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November 25, 1975

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ATTENTION: J. A. PORTER

NITRITE INGROWTH AND STRESS CORROSION CHARACTERIZATION OF TANK 11H SUPERNATE

INTRODUCTION AND SUMMARY

Waste supernate stored in Tank 11H was analyzed periodically from May 1973-August 1975 to determine the rate of nitrite ingrowth by radiolytic decomposition of nitrate. This waste was transferred to tank 33F in accordance with TA 2-892, Rev. 1, "Use of Cracked Tank for Fresh High Level Waste," during the week of November 10, 1975. This letter summarizes analytical and corrosion characterizations wich indicate that this transfer should not increase the risk of stress corrosion cracking in F Area non-stress-relieved tanks. An interpretation of the nitrite ingrowth data is presented and used as a basis for concluding that the crack in Tank 11H occurred early in 1974.

The formation of nitrite in waste supernate was followed for $2\frac{1}{4}$ years during the last filling and storage cycle in 11H. The conversion of nitrate to nitrite in the $1\frac{1}{2}$ year period after filling was 4.9×10^{-11} mol NO_2^-/ℓ BTU of fission product heat. The energy released during the period was 1.15×10^{10} BTU with a corresponding increase in nitrite of 0.56 mol/ℓ.

The crack that was first observed in Tank 11H in April 1974 probably made its final penetration through the wall in March 1974 based on nitrite in-growth calculations and analyses of supernate for the NO_3^-/NO_2^- ratio. Analyses for $^{137}Cs/^{134}Cs$ in the dried salt crust did not yield a definitive estimate of the time of penetration because waste from high-burnup, off-site fuel made up the last 20% of the present fill.

Laboratory tests indicate that the OH^-(1.5M) and NO_2^-(1.2M) concentrations present in Tank 11H prior to transfer to F Area should sufficient for efficient inhibition of nitrate stress corrosion cracking. Electrochemically controlled tensile tests of A285-B steel specimens in synthetic 11H supernate at 100°C showed almost no loss of mechanical properties, and there was no visible evidence of crack propagation in precracked and stressed (45 kpsi $\sqrt{\text{in.}}$) wedge opening loaded specimens after 1000 hours exposure in synthetic supernate at 97°C. These tests are more severe than the actual tank conditions; 11H supernate was about 40°C when transferred.

DISCUSSION

Nitrite Ingrowth

Basic nitrite is a well known corrosion inhibitor for mild steel. In high activity wastes (HAW) caustic is added to neutralize the solution prior to storage, and radiolysis of nitrate occurs during storage to form nitrite. The presence of an inhibitor such as basic nitrite is important to HAW tank lifetime because stress corrosion cracking can be prevented by inhibiting the initiation phase of micropitting or intergranular trenching. Stress corrosion cracking could then only initiate at very narrow structural flaws.

The nitrite concentration in fresh waste is too low to be an effective inhibitor. However, nitrite is formed from nitrate by radiolysis. Prior to this work the rate of production of nitrite in HAW was not known for two reasons:

1) the radioactive dose rate has been calculated but not measured

2) the effect of prolonged high dose rates on nitrite was unknown for complex waste solutions.

The conversion of nitrate to nitrite and chemical composition were followed for a period of 2¼ years ending in August 1975 with samples for a proposed transfer of the waste supernate to 33F in November 1975.[1] Tank 11H had been emptied to a 35 inch level on March 29, 1973 and at that stage contained mostly sludge. Because of the possible delaying effect of basic nitrite on stress corrosion cracking a 30 inch heel (81,300 gal) of aged HAW was added to the sludge layer of 11H from 3H. The density and concentrations of nitrate, nitrite, hydroxide, aluminate, sulfate and chromate ions in the waste were measured periodically. The major sampling point was Riser #3 about 15 ft from the waste entry point. Samples were taken at the surface.

Variations in density, nitrate, nitrite and hydroxide during the 27 months prior to August 1975 are shown in Figure 1. The small amount of supernate left on the sludge contained about 2.5M NO_3^-, and 1M each NO_2^- and OH^- as indicated by the first point. The values at the second point, 2.4M NO_3^-, 3.6M NO_2^-, 3.2M OH^- and 1.42 g/ml were approximately the values of the 3H supernate added because of the small effect of the residual 11H supernate left on the sludge.

