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LWR FUEL REPROCESSING AND RECYCLE PROGRESS REPORT FOR JANUARY 1 - MARCH 31, 1977

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April 1977

Allied Chemical
IDAHO CHEMICAL PROGRAMS
IDAHO NATIONAL ENGINEERING LABORATORY
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PROGRESS REPORT FOR JANUARY 1 - MARCH 31, 1977

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ABSTRACT

Quarterly progress is reported on development studies for the Savannah River Laboratory on light water reactor (LWR) fuel reprocessing and recycle. Off-gas studies are reported on the reaction between NO_x and NH_3 and on the adsorption of gaseous iodine on silver-exchanged mordenite. Studies reported on LWR high-level liquid waste include waste evaporation characteristics, small-scale evaporator design, and corrosion of Type 304L stainless steel under various conditions.

SUMMARY

LWR OFF-GAS TREATMENT

A computer program was written to fit experimental data for the catalyzed reaction between NO_x and NH_3 to a bimolecular surface reaction rate expression by iterative non-linear least-squares analysis. Introductory sections of a topical report dealing with the NO_x - NH_3 reaction catalyzed by hydrogen mordenite were written. The LWR off-gas program was rescheduled for termination at the end of FY 1977; preparation for laboratory experimentation has been discontinued.

IODINE-129 ADSORBENT AND STORAGE DEVELOPMENT

The silver in silver-exchanged mordenite (AgZ) may exist both as the oxide and the metal. The metallic state appears to be more reactive and has a higher iodine-loading capacity. In test streams with a dew point of 23°C, iodine loadings of 137 and 71 mg I_2/g AgZ can be obtained on H_2-pretreated and untreated AgZ, respectively. The mass transfer zone for iodine adsorption is between 7.5 and 10 cm from the inlet with a dew point of 23°C, bed temperature of 100°C, and a face velocity of 15 m/min.

A rough draft of a topical report entitled "Airborne Elemental Iodine Loading Capacities of Metal Zeolites and a Dry Method for Recycling Silver Zeolite", has been written. The report includes a process-flow diagram illustrating full-scale application of AgZ regeneration and recycle to iodine recovery from the DOG of LWR fuel reprocessing plants.

WASTE MANAGEMENT

Laboratory evaporations were performed with simulated high-level liquid waste (HLLW) solutions having compositions expected during early operation of the Barnwell Nuclear Fuel Plant (BNFP); this waste contains a lower corrosion product concentration and a lower phosphate composition than the previous waste solutions studied; it also contains gadolinium as a nuclear poison. The HLLW-BNFP, concentrated to 336 l/MTU, contained approximately 12.8M nitric acid and smaller amounts of undissolved solids than previous waste solutions at the same acidity.

Physical properties of HLLW-BNFP are presented and include density, boiling point rise, and percent of undissolved solids. Viscosities are reported for several types of HLLW at various degrees of evaporation and temperatures. Slurries were about 1.5 times as viscous as their supernates.

Construction of the small-scale Type 304L stainless steel evaporator has been completed. Preliminary runs have been made with water and nitric acid at approximately one ft/sec vapor rate in the reboiler tube. Run plans and operating procedures have been prepared for testing of Type 304L stainless steel reboiler tube specimens.

Construction of the laboratory, glass-fabricated storage tank, which models selected conditions of a BNFP-type liquid waste storage tank, has been completed. The tank will be used to obtain preliminary heat transfer data and to provide design criteria for a small-scale stainless steel storage tank.

Corrosion rates obtained by continuous monitoring of HLLW solutions using Type 304L stainless steel probes compare well with coupon data obtained in the same solution. An average rate of 0.35 mpy was obtained at 60°C for a HLLW solution containing low concentrations of process contaminants and additives.

Corrosion rates are reported for HLLW solutions containing varying amounts of corrosion products. These data indicate that the total corrosion product accumulation in test solutions should be limited to about 0.6 g/l during operation of the small-scale evaporator.

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INTRODUCTION

This quarterly report is the fourth to be issued by Allied Chemical Corporation Idaho Chemical Programs at the INEL on the LWR Fuel Reprocessing and Recycle national programs which are administered by Savannah River Operations, ERDA, and the Savannah River Laboratory. The previous quarterly reports were published as ERDA reports ICP-1101, ICP-1108 and ICP-1110.

Off-Gas Treatment:	F-ID-13-001
Waste Management:	F-ID-13-002
^{129}I Adsorbent and Storage Development:	F-ID-13-004

RESULTS

I. LWR OFF-GAS TREATMENT

(R. A. Brown, D. H. Munger, T. R. Thomas)

Preparation for laboratory study of the NO_x-NH_3 reaction catalyzed by hydrogen mordenite was continued. All required equipment has been ordered. Each of the reactions of NH_3 with NO, NO_2, O_2, and N_2O is assumed to be described by the bimolecular surface reaction rate expression:

$$r = \frac{-d(A)}{dt} = \frac{K(A)(NH_3)}{(1 + \alpha A + \beta NH_3)^2}$$

where r = the rate at which NO, NO_2, O_2, or N_2O disappears, α and β are the equilibrium adsorption constants of A and NH_3, K is the rate constant, and t = the contact time in the plug-flow reactor. A computer program was written which uses iterative non-linear least-squares analysis to estimate all constants. A 5-cm-diameter by 60-cm-long stainless steel reactor with thermocouple and pressure transducer ports was fabricated. A new chemiluminescence monitor for NO_x analysis, which was made available from another project, was checked out. Construction of the test apparatus was scheduled to begin in April. However, due to termination of this program at the end of FY 1977, further preparation for a laboratory study is being discontinued.

A topical report is being written to summarize the thermodynamics, gas-phase kinetics and bimolecular surface reaction kinetics of the NO_x-NH_3 reaction. The report will also include a survey of other publications on the catalyzed NO_x-NH_3 reaction, published and unpublished experimental data previously obtained by the authors, and a description of the experimental system and procedure.

Future Plans

A topical report on the NO_x-NH_3 reaction catalyzed by hydrogen mordenite will be prepared.

II. ^{129}I ADSORBENT AND STORAGE DEVELOPMENT

(J. T. Nichols, L. P. Murphy, B. A. Staples, T. R. Thomas)

The effects of pretest purge and hydrogen pretreatment on the iodine loading of silver-exchanged mordenite Zeolon 900 (AgZ) were examined. Five-cm-deep beds, containing 10-20 mesh AgZ, were loaded with $I_2(g)$ in a dry airstream at a superficial face velocity of 15 m/min and a bed temperature of 100°C until breakthrough was detected (DF > 500). The results are given in Table 1.

TABLE 1

Dry Air Effect Test on the $I_2(g)$ Loading of AgZ

Pretest Purge (hr)[a]	H_2 Pretreatment[b]	No. of Replicate Tests	Loading[c] (mg I_2/g AgZ)
1	no	1	60 ± 9[d]
1	yes	1	67
16-64	no	4	24 ± 9
16-120	yes	3	62 ± 9

---

[a] Purged by dry air at 100°C

[b] Exposed to pure H_2 stream at 500°C for 20 hr

[c] Based on a dry density of 0.79 g/cm^3 for AgZ

[d] The 95% confidence interval based on a pooled variance

The data indicates that increased exposure of the AgZ to dry air at 100°C decreases the iodine loading about 60%. However, this effect is eliminated by pretreating the AgZ with H_2.

Tests were repeated using the conditions which gave the low results in Table 1 (i.e., 24 mg I_2/g AgZ) except that the bed temperature was raