N

DP-MS-77-109

Conf-780308--2

INVESTIGATION OF COOLING COIL CORROSION IN STORAGE TANKS FOR RADIOACTIVE WASTE

R. S. Ondrejcin

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, SC 29801

MASTER

A paper prepared for presentation at the Corrosion/78 in Houston, Texas on March 6-10, 1978.

This paper was prepared in connection with work under Contract No. AT(07-2)-1 with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

ep

DP-MS-77-109

INVESTIGATION OF COOLING COIL CORROSION IN STORAGE TANKS FOR RADIOACTIVE WASTE*

R. S. Ondrejcin
Savannah River Laboratory
E. I. du Pont de Nemours & Co.
Aiken, SC 29801

ABSTRACT

The high frequency of cooling coil leaks observed in high-heat waste storage tanks soon after sludge removal operations is attributed to pitting, according to laboratory corrosion studies. Experiments show that the most likely series of events leading to coil leakage is 1) excessive dilution of basic nitrite in the supernate, 2) initiation of attack in crevices due to oxygen depletion cells, and 3) acceleration of the attack by sulfate dissolved from the sludge.

When sludge was slurried with water, the interstitial liquid was diluted. Nitrite, the anodic inhibitor that prevented attack on coils and tanks in normal operation when its concentration was 0.5 to 3.0M, could accelerate attack when diluted to 10^{-4} to 10^{-3}M. Attack was presumably initiated at oxygen depletion cells. The presence of sulfate, leached from the sludge, produced a conductive solution that could produce high current densities at the corroding steel surface.

The proposed series of events leading to coil leakage agrees with the observations previously made on one leaking coil removed from Tank 2F after sludge removal in 1967. Examination revealed pitting that had originated on the outside of the coils. This pitting was attributed to oxygen depletion cells in coil crevices.

To prevent recurrence of pitting attack on cooling coils during future sludge removal operations, the sludge should be slurried 1) with waste diluted less than one hundredfold with water, or 2) with a 500-ppm nitrite-H_2O solution at pH 12. Either method should preclude pitting damage to the coils.

---

* The information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U. S. Department of Energy.

INTRODUCTION

This report summarizes results of laboratory studies on pitting corrosion of mild steel associated with leaks of cooling coils in tanks used for storage of liquid high-heat waste (HHW) at the Savannah River Plant (SRP). The objective of this work was to establish the cause of frequent cooling coil leaks in HHW tanks following sludge removal operations and to develop methods to prevent recurrence of leaks. The sludge was removed by slurrying with water after the supernate had been removed.

During 1966-1969, supernate was pumped from five HHW tanks and the remaining sludge was slurried with water and pumped to other tanks. An average residual sludge depth of about two inches remained. During and shortly after sludge removal, cooling coil leaks were much more frequent than during normal operating conditions. Coil leaks cannot allow escape of radioactivity from the tanks, and since spare cooling coils were installed when the tanks were constructed, the coil failures have not had a significant effect on waste management operation.

Sludge removal will continue to be necessary for efficient waste management. For example, tentative plans call for removing the sludge from Tank 16H to prepare the tank for retirement. Later, sludge may be removed from other tanks for incorporation into concrete or glass as part of the long term waste management program to solidify defense liquid waste for eventual shipment to a federal repository.[1]

BACKGROUND

Waste Storage Operations

HHW's from SRP's nuclear fuel reprocessing areas are stored in large underground carbon-steel tanks (Figure 1). Radioactive decay heat must be extracted from the wastes during the first several years of storage until short-lived radioisotopes have decayed. Decay heat is removed by corrosion-inhibited cooling water flowing through carbon steel pipes (cooling coils) to exterior heat exchangers.

Most of the wastes in the tanks are byproducts of separations processes that produce acidic wastes containing suspended manganese dioxide. The wastes are made basic with sodium hydroxide before storage in tanks. The major constituents of the basic wastes are Na^+, NO_3^-, $Al(OH)_4^-$, and OH^-. Some of the nitrate is converted to nitrite by radiolysis and nitrite then becomes a major constituent of the waste. The hydroxide addition causes insoluble hydrated oxides, mainly of iron, aluminum, and mercury, to precipitate. The insoluble constituents settle to the bottom of the waste tanks as a sludge.[2]

After the waste is stored for about one year to allow short-lived isotopes to decay and the sludge to separate, the supernate is removed and evaporated to reduce waste volume. The condensed evaporator overheads are passed through a bed of zeolite ion exchanger for removal of traces of ^{137}Cs, and after being monitored for radioactivity are discarded to a seepage basin. The hot, concentrated evaporator bottoms are returned to other waste tanks in the tank farm where the solutions cool and salts crystallize out. The remaining supernate is subsequently recycled through the evaporator for additional volume reduction.

The waste tank farm is managed so that certain tanks are used to store fresh waste and to accumulate sludge, and other tanks are used as salt receivers. HHW tanks can therefore be classified on this basis. However, in the early stages of separations plant operation, most tanks received fresh waste and contained some sludge; later the concept of crystallizing the salt was adopted to minimize the waste volume and to decrease waste mobility. Sludge was therefore removed to a residual depth of about two inches from five tanks during 1966-1969. These five tanks are now filled to practical limits with salt and are quiescent.

In the twenty years of waste tank operation, several cooling coils have leaked. The frequency with which new leaks developed in the cooling coils was unusually high during and immediately after sludge was removed from the tanks.