Early addition from the HM process were obviously very high in NO_3^- and very low in OH^- and NO_2^-, which is typical of fresh 221H waste. Additions of waste from the HM process continued until 11/14/73 when the tank was topped off with 120,000 gallons of waste from electrolytically dissolved off-site fuel. This waste could not go through nitric acid recovery because of the high chromium content and was added to HAW after neutralization. This waste was apparently low in nitrate and high in hydroxide.

Ingrowth of NO_2^- from radiolysis of NO_3^- for the 18 months after filling was 4.7×10^{-14} mole NO_2^-/ℓ joule of fission product heat or 4.9×10^{-11} mole NO_2^-/ℓ BTU. Total dose was calculated from the fission product inventory based on fuel irradiation and accountability data and the estimate of ingrowth is only as accurate as those data. The total energy output was 1.15×10^{10} BTU and the nitrite concentration increase was 0.56M.

Crack Propagation Through 11H Primary

Waste leaked through the primary tank wall at some time between June 1972 and April 1974, when a crack with a dried salt encrustation was observed at the top weld near the west annulus riser, as shown in photographs by Reactor Technology, Figure 2. During this time there were only two periods, June to mid-October 1972 and January to April 1974, when waste could have leaked out because of the liquid level in the tank. Between these two periods the liquid level was below the weld as shown in Figure 3. The leak is believed to be a stress corrosion crack.

Analyses of salt from the leak showed a NO_3^-/NO_2^- ratio of 5/1 which indicated that final penetration occurred in early 1974 based on nitrite ingrowth calculations given in the previous section, and analyses of waste supernate. Analysis of a 7/11/72 sample showed a 6/1 NO_3^-/NO_2^- ratio; a ratio of 5/1 would have been attained in the supernate in March 1973, based on the nitrite ingrowth data. At that time the liquid level was below the crack and the tank was being emptied (Figure 3). Waste supernate samples taken in 1973-4 show a 5/1 NO_3^-/NO_2^- ratio in March 1974 (Figure 1), just prior to the April photograph of the salt leak.

Analysis of the salt for $^{137}Cs/^{134}Cs$ ratio was not helpful in establishing the date of the leak. The ratio of 2.7 indicated an age of 3-3.5 years for HM waste, which would indicate that the leak occurred in 1972; however the mixture of waste from high burnup off-site fuel and HM in early 1974 could easily have the same ratio.

Only the time of final penetration of the crack through the primary can be deduced from the above argument; the time for initiation cannot. The results infer that once initiated cracks can propagate in the 50-60°C temperature range (Figure 3) if there has been enough penetration, even though the bulk supernate contains sufficient NO_2^- and OH^- to inhibit stress corrosion under freely corroding conditions. The inside surfaces of all unstress-relieved, cooled HAW tanks that have received fresh 221-H waste are probably cracked, as shown in Figure 16 of DP-990, "Leaks in Radioactive Waste Tanks." Since solution chemistry at the tip of a long crack is not the same as the bulk solution in the tank, occasional minor cracking can be anticipated. Controls on supernate concentration should prevent new cracking, and also reduce the frequency of penetrations due to propagation of existing cracks.

Analysis and Stress Corrosion Characterization

Tank 11H waste was a combination of about 65% HM HAW, 21% electrolytically dissolved off-site fuel waste, and 14% 31H heel. Samples were taken at the surface and eight feet below the surface to establish the degree of homogeniety of the solution within the tank. The results are shown in Table I.

TABLE I

Analyses of Tank 11H Supernate[a]

	7/17/75 Top	8/8/75 8 ft.	Synthetic Test Solution
NO_3^-	3.6	3.6	3.6
NO_2^-	1.2	1.2	1.2
$Al(OH)_4^-$	0.58	0.55	0.6
OH^-	1.5	1.5	1.5
CO_3^{2-}	0.01	0.01	0.01
SO_4^{2-}	0.03	0.03	0.03
CrO_4^{2-}	0.004	0.004	0.004
Hg, mg/ℓ	480	520	500
Density, g/ml	1.32	1.32	-
^{137}Cs, d/(min)(ml)	3.0×10^9	3.0×10^9	-
^{134}Cs, d/(min)(ml)	5.5×10^8	5.4×10^8	-

(a) All concentrations are M except as indicated.

Potentiostatic polarization tests were made of the actual waste to determine whether it could act in an aggressive manner in the event that electrochemical corrosion cells form on the steel. A major feature in this test is a high current peak when the steel is anodic. This characteristic would indicate a high probability of localized rapid corrosion and possible cracking if the steel were susceptible. For Tank 11H the current density peak was slightly higher at 1.0 ma/cm^2 than 32H transferred in 1974.[2] The open circuit potential was -0.16 V referenced against a saturated calomel electrode. This potential is in the lower part of the cracking range by pure $NaNO_3$ solutions.

