.

TABLE 3

Inspection Results for Cracked Tanks

Tank Design	Tank No.	Service Date	First Leak Site Observed	Observed No. of Leak Sites	Salt Depth in Annulus, in.
Type I	1	1954	1969	-	0 - 1/4
	9	1954	1957	-	8 - 10
	10	1955	1959	-	2 - 3
	11	1955	1974	1	None
	12	1956	1974	1	None
Type II	13	1956	1977	1	0 - 1/4
	14	1957	1959	50	12 - 13
	15	1960	1972	15	None
	16	1959	1959	300	Being Removed

TABLE 4

Effect of Temperature on Tensile Properties[a]

| Temperature, °C | Per Cent of Values in Air | | |
	Ultimate Strength	Elongation	Reduction in Area
50	100	100	100
75	95	50	70
100	65	30	20

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a. A 285-B steel in 221-H waste at 0.2 mA/cm^2.

TABLE 5

Required Minimum OH$^-$ and NO$_2^-$
Concentrations in SRP Wastes

Concentration, M		
NO$_3^-$	OH$^-$	OH$^-$ + NO$_2^-$
3-5.5	0.3	1.2
1-3	0.1 [NO$_3$]	0.4 [NO$_3$]
<1	0.01	-
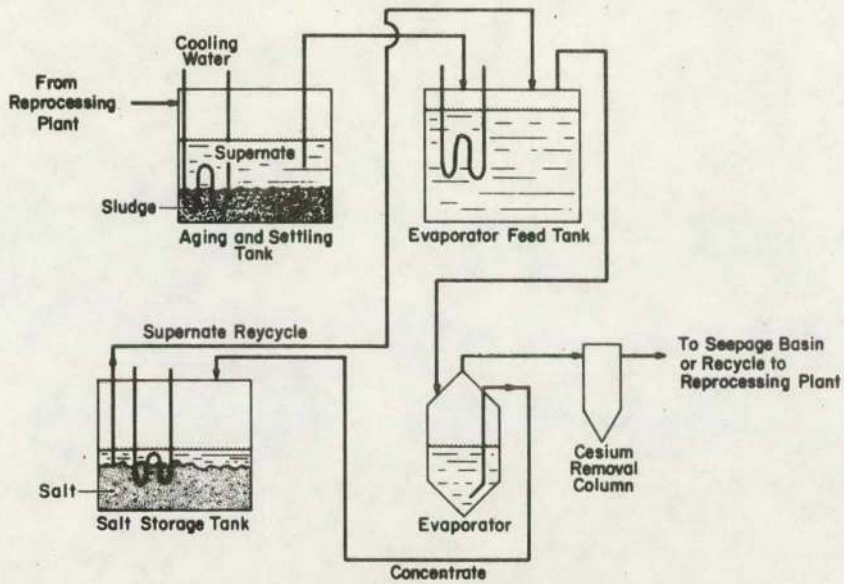
FIGURE 1. High-Heat Waste (HHW) Processing in Tank Farm
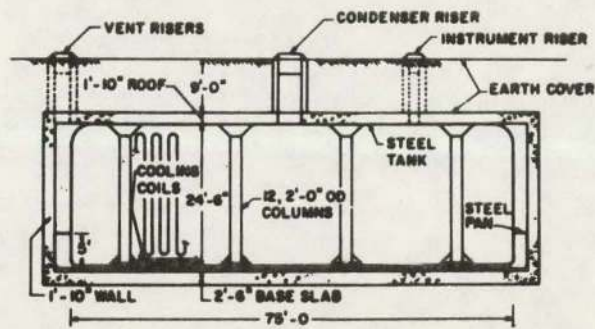
FIGURE 2. Type I Waste Storage Tanks (1951-53)
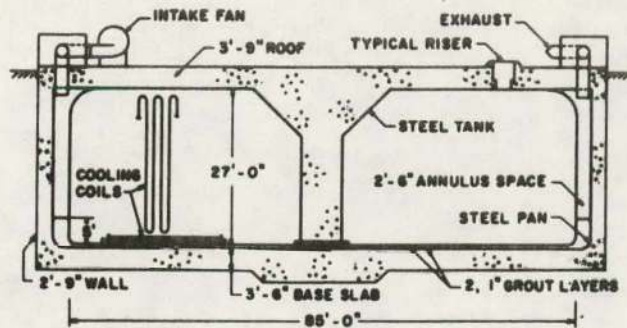
FIGURE 3. Type II Waste Storage Tanks (1955-56)
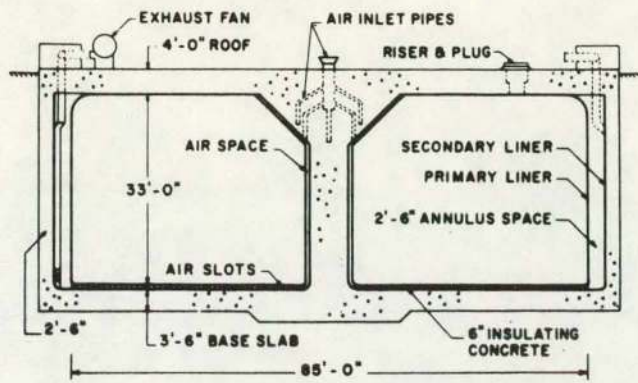
FIGURE 4. Type III Waste Storage Tanks
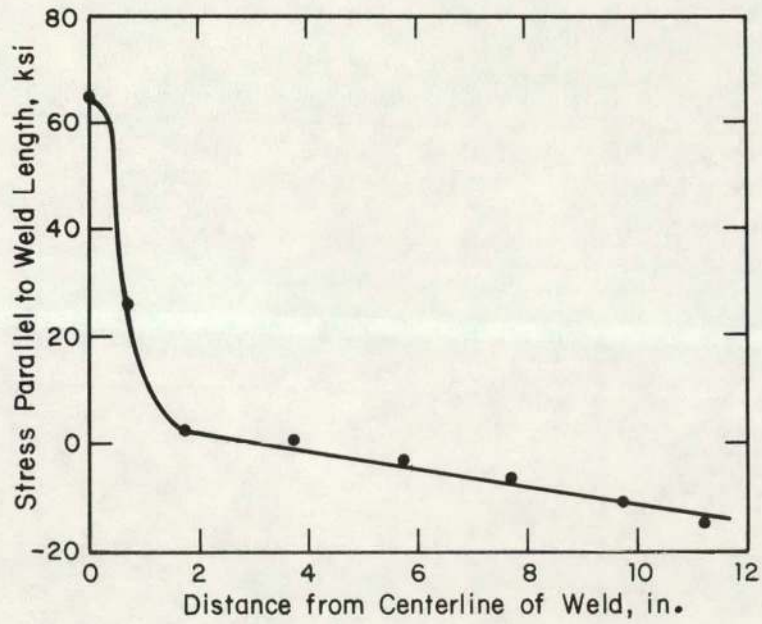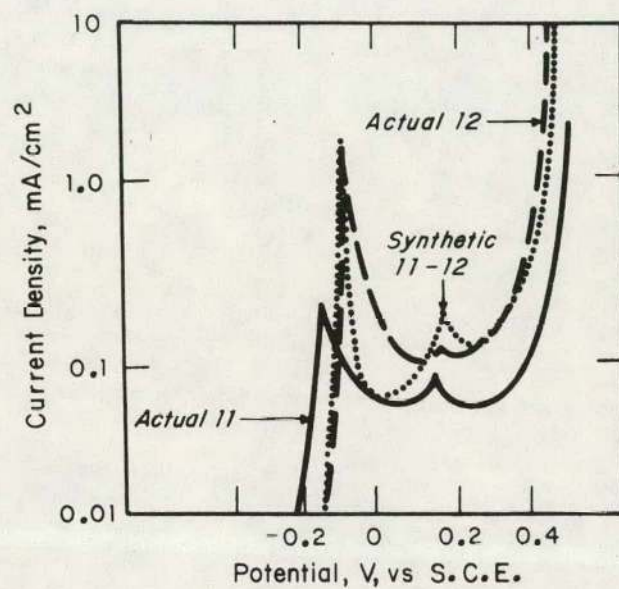

