

CORROSION PROTECTION FOR THE IN-TANK PROCESSING OF HIGH-LEVEL NUCLEAR WASTE AT THE SAVANNAH RIVER SITE (U)

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ABSTRACT

New chemical processes for preparing high-level nuclear waste for vitrification and cementation will be carried out in modified Type III waste tanks at the Savannah River Site (SRS). An extensive test program has been carried out to determine the susceptibility of the tanks to stress corrosion cracking and pitting corrosion during these processes. Laboratory tests have indicated that the tanks should not be susceptible to stress corrosion cracking at expected operating conditions. Active measures must be taken, however, to prevent pitting corrosion. These measures include controlling the chemistry of the liquid phase and limiting the tank steel temperature. Equations have been developed which specify minimum inhibitor requirements based on the temperature and nitrate concentration of the liquid phase.

INTRODUCTION

High-level nuclear waste (HLW) from chemical separations processes at the Savannah River Site (SRS) is currently stored in underground carbon steel tanks. This waste contains radioactive byproducts, nonradioactive reactor tubing cladding materials, and processing chemicals. The nitric acid processing solutions are neutralized with sodium hydroxide prior to storage in the tanks to prevent attack of the carbon steel. Approximately 90% of the waste consists of water soluble salts such as sodium nitrate. The remaining 10% is a sludge consisting of transition metal, aluminum, and transuranic hydroxides and oxides formed upon neutralization of the acid processing solutions.

Facilities are under construction to immobilize greater than 99.999% of the radionuclides in a borosilicate glass. This process will also produce a low-level liquid waste (LLW), which will be immobilized in a cement. The borosilicate glass will be stored on site until the federal repository is ready to receive the glass canisters for permanent emplacement. The cement wasteform, saltstone, will be permanently stored in an engineered vault on site.

Initial preparation of feed streams for vitrification and cementation will be carried out in carbon steel tanks which have been modified for chemical processing. Radionuclides will be separated from the soluble salt and stored for feed to the vitrification facility. The decontaminated salt will be stored for feed to the cementation facility. The sludge waste will be treated to reduce the soluble salt content and will be stored for feed to the vitrification facility.

Stress corrosion cracking and localized corrosion of the steel tanks were identified as possible corrosion mechanisms during these HLW processing operations. An extensive research program was conducted to determine the susceptibility of the tanks to these types of corrosion and, if necessary, to develop suitable control measures to prevent corrosion and the possible formation of leak sites which could result in the release of nuclear waste.

RESULTS AND DISCUSSION

In-Tank Precipitation and Sludge Processing Operations

For removal of radionuclides from water soluble salt, the HLW will be treated with (1) sodium tetraphenylborate to precipitate cesium and (2) monosodium titanate to adsorb strontium. The solid phase will be filtered, washed, and stored for feed to the vitrification facility. The decontaminated filtrate will be stored for feed to the cementation facility. These steps are referred to as the In-Tank Precipitation (ITP) process.

The sludge HLW will be treated to reduce aluminum and soluble salt concentrations prior to transfer to the vitrification facility. Wash water will be added to the sludge, the slurry will be agitated, and then the agitation will be stopped to allow the sludge solids to settle. The supernate will be removed from the top of the settled sludge. Fresh wash water will be added and the process will be repeated until the soluble salt content is sufficiently low to meet vitrification feed requirements.

Some of the sludge which will be processed contains unacceptably high levels of aluminum. To reduce the aluminum content in the Defense Waste Processing Facility (DWPF) feed, these sludges will be treated with sodium hydroxide at elevated temperatures to dissolve most of the aluminum. After dissolution, the sludge will be washed to remove the water soluble salts. The sludge washing and aluminum dissolution steps are referred to as Sludge Processing (SP).

Type III Waste Tank Design

The ITP and SP processes will be carried out in Type III waste tanks, which have been modified for chemical processing. Type III tanks are the most recently designed tank at SRS and have an operating capacity of 1.3 million gallons. These tanks are double shelled and are cooled by circulating water through vertical coils passing throughout the tank. The primary and secondary shells are constructed of ASTM type 357 normalized carbon steel which has been

stress relieved. The cooling coils are fabricated from ASTM A53 or A106 carbon steel. Specially designed slurry pumps have been installed in each tank for mixing. A cross-sectional diagram of a Type III tank is given in Fig. 1.