Description of Cooling Coils

The HHW tank cooling coils are fabricated from ASTM Grades A 53 and A 106 mild steels, nominal 2-in. schedule 40 pipe [3.91 mm (0.154-in.)-thick wall]. The type I tanks contain 34 vertical and 2 horizontal coils; Type II tanks have 40 vertical and 4 horizontal coils. The total length of the vertical coils is about seven times that of the horizontal coils.

Approximately ten percent of the cooling coils now leak, as shown in Table 1. When coil leakage is discovered, flow of cooling water through the leaking coil is discontinued; the result is decreased cooling capacity of the coil system. In Tank 11H, for example, cooling capacity is reduced by the eighteen coils that no longer function, although sufficient cooling capacity remains for its continued use.

History of Cooling Coil Leakage

Tank 10H was the only tank to experience any cooling coil leaks during the first ten years of operation. After seven leaks in coils had been found in Tank 10H, a caustic deficiency in the supernate was discovered, and the deficiency was corrected by the addition of 161,000 liters (42,500 gallons) of 50% NaOH over a period of several months beginning in April 1957. The NaOH was added to combat potential corrosion conditions; no other coils leaked in Tank 10H until sometime after sludge removal was completed. Only four other cooling coils in the remaining fifteen Types I and II waste tanks leaked prior to sludge removal operations. Thus, if the Tank 10H experience is discounted, the incidence of cooling coil leakage prior to sludge removal was approximately 0.02 leaks per tank year of operation. The causes of the other leaks that were observed before sludge removal are unknown, but if they were corrosion induced, they did not proceed according to the mechanism described in this report.

Sludge removal operations were attempted on seven tanks beginning in 1967. From 2 weeks to 7 months after sludge removal, the incidence of cooling coil leakage increased, and four tanks had 33 leaks in cooling coils during the short periods that the tanks contained a residual of sludge-slurry water. Coil leaks in Tanks 11H and 14H began about two weeks after sludge removal; addition of evaporator bottoms to tanks that contained the residual sludge sharply reduced the incidence of coil failures.

A summary of the rate of cooling coil leaks is shown in Figure 2. Coils leaked 500 times more frequently shortly after sludge removal than during normal storage. Furthermore, leaks were also five times more frequent after the tanks were returned to service than before sludge removal, probably because many of the coils that did not leak had been damaged during sludge removal.

Tank 10H is omitted from Figure 2 because it appears to be a special case in which the caustic deficiency may have caused corrosion of coils before sludge removal. Although after sludge removal and salt addition, the coils in Tank 10H were exposed to sludge-water slurry for eight months with no additional coil leaks, eleven coils leaked during the following four years. These later leaks also appear to be a special case. During the four-year period, flow through the cooling coils was stopped to maintain tank temperature in the 85 to 100°C range. During the stagnant period, the chromate corrosion inhibitor normally in the cooling water probably became depleted to a concentration at which it acted as a pitting agent.[3] The resulting pitting would progress from the inside out and eventually cause the pitted coil to leak. Corrosion of coils in Tank 10H was probably associated with chromate-depleted cooling water. Corrosion by chromate-depleted water was prevented either by periodic flushing of coils or by a continuous, but low coolant flow (restricted by an orifice) to avoid stagnation.

Actual leak sites have been examined in only one cooling coil. In 1967, leaks were located in both horizontal and vertical coils of Tank 2F. A 0.40-m (16-in.) section was removed from the upper horizontal coil; mechanical interferences prevented removal of a vertical coil section. The leaks in the horizontal section of coil were caused by pitting from the outside (Figures 3 and 4) and apparently occurred during sludge removal. Pitting initiated under loose porous material and was attributed to an oxygen depletion cell. Intergranular attack was also observed under some of the scale (Figure 5).

Further attempts have been made to locate leaks in cooling coils by several methods, but none have been located; therefore, no additional leaking sections of coils were removed for examination.

EXPERIMENTAL RESULTS

Miniature Cooling Coil Tests

Preliminary tests were performed with miniature cooling coils of A 106 steel that were cooled with circulating tap water while they were immersed in various test solutions that could be heated if desired.

Pitting from slurrying operations alone was apparently greatest in Tank 11H. Consequently, supernate and sludge compositions in the pitting studies discussed below were based, as much as possible, on compositions in this tank. Observed pitting of cooling coils may have been caused by supernate. However, this could not be verified with actual supernate because Tank 11H supernate had lost its identity when it was mixed with other supernates and the mixture evaporated. Consequently, pitting tests were made by immersing miniature cooling coils in a synthetic Tank 11H supernate. The miniature coils were not attacked at 92°C, but became coated with a thin layer of insoluble salts. The metal under the salts remained shiny.

An equal volume of synthetic sludge was then added to the supernate at 40°C. The sludge contained 14 constituents and was formulated according to Savannah River Laboratory studies of solid waste forms for analyses made in high-level wastes.[4] Only mild pitting, a rate of <0.30 mm/yr (<0.012 in./yr), was observed. Pitting rate was not increased following a one-thousandfold dilution, and the metal stayed bright and shiny without becoming coated. The only inhibitor in HHW that could keep steel bright and shiny was basic nitrite; other components were too dilute when diluted by one thousand.

A ten-thousandfold dilution of Tank 11H synthetic supernate with sludge addition increased the pitting rate at 40°C by about a factor of three, to 0.91 mm/yr (0.036 in./yr). Although slurrying sludge with very dilute supernate did increase the pitting rate, the rate was far too low to account for the 46 mm/yr (1.8 in./yr) penetration that was observed in Tank 11H on 18 coils during sludge removal.