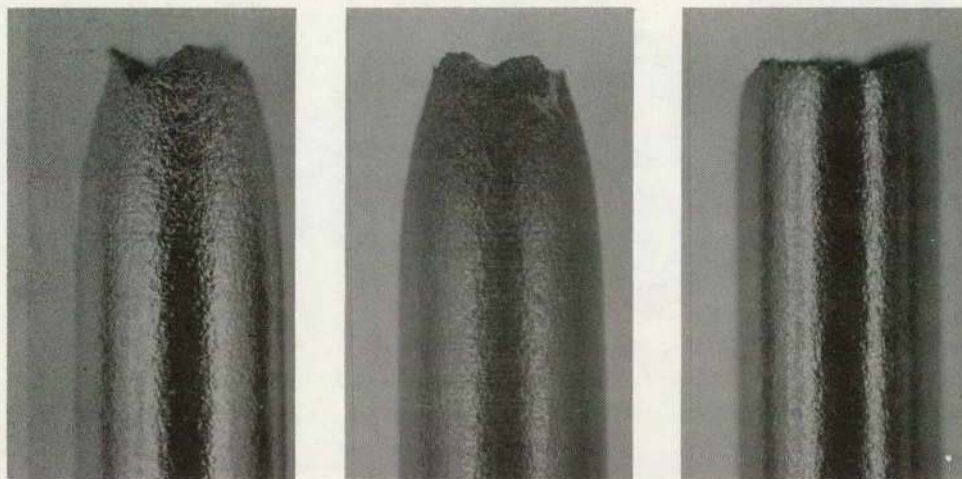FIGURE 5. Residual Stress in Butt Welds

FIGURE 6. Anodic Potentiodynamic Polarization of A 285-B
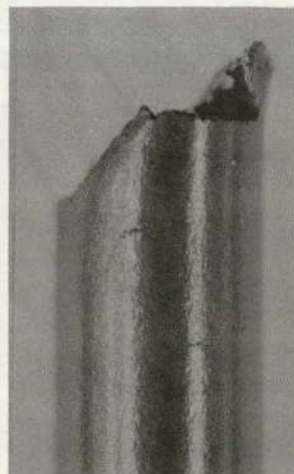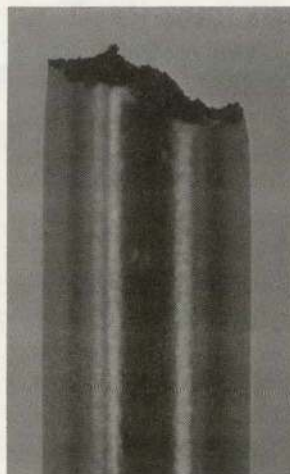Carbon Steel in SRP Waste Supernate