Formation of flammable hydrogen/air mixtures in the vapor space is prevented by continuously purging the tank with air. Before release to the atmosphere, the purge air is filtered through a nuclear grade HEPA filter to prevent the release of radioactivity. The ITP processing and storage tanks are also equipped with a nitrogen blanketing system. The purpose of the nitrogen blanketing is to reduce the concentration of oxidants which would be available to support the combustion of flammable vapor mixtures and flammable solids in these tanks.

Corrosion Testing Methods

Corrosion tests were carried out using simulated and actual wastes for both the SP and ITP processes. Corrosion tests were carried out over a range of compositions because of the large changes in the soluble salt concentrations during each process. The range of soluble salt concentrations tested are provided in Tables I and II. The unwashed com-

position represents the initial soluble salt concentration at the start of washing operations. The washed composition represents the soluble salt concentration at the conclusion of washing. Variations in the concentrations of individual salt species were also tested based on known variations in each type of HLW generated at SRS.

Modified wedge-opening loaded (WOL) tests (5) and constant extension rate tests (CERT) (6) were performed to predict the susceptibility of the steel to stress corrosion cracking. All of the WOL specimens (ASTM A537) were fatigued to produce an initial crack of about 0.1 inches. The specimens were stressed and immersed in the test solution for a total time of 218-259 days. The CERT were conducted at an initial strain rate of $1.0 \times 10^{-7} \text{ sec}^{-1}$ over a range of applied potential from -0.18 to -0.66 volts versus a saturated calomel electrode.

Cyclic polarization scans were used as a rapid test method to determine the tendency for pitting corrosion. (3-5) For evaluation of the pitting potential, the pH of the test solution was adjusted to that which would be reached at steady-state conditions upon adsorption of atmospheric carbon dioxide.