Analyses of HHW supernates account for only 10 to 30% of the sulfate predicted from process flowsheets.[2] Recently, analyses showed the sludge in Tank 16H was 0.09 molal in SO_4^{2-}, and 50% of this dissolved in water washes.[5] Thus, the original sludge removal operations that involved pumping out the supernate, then slurrying the sludge with water, could increase the concentration of sulfate relative to the other components in the liquid phase of the slurry.

The combination of increased sulfate and dilution of basic nitrite inhibitor in the waste could lead to rapid perforation of the steel coils. Sulfate that is present in the sludge and then dissolved in the slurry solution should promote pitting.[6] Dilution of an anodic inhibitor, such as nitrite, below the level of effective inhibition is considered an improper practice that can cause pitting and sometimes accelerate corrosion.[7] The possible extent of such acceleration was estimated by several experiments designed to establish the electrochemistry of pitting in sludge-supernate-water solutions.

Polarization Studies

In polarization studies of steel specimens, surface current densities were measured continuously as a function of applied potential. The anodic polarization curve corresponds to oxidation at the test electrode; conversely, the cathodic polarization curve corresponds to reduction at the test electrode. Mild steel specimens were immersed in diluted (ten-thousandfold)

Tank 11H supernate containing 0.03M SO_4^{2-} to simulate slurries developed in waste tanks. The polarization curves for such specimens are shown in Figure 6. The 0.03M SO_4^{2-} concentration was selected to represent that which is produced by slurrying $CaSO_4$, a possible sludge sulfate, which is relatively insoluble.

The maximum current density possible under the test conditions can be defined from the intersection of the anodic and cathodic Tafel[7] slopes (Figure 6). The steep anodic Tafel slope shows that the cell is under anodic control[8] and that the basic nitrite, an anodic inhibitor, is not effective at this concentration when sulfate is present. The uniform corrosion rate, Rm, calculated by Faraday's Law for this specimen is 15 mm/yr (0.60 in./yr). If the corrosion were localized as pitting, the rate could easily be as high as that observed in coil penetrations, viz., 46 mm/yr (1.8 in./yr).

Interpretation of Curves Related to Pitting

The hyperbolic shape of the anodic polarization curve for the test solution demonstrates a freely corroding system; the curve for steel in waste at the same dilution but without sulfate (see inset in Figure 6) shows a limited current density until O_2 evolution at high anodic potentials. The possible corrosion rate without sulfate is about 0.002 of the rate calculated for the freely corroding system with sulfate.

The specimen used in the determination of the anodic polarization curve in solutions that contained sulfate was pitted and corroded. Pitting can be initiated either by an anodic discontinuity in the metal or by a differential aeration cell. One common mode of pit formation is by an oxygen depletion cell which may develop in a crevice that restricts solution circulation. In an idealized reversible depletion cell when the Nernst equation would apply, for example, with platinized platinum electrodes, an emf of a few hundredths of a volt is developed in a dilute electrolyte saturated with oxygen at 0.2 atm pressure at the anode and a similar medium saturated at 1 atm pressure at the cathode.

Under actual cell conditions, if iron electrodes are used, an electrically conductive iron oxide forms at the cathode and acts as an oxygen electrode; iron dissolves at the anode to form Fe^{2+}. The Nernst equation predicts a potential of 1.26 V for an Fe^{2+} concentration of 0.1M at the anode, a pH of 7, and an O_2 pressure of 0.2 atm (air-saturated) at the cathode. In practice, the actual potential is lower because the Nernst equation requires reversible reactions, and the reduction reaction at the iron oxide cathode is not reversible. However, actual potential differences of 0.5 to 0.6 V between an active pit (anode) and a conductive steel oxide have been measured.[9,10]

Pitting Demonstration and Pitting Prevention

In laboratory demonst-ations, classical active-passive pitting occurred when a potential of 0.5 V was applied to steel samples in the same pH 9 synthetic solution that was used to determine polarization curves (with $CaSO_4$) shown in Figure 6. The active portion of the cell is the bottom of the pit (anode), where iron is oxidized, $Fe \rightarrow Fe^{2+} + 2e^-$. The passive portion of the cell is the iron oxide ring (cathode) around the pit, where oxygen is reduced, $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$ (Figure 7). The 0.5-V potential produced a pitting rate sufficient to perforate a cooling coil pipe with a 0.15-in. (3.81 mm) wall thickness in six days, and thus could explain the coil perforations produced during sludge removal. Less severe pitting but more severe general corrosion occurred at lower potentials, and at 0.4 V, the pitting was still sufficient to produce cooling coil perforation in 10 to 15 days.

Pitting of the steel did not occur when the waste was not excessively dilute or when adequate inhibitor was used. Figure 7b shows the same steel subjected to the same conditions of potential, viz., 0.5 V anodic to open circuit, time 1/2 hr, and room temperature. The steel was not attacked when exposed to Tank 11H solution diluted one hundredfold or to water at pH 12 containing 500 ppm NO_2^-. The small spots seen in Figure 7b are artifacts on the steel surface.

PITTING MECHANISM AND PREVENTION

The experimental studies indicate that cooling coils can be perforated by pitting corrosion after sludge removal if residual sludge and water remain in the tank. This conclusion is based on tests with synthetic wastes. The proposed mechanism for pitting is initiation at oxygen depletion cells which may develop in crevices. Initiation is followed by rapid corrosion accelerated by dilution of the anodic inhibitor, basic nitrite, and by sulfate that dissolved from the sludge during removal operations. This mechanism indicates that pitting attack of coils should not occur under normal operating conditions, because the solution compositions are not conducive to it.