The synthetic solution (Table I) was used for laboratory stress corrosion tests of A285-B steel specimens. The combined hydroxide and nitrite ion concentration of 2.7M is well within the range believed to provide effective inhibition of nitrate stress corrosion cracking.[3] Polarization curves of the synthetic and actual wastes were almost identical, so that test results with the synthetic solution should be valid for actual waste. Both electrochemically controlled tensile specimens and precracked wedge opening loaded specimens were tested. The tensile tests were performed in duplicate at 100°C. The ultimate tensile strength was the same as the value measured in air 68 kpsi. Tensile elongation decreased from 18% in air, to 17% in this test, in good agreement with the predicted value of 16%. The duplicate wedge opening loaded specimens were precracked by fatigue, stressed to 45 kpsi $\sqrt{\text{in.}}$ and immersed in synthetic waste at 97°C. There was no visible evidence of crack propagation after 1000 hours exposure. The ~100°C test temperatures were severe when compared to the Tank 11H supernate temperature, which was 40°C.

Thus, the laboratory test data indicate that the transfer will not increase the risk of stress corrosion in F Area tanks. These data include:

a) 11H supernate is within compositional limits for inhibition of nitrate stress corrosion cracking

b) There was almost no loss of mechanical properties in electrochemically controlled tensile tests.

c) Cracks did not grow in highly stressed wedge opening loaded specimens after 1000 hrs.

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Attachments

REFERENCES

1. Waste Management Operating Schedule No. 10 August 1975 to August 1976 TO: R. Maher FROM: A. A. Barab - F. E. McKay September 3, 1975.
2. DP-75-1-7, Savannah River Laboratory Monthly Report p 45 July 1975.
3. DP-75-1-7, Savannah River Laboratory Monthly Report pp 48-49 July 1975.