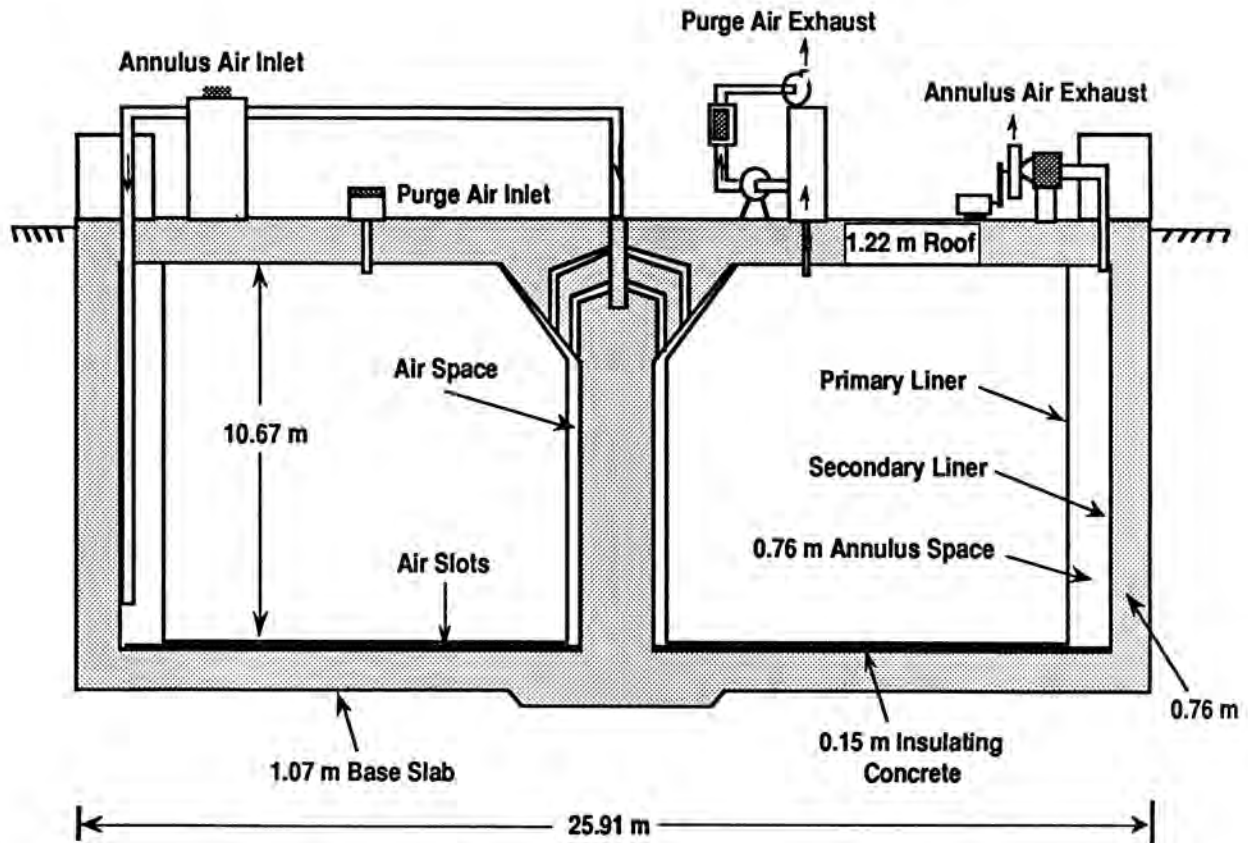


Fig. 1. Type III tank diagram.

TABLE I
In-Tank Precipitation Stream

Species	Average Soluble Salt Concentration (mole/L)		
	Unwashed	Washed	Variation
Nitrate	1.9	0.028	+ 30%
Hydroxide	1.3	0.024	-
Aluminate	0.31	0.0045	-
Carbonate	0.16	0.0023	-30%
Sulfate	0.14	0.0020	+ 30%
Chloride	0.022	4.0×10^{-4}	+ 30%
Fluoride	0.014	2.2×10^{-4}	+ 30%
Phosphate	0.0085	1.2×10^{-4}	-30%
Silicate	0.0038	5.4×10^{-5}	-30%
Chromate	0.0033	4.7×10^{-5}	-30%
Tetraphenylborate	0.0026	7.7×10^{-4}	-

TABLE II
Sludge Processing Stream

Species	Average Soluble Salt Concentration (mole/L)		
	Unwashed	Washed	Variation
Nitrate	2.9	0.041	+ 100%
Hydroxide	1.2	0.031	-
Aluminate	0.12	0.0017	-
Carbonate	0.056	8.0×10^{-4}	-
Sulfate	0.13	0.0019	+ 40%
Chloride	0.035	5.0×10^{-4}	+ 60%
Fluoride	0.014	2.0×10^{-4}	+ 30%
Phosphate	4.1×10^{-4}	5.8×10^{-6}	-93%
Silicate	3.4×10^{-4}	5.0×10^{-6}	-83%
Chromate	0.0019	2.7×10^{-5}	-8.0%
Oxalate	0.0048	6.8×10^{-5}	-6.0%

Based on the results of the polarization tests, coupon tests were carried out to assess minimum inhibitor requirements as a function of the concentration of aggressive species and the temperature. The coupon tests were not pH adjusted and were carried out for a minimum of four months. Conditions were maintained as close as possible to that which will occur during preparation and storage of the DWPF feed streams. Upon completion of the test, specimens were cleaned with Clarke's solution and examined for evidence of corrosion. (6)

Stress Corrosion Cracking Test Results

Because of the high salt concentration and the high temperature during alumina dissolution, the possibility of stress corrosion cracking was investigated. The open-circuit potentials (OCP) of ASTM A537 carbon steel specimens were measured at elevated temperatures and in various simulated solutions containing sodium hydroxide, sodium nitrate, sodium nitrite, and sodium aluminate. The concentration and temperature ranges were selected to bound the

TABLE III

Experimental Conditions for Stress Corrosion Cracking Testing

Temperature	60 - 100°C
[NaOH]	3.0 - 8.0 M
[NaNO ₃]	0.020 - 2.0 M
[NaNO ₂]	0.0050 - 0.5 M
[NaAl(OH) ₄]	0.0 - 1.0 M

expected conditions which will occur in SP operations. These ranges are given in Table III.

The measured OCP ranged from -185 to -786 mV(SCE). This is outside the range for caustic cracking (-800 to -1000 mV), but does overlap the range for nitrate cracking (-300 to -1100 mV). These results suggest that the tanks should not be susceptible to caustic cracking, but may be susceptible to nitrate cracking. Therefore, WOL tests and CERT were conducted over the same range of experimental conditions to assess cracking susceptibility. These tests showed no susceptibility of the steel specimens to stress corrosion cracking. In order to maintain non-corrosive conditions during alumina dissolution, the following limits have been recommended; (1) limit the hydroxide concentration to ≤ 8.0 molar, (2) limit the temperature to $\leq 90^\circ\text{C}$, and (3) require that there be ≥ 0.20 molar nitrate in the liquid phase.