Crevices are abundant in the waste tanks, especially around vertical cooling coil supports as shown in Figure 8. Corrosion, started as oxygen depletion cells in the crevices, can eventually produce potentials of the order of 0.5 V between pits and matrix metal in a sludge-water slurry. Sulfate and dilute nitrite can accelerate this corrosion. Any crevice would be suitable for pit initiation, even if the crevice were formed by insoluble salts precipitated on the cooling coil pipes.

Coil perforation did not occur in all tanks because the basic nitrite inhibitor was not sufficiently diluted during slurrying of sludge. Basic nitrite is an effective inhibitor in SRP waste diluted one thousandfold or less, although crevices reduce its effectiveness to some extent. Cooling coils in Tank 10H survived eight months in a slurry of sludge without cooling coil damage, but 18 coils in Tank 11H leaked after only one month in a similar slurry. Apparently, the wastes in Tank 10H were not diluted as much as were those in Tank 11H, and the basic nitrite remained effective even though sulfate was present. The conclusion on waste dilution in Tanks 10H and 11H was later verified through plant records.

In future sludge removal operations, the waste supernate should not be diluted by more than a factor of one hundred. Corrosion of the cooling coils should be precluded by this limited dilution. If supernate diluted by one hundredfold is not a satisfactory medium for slurrying sludge, an aqueous solution containing 500 ppm nitrite at pH 12 could be used. This would be a minimal increase in the total waste burden, requiring about 7500 lb (3401 kg) of sodium nitrite per million gallons (3.78×10^6 liters) of slurry water.

ACKNOWLEDGMENT

The cooling coil examinations shown in Figures 3-5 were performed by the Equipment Engineering Division of the Savannah River Plant.

REFERENCES

1. *Integrated Radioactive Defense Waste Management Plan.* USERDA Report SRO-TWM-77-1. Savannah River Operations Office, Aiken, SC (1977).
2. R. S. Ondrejcin. *Chemical Compositions of Supernates Stored in SRP High Level Waste Tanks.* USAEC Report DP-1347, E. I. du Pont de Nemours & Company, Savannah River Laboratory, Aiken, SC (1974).
3. C. C. Nathan, ed. *Corrosion Inhibitors.* p 133, National Association of Corrosion Engineers, Houston, TX (1973).
4. R. M. Wallace, H. L. Hull, and R. F. Bradley. *Solid Forms of Savannah River Plant High Level Waste.* USAEC Report DP-1335, E. I. du Pont de Nemours & Company, Savannah River Laboratory, Aiken, SC (1973).
5. L. W. Gray and R. S. Ondrejcin. "Chemical Characterization of SRP Waste Tank Sludges and Supernates." Presented at the *18th Conference on Analytical Chemistry in Nuclear Technology,* Gatlinburg, TN, October 22-24, 1974.
6. S. Matsuda and H. Uhlig. *J. Electrochem. Soc. 111,* 156 (1964).
7. *NACE Basic Corrosion Course.* p 9, National Association of Corrosion Engineers, Houston, TX (1971).
8. W. H. Ailor, ed. *Handbook on Corrosion Testing and Evaluation.* p 661, John Wiley and Sons, New York (1971).
9. W. H. Ailor, ed. *Handbook on Corrosion Testing and Evaluation.* p 681-4, John Wiley and Sons, New York (1971).
10. H. Uhlig. *Corrosion and Corrosion Controls.* p 273, John Wiley and Sons, New York (1971).

TABLE 1

HHW Tank Cooling Coil Failure History

Tank[a]	Vertical		Horizontal	
	Total	*Leaking*	*Total*	*Leaking*
1F[b]	34	2	2	0
2F[b]	34	6	2	1
3F[b]	34	1	2	0
4F	34	0	2	0
5F	34	0	2	0
6F	34	0	2	0
7F	34	0	2	0
8F	34	1	2	0
9H[b]	34	6	2	2
10H[b]	34	19	2	2
11H[c]	34	17	2	1
12H	34	0	2	0
13H	40	0	4	0
14H[c]	40	4	4	2
15H	40	0	4	0
16H	40	0	4	0
Total	568	56	40	8

---

[a] Tanks 1F-8F, 9H-12H; Type I, 2.84 × 10^6 liters (0.750 × 10^6 gal.), 12 internal support columns. Tanks 13H-16H; Type II, 3.90 × 10^6 liters (1.03 × 10^6 gal.), 1 internal support column.

[b] Sludge successfully removed; since used as salt receiver.

[c] Sludge partially removed; since used as fresh or aged waste receivers.

FIGURE 1. HHW Storage Tank
[Type I, 2.84×10^6-liter (750,000-gal) Capacity]

FIGURE 2. Incidence of Cooling Coil Leaks in Tanks 1F-8F, 9H, and 11H-16H

FIGURE 3. Perforated Upper Horizontal Cooling Coil, Tank 2F

FIGURE 4. Pits Beneath Loose Porous Material on Cooling Coil

a. Porous Material and Pits

b. Transverse Section of Pits Shown Above

FIGURE 5. Microstructure of Cooling Coil Under Porous Material

FIGURE 6. Polarization Curves of Steel in Dilute (ten-thousandfold) Synthetic Tank 11H Waste With and Without $CaSO_4$

FIGURE 7. Pitting and Prevention of Pitting in A 106 Mild Steel

a. Active-Passive Pitting at Ten-Thousandfold Dilution of Tank 11H Supernate

b. No Attack at One-Hundredfold Dilution of Tank 11H Supernate

FIGURE 8. Typical Crevices Formed by Cooling Coil Supports in Tanks 1F-8F and 9H-12H