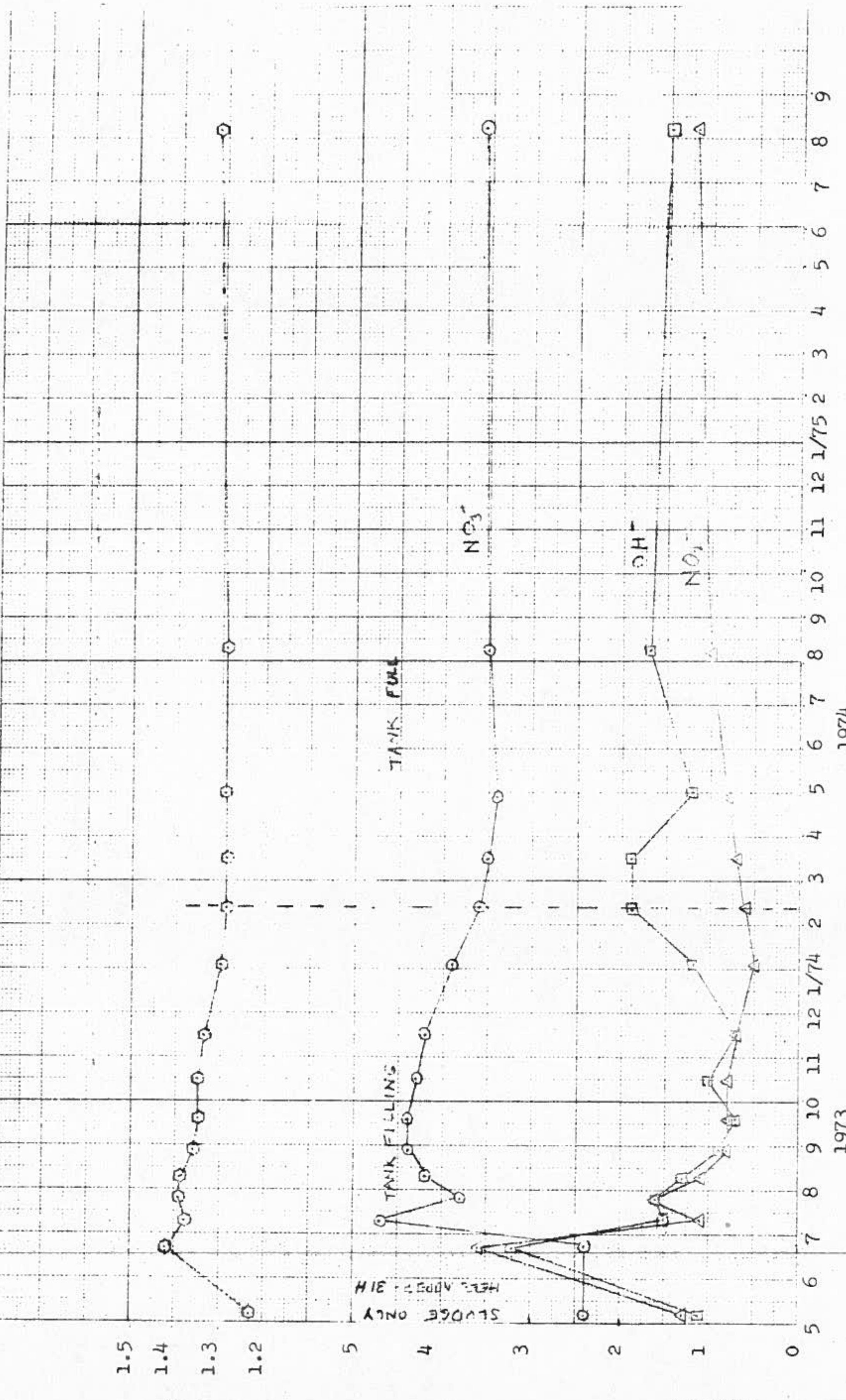

FIG 1. 11H SUPERNATE VARIATION

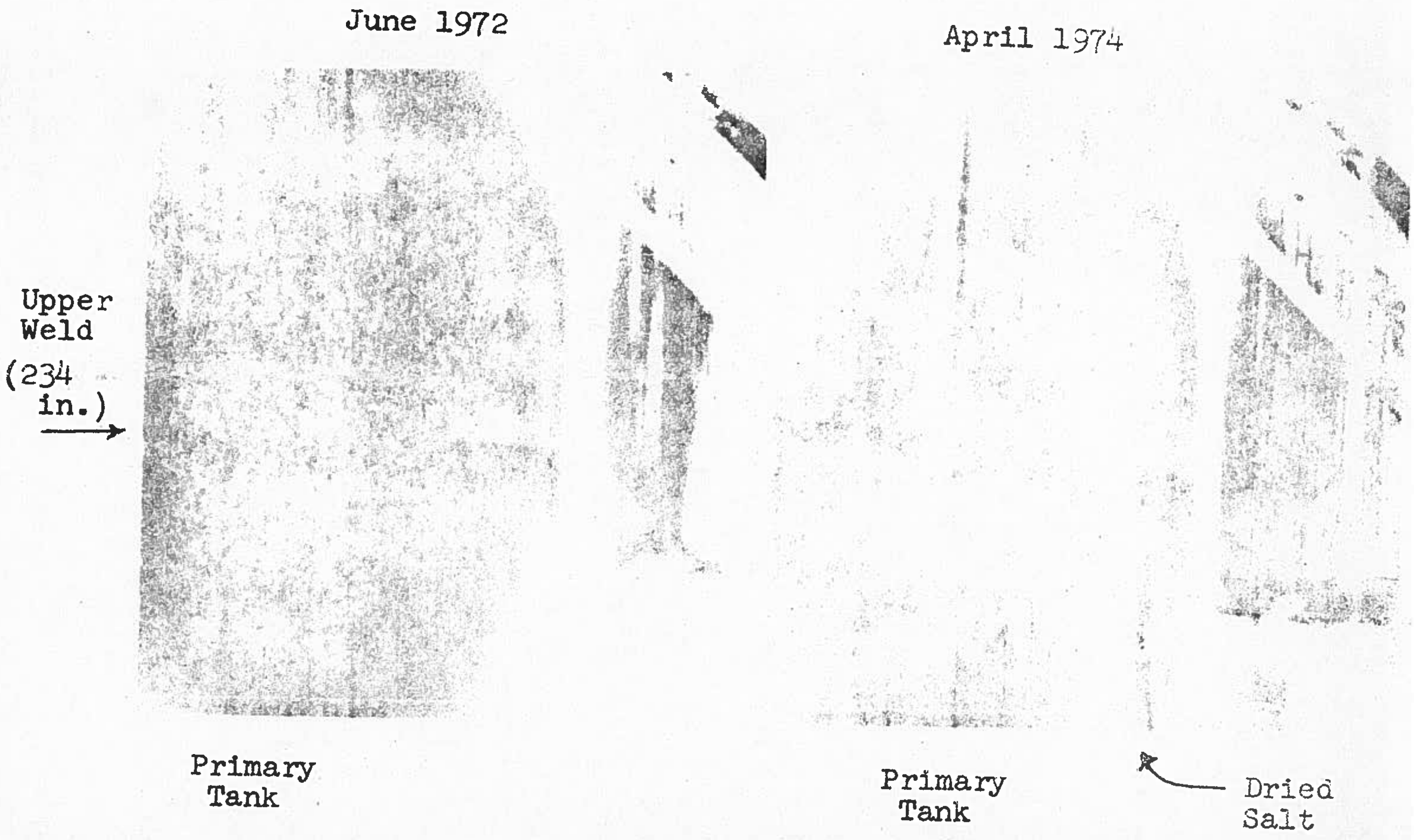