Pitting Corrosion

During the ITP and SP operations, the soluble salt concentration will be diluted by a factor of up to about 70. As a result the hydroxide concentration, which is the predominant inhibitor against pitting corrosion, will be significantly reduced. The concentrations of aggressive species, such as nitrate, chloride, fluoride, and sulfate, will still be sufficiently high that attack of the steel surface can occur. If the hydroxide concentration in the liquid phase is further reduced by some mechanism, then localized attack of the steel could occur. Polarization and coupon tests confirmed that pitting corrosion could occur if the hydroxide concentration were decreased to below about 0.01 molar.

Two mechanisms were identified that could reduce the hydroxide concentration; (1) absorption and reaction of atmospheric carbon dioxide and (2) radiolytic generation of weak acids from tetraphenylborate salts. The latter mechanism would occur only in the ITP tanks and not in the SP tanks. Atmospheric carbon dioxide is continuously passed through the tank as a result of the vapor space purging system. Because of the high pH, the HLW will absorb the carbon dioxide and react with hydroxide to form bicarbonate and carbonate species. Monitoring of HLW tanks indi-

cates that approximately 75% of the atmospheric carbon dioxide entering a tank is absorbed by the waste.

Visual inspection of the waste tanks reveals a thin wetted region extending up the tank wall or cooling coil from the bulk liquid. Because of the small volume element in this region, there is a limited amount of hydroxide. Because of the much higher ratio of the surface area to the volume in this region as compared to the bulk liquid, much more rapid depletion of the hydroxide may occur. Modeling indicates that the absorption and reaction of carbon dioxide is much more rapid than diffusion of hydroxide from the bulk solution. Therefore, the hydroxide concentration at the liquid/vapor interface is reduced and the steel in this region can be susceptible to attack.

Tests indicate that tetraphenylborate salts are decomposed upon exposure to high radiation fields. A variety of decomposition products are produced including weak acids such as phenol and phenylboric acid. These acids will react with hydroxide to reduce the hydroxide concentration in the bulk solution. During storage of washed precipitate slurry, the rate of hydroxide depletion is dominated by this mechanism.

Laboratory tests indicated that corrosive solutions are produced during ITP and SP, which can result in pitting of the carbon steel. Attack was observed to occur more often at the liquid/vapor interface in the coupon tests, but was evident under certain conditions in the bulk liquid. The extent of the attack increased with higher concentrations of aggressive ions and higher temperatures.

Corrosion Control Measures

An extensive test program was carried out to develop control measures to prevent this type of attack during ITP and SP operations. Measures which were considered included (1) the removal of carbon dioxide from the air passed through the tanks, (2) lower steel temperatures, (3) alternate processing steps, and (4) the addition of corrosion inhibitors. The addition of corrosion inhibitors and the limiting of tank steel temperatures were selected as control parameters to prevent pitting corrosion, based on effectiveness, current facility capabilities, impact on downstream processes, and costs.

Laboratory tests identified a number of effective inhibitors including nitrite, hydroxide, chromate, and perrhenate. Hydroxide is depleted as a result of absorption and reaction with atmospheric carbon dioxide and radiolytic generation of weak acids. Based on the estimated hydroxide depletion rates, the amount of sodium hydroxide that would be added to prevent corrosion would result in an unacceptably high sodium ion content in the vitrification feed stream. Therefore, hydroxide cannot be used as a corrosion inhibi-

tor for the storage of the washed precipitate and sludge slurries.

Chromium oxides have a limited solubility in the borosilicate glass formulation and consequently, insoluble chromium oxide phases would be produced in the melter at the projected usage requirements. Per technetate was shown to be an effective inhibitor at very low concentrations. However, even at the very low concentrations necessary to inhibit pitting, the volume of waste requiring inhibition demands more per technetate than is commercially available.

Nitrite was selected as the preferred inhibitor, based on its effectiveness and overall compatibility with the ITP, SP, saltstone and DWPF operations. Nitrite is a well-known anodic inhibitor for carbon steel and was observed to be an effective inhibitor in the ITP and SP systems. Based on the projected usage of sodium nitrite, sodium ion limits in the DWPF melter feed can be met. However, the use of nitrite does impact the salt processing cell of the DWPF. In order to minimize the impact, additional washing of the precipitate slurry has been recommended to reduce the amount of nitrite sent to the DWPF.

Nitrite Inhibitor Requirements

Electrochemical and coupon tests indicated that the amount of nitrite necessary to inhibit is dependent on the nitrate concentration, the hydroxide concentration, and the steel temperature. Fig. 2 shows a plot of the minimum nitrite concentrations required to inhibit precipitate and sludge slurries at 40°C as a function of nitrate concentration. The

similar plots are consistent with the similar solution chemistry of each slurry.