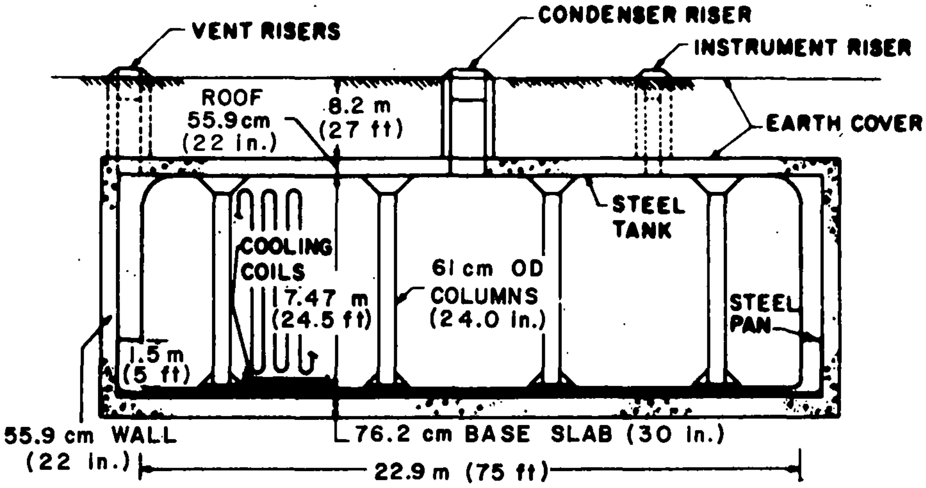

VENT RISERS
CONDENSER RISER
INSTRUMENT RISER
ROOF
55.9 cm
(22 in.)
8.2 m
(27 ft)
EARTH COVER
STEEL TANK
COOLING COILS
7.47 m
(24.5 ft)
61 cm OD COLUMNS
(24.0 in.)
STEEL PAN
1.5 m
(5 ft)
55.9 cm WALL
(22 in.)
76.2 cm BASE SLAB (30 in.)
22.9 m (75 ft)

FIG. 1

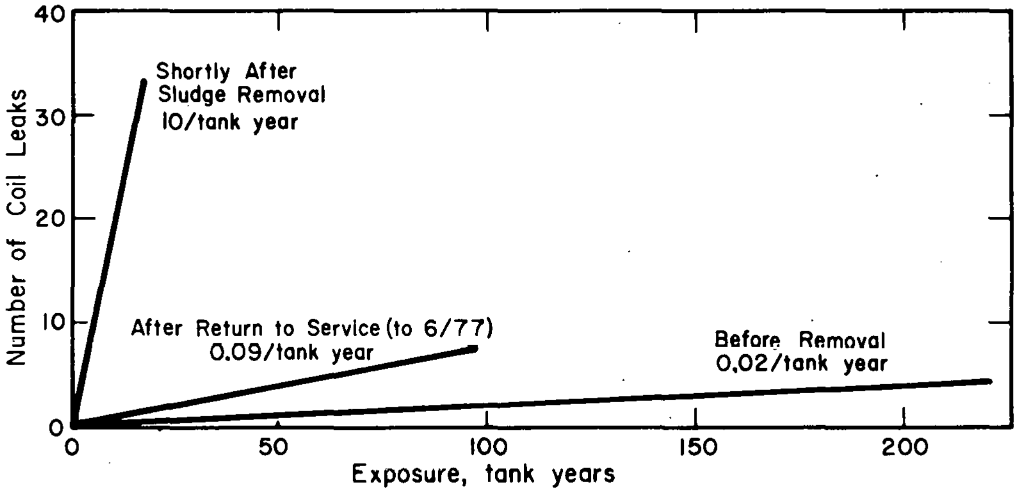

Number of Coil Leaks
40
30
20
10
0
Shortly After
Sludge Removal
10/tank year
After Return to Service (to 6/77)
0.09/tank year
Before Removal
0.02/tank year
0
50
100
150
200
Exposure, tank years