Air   Tank 1 Synthetic   Tank 9 Synthetic

|— 4 mm —|

Tank 8 Synthetic   Tank 14 Synthetic

FIGURE 7.   Appearance of Fractures in Electrochemical Tensile Test
A 285-B steel tested in various wastes at 100°C -
0.5 mA/cm^2.
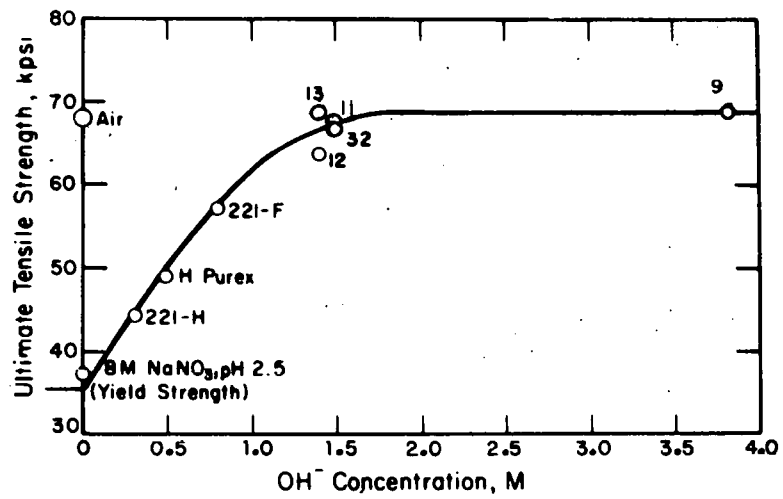
FIGURE 8. Effect of OH⁻ Concentration on Electrochemical Tensile Test. A 285-B steel tested in synthetic wastes at 100°C and 0.2 mA/cm².
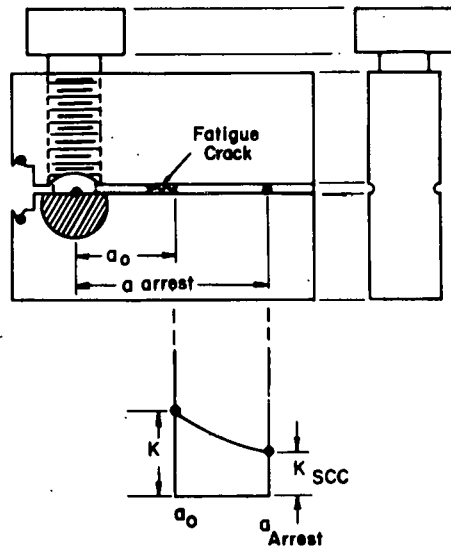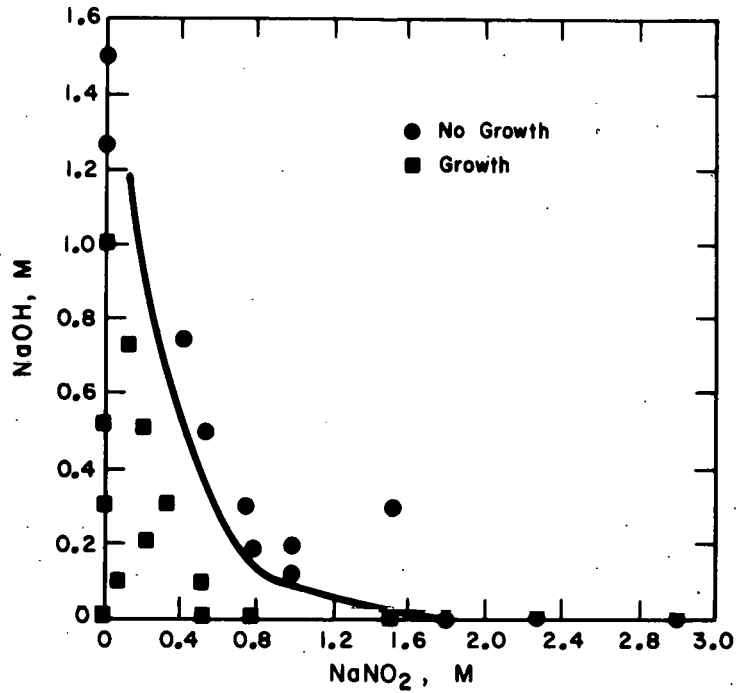

FIGURE 9. Modified WOL Specimen

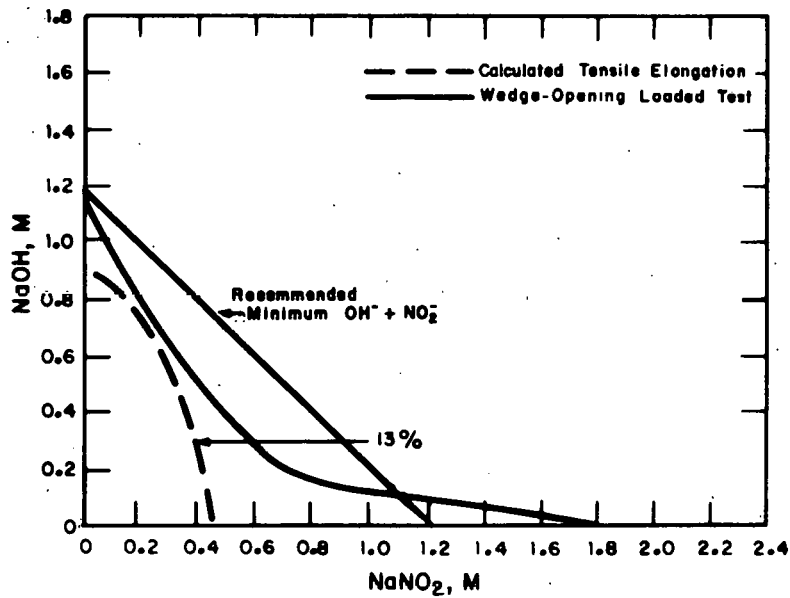FIGURE 10. Influence of NO_2^- and OH^- on Crack Growth of A 285-B Steel in 5M $NaNO_3$

FIGURE 11. Effect of $NaNO_2$ and $NaOH$ on Stress Corrosion Cracking of A 285-B Steel in 5M $NaNO_3$ at 97°C