Equations were developed to provide minimum nitrite concentrations during processing and storage of ITP and SP slurries. The equations were developed by fitting the experimental data to a curve and applying a 50% safety factor to allow for compositional variation and experimental errors. Equations for ITP and SP slurries are shown below for a maximum temperature at 40°C.

ITP Slurries:

$$[\text{NO}_2^-] = 0.014 + 1.4[\text{NO}_3^-] - 2.5[\text{NO}_3^-]^2 + 3.8[\text{NO}_3^-]^3 \quad (\text{Eq. 1})$$

SP Slurries:

$$[\text{NO}_2^-] = 2.0[\text{NO}_3^-] - 0.8[\text{NO}_3^-]^2 \quad (\text{Eq. 2})$$

where $[\text{NO}_3^-]$ = nitrate concentration in moles/Liter.

Because of the high decay heat in the ITP and SP slurries, heat generated by operating the slurry pumps, and seasonal variation in the cooling water temperatures, slurry temperatures may exceed 40°C. Therefore, experiments were carried out to determine the effects of temperature on the inhibitor requirements. As expected, temperature has a significant effect on the inhibitor requirements. For ITP slurries, the inhibitor requirements increase over those at 40°C by factors of 1.25 at 50°C and 2.0 at 60°C. For SP slurries, the effects of temperature are more significant.

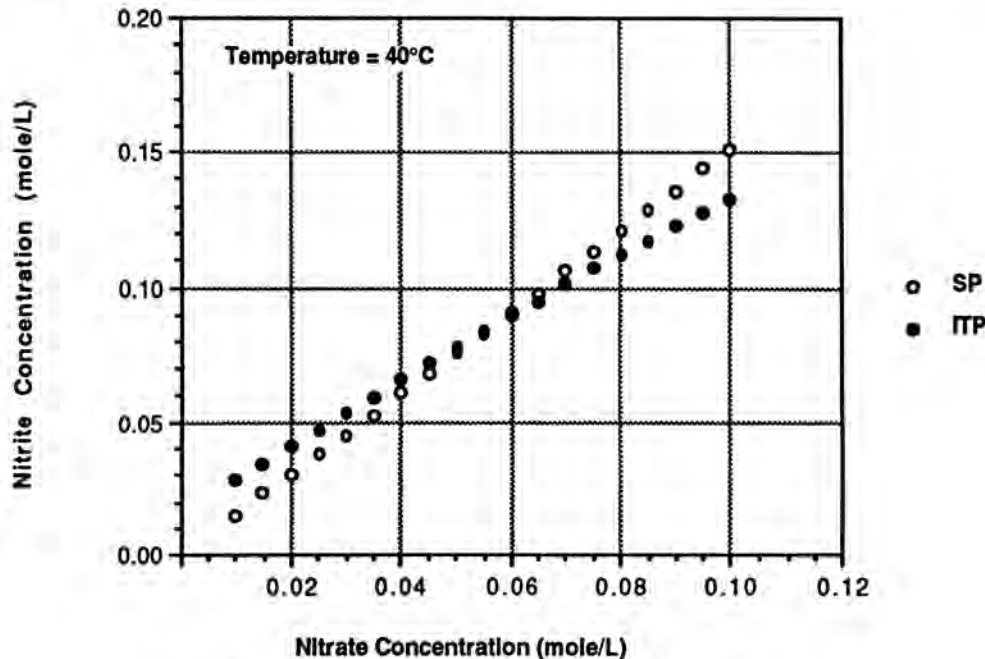


Fig. 2. Minimum nitrite requirements for ITP and SP.