FIG. 2

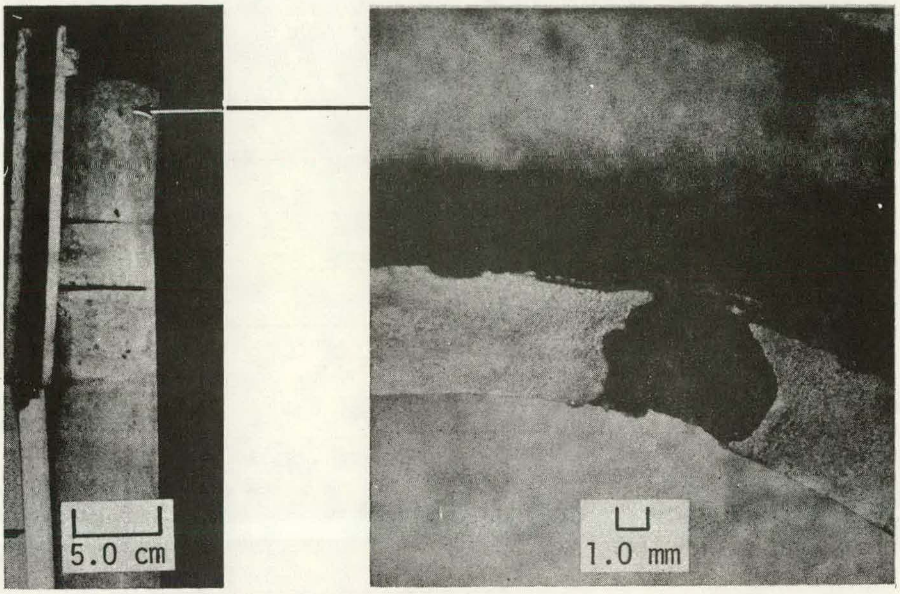
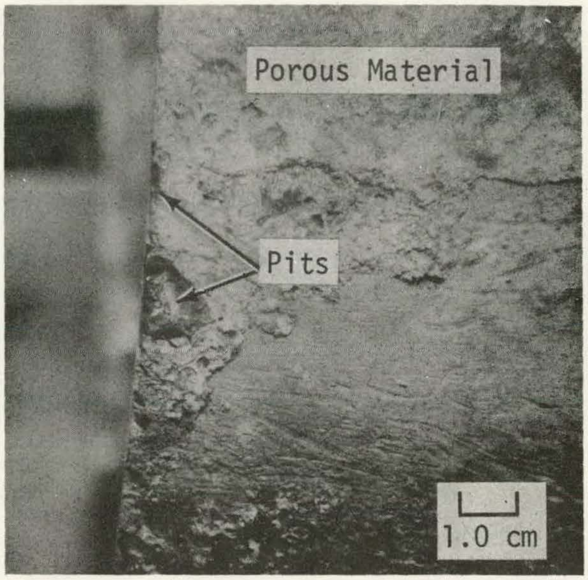
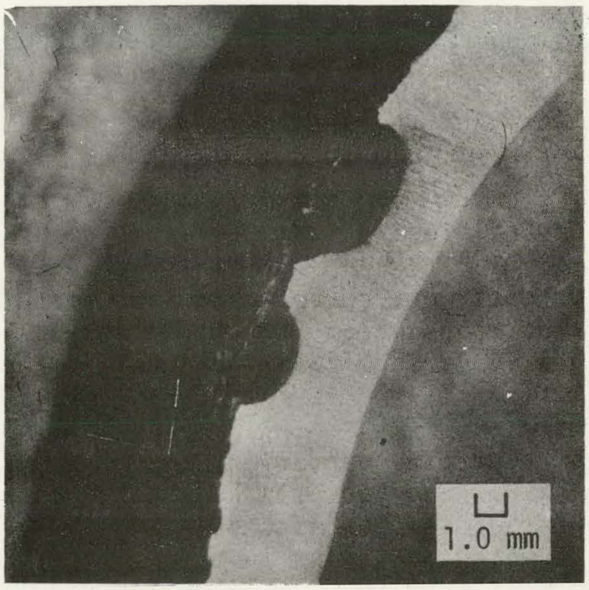