FIG 2. TANK 11H SHOWING SALT LEAK

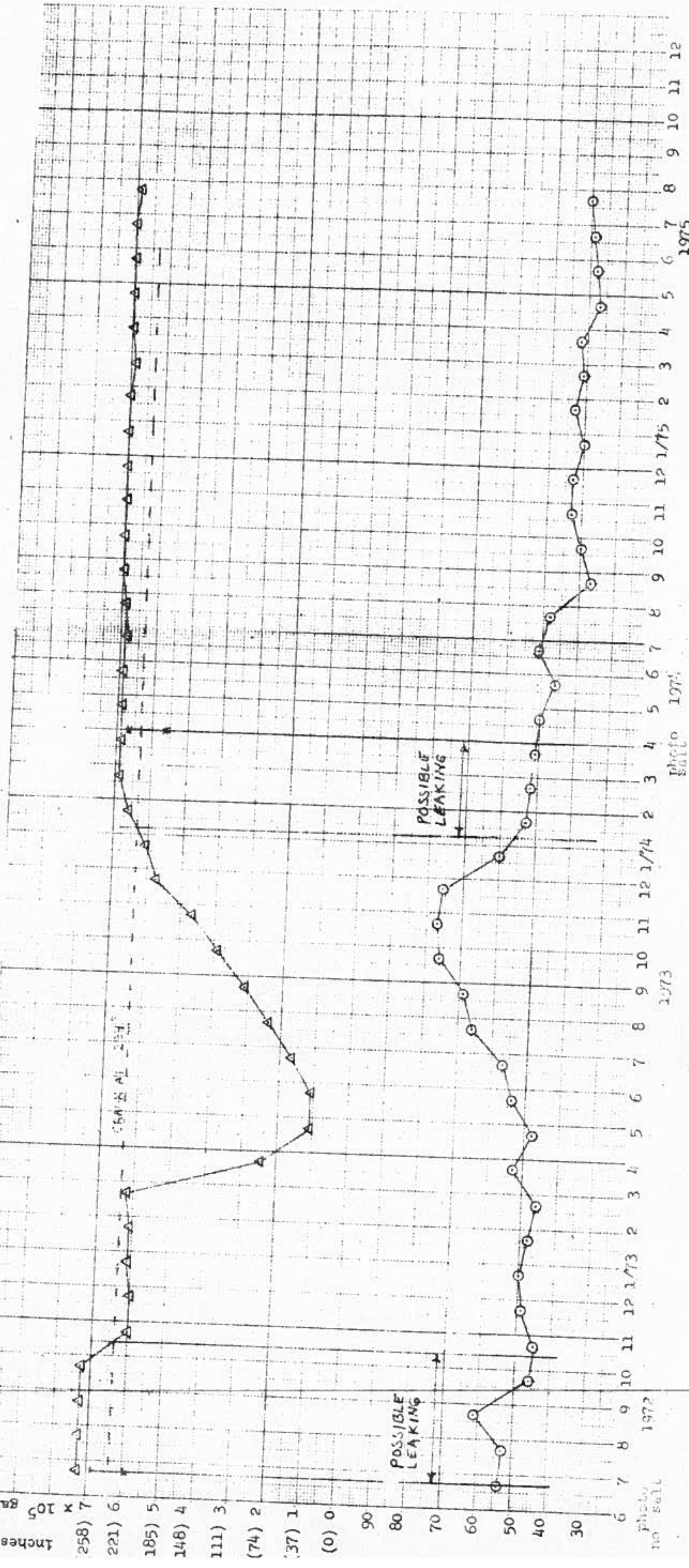

FIG. 3. LIQUID LEVEL AND TEMPERATURE OF 11H