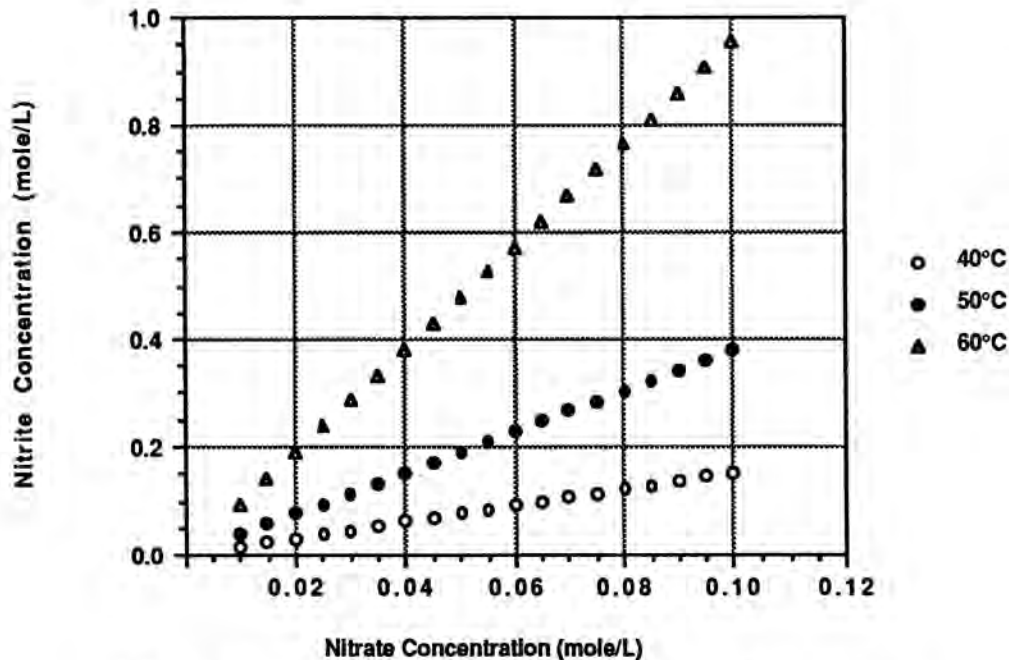


Fig. 3. Sludge processing nitrite requirements at elevated temperatures.

This may be due to the inhibiting/passivating effect of a tetraphenylborate precipitate coating on the steel surface.

Equation 3 gives the inhibitor requirements for sludge slurries as a function of nitrate and temperature. This equation was developed by multiple regression analysis of the experimental data and applying the same 50% safety factor discussed above. Figure 3 shows a plot of the nitrite concentration as a function of the nitrate concentration at 40°, 50°, and 60°C.

$$[\text{NO}_2^-] = 0.038[\text{NO}_3^-] \cdot 10^{(0.041 \cdot T)}$$

where T = temperature in °C.

Under certain conditions, the nitrite concentration can be dependent on the concentration of other aggressive ions such as chloride, fluoride and sulfate. However, under normal operating conditions, the concentrations of halides and sulfate are not expected to significantly increase relative to that of nitrate and become the inhibitor controlling species.

Tank Chemistry and Surveillance

Periodic inspections are made of the tank interior and annulus as part of a program to monitor the integrity of the tank and to prevent the release of HLW from a waste tank. These inspections are conducted using a number of techniques including: periscopic, direct photography, wide-angle photography, and video camera. The frequency of the inspections is established based on the current operations as well as the history of each tank. Tanks which have known leaks are inspected at least annually.

The liquid phase of each tank is periodically sampled and the concentration of aggressive species and inhibitors are determined by a variety of analytical techniques. Based on the analytical results, inhibitors are added as needed to maintain non-corrosive conditions. The sampling frequency is established based on the use of the tank. For the tanks involved with ITP and SP, the sampling frequency ranges from 1 month to 6 months.

In addition to visual inspection and the tank chemistry programs, floating racks containing specimens of ASTM A537 carbon steel will be placed in each of the ITP and SP tanks during the first two years of operation. The racks have been designed such that the specimens will be partially submerged. This will allow for evaluation of pitting corrosion at the liquid/vapor interface. Over the two year period, specimens will be removed periodically and inspected for evidence of corrosion.

SUMMARY

New chemical processes for preparing high-level nuclear waste for vitrification and cementation at SRS will be carried out in modified Type III waste tanks. Laboratory tests have indicated that the tanks should not be susceptible to stress corrosion cracking provided the concentrations of hydroxide and nitrate and the steel temperatures are maintained within recommended limits. However, pitting corrosion is possible as a result of the depletion of hydroxide in the liquid phase.

The addition of corrosion inhibitors and limiting the tank steel temperature will prevent pitting corrosion during these processes. Minimum inhibitor requirements have been determined for both processes and are based on the temperature and nitrate concentration of the liquid phase. During ITP and SP operations, the composition of the liquid phase will be determined by periodic sampling of each tank and inhibitors will be added as needed to maintain non-corrosive conditions. Corrosion test specimens will be placed in each tank and monitored on a periodic basis during the first two years of operation. Periodic inspections of each tank will also be made to determine any changes in the tank integrity.

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