FIG. 3



a. Porous Material and Pits



b. Transverse Section of Pits Shown Above

FIG. 4

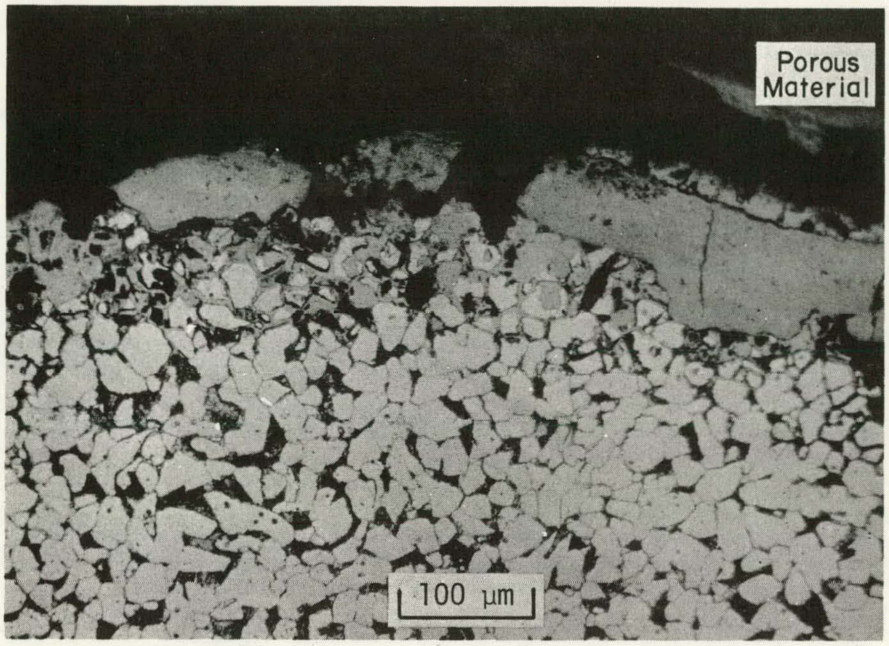

Porous Material
100 µm

FIG. 5

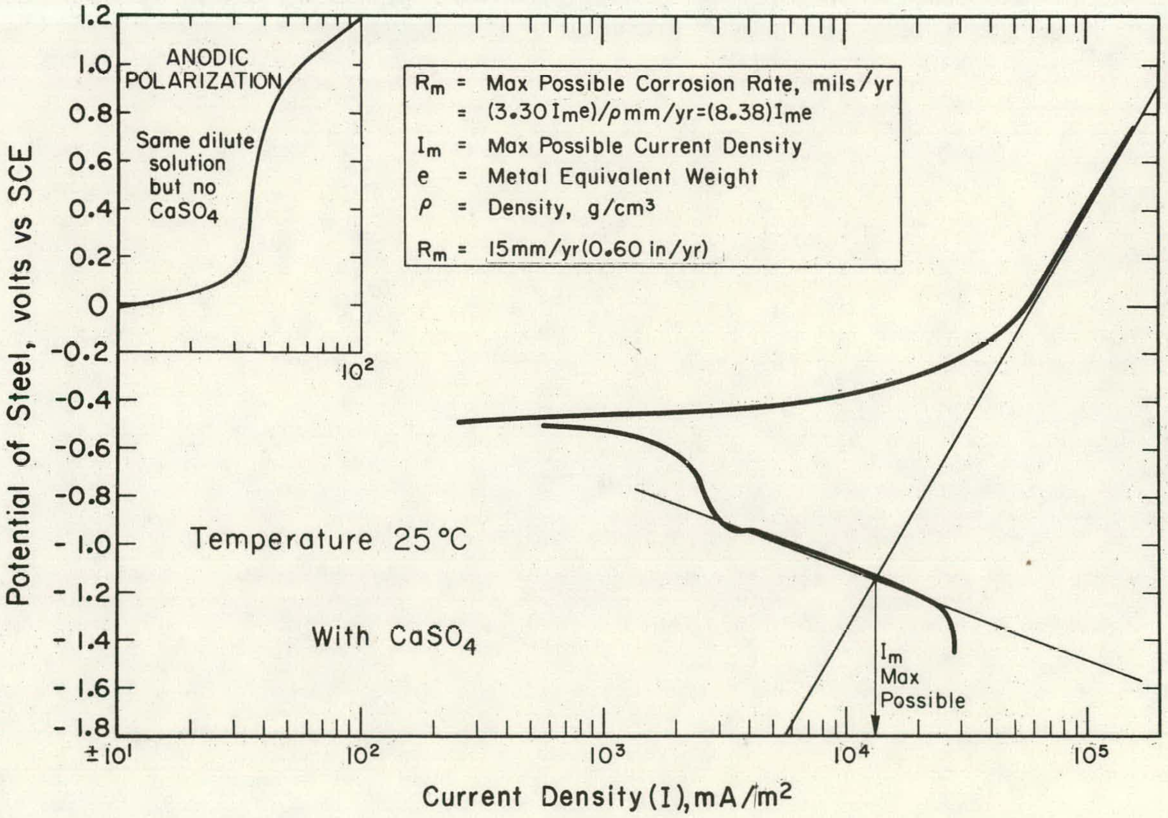
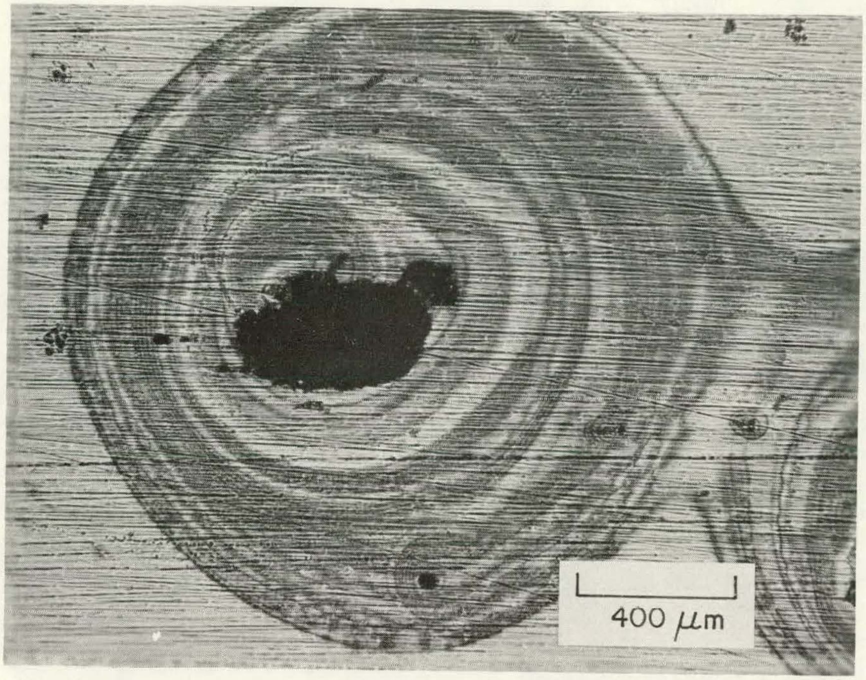
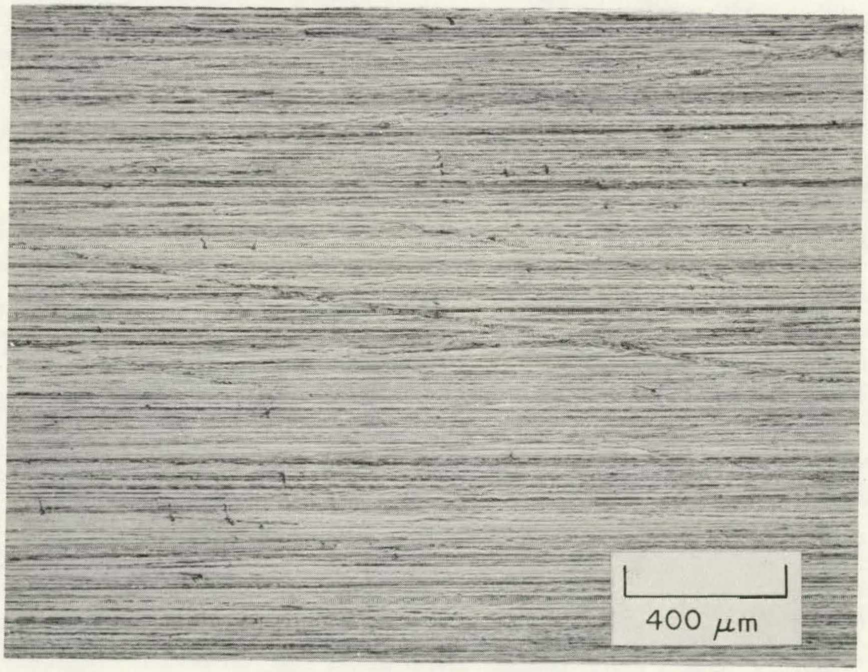

ANODIC POLARIZATION
Same dilute solution but no $CaSO_4$
R_m = Max Possible Corrosion Rate, mils/yr
= $(3.30 I_m e)/\rho$ mm/yr = $(8.38) I_m e$
I_m = Max Possible Current Density
e = Metal Equivalent Weight
ρ = Density, g/cm^3
R_m = 15mm/yr(0.60 in/yr)
Temperature 25 °C
With $CaSO_4$
I_m Max Possible
Potential of Steel, volts vs SCE
1.2
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
$\pm 10^1$
10^2
10^3
10^4
10^5
Current Density (I), mA/m²

FIG. 6



a. Active-Passive Pitting at Ten-Thousandfold Dilution of Tank 11H Supernate



b. No Attack at One-Hundredfold Dilution of Tank 11H Supernate

FIG. 7

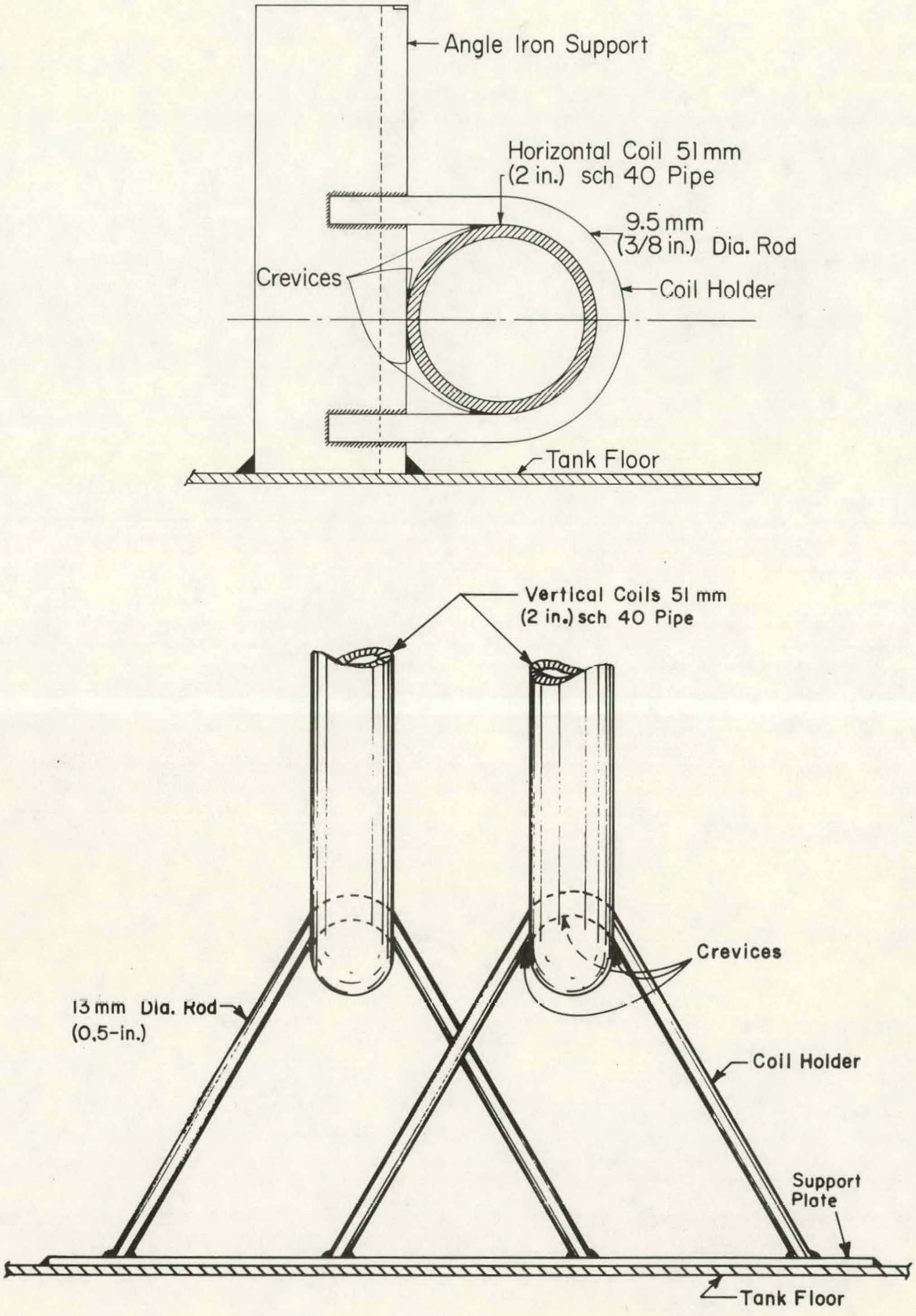

Angle Iron Support
Horizontal Coil 51 mm
(2 in.) sch 40 Pipe
9.5 mm
(3/8 in.) Dia. Rod
Crevices
Coil Holder
Tank Floor
Vertical Coils 51 mm
(2 in.) sch 40 Pipe
Crevices
13 mm Dia. Rod
(0.5-in.)
Coil Holder
Support
Plate
Tank Floor

FIG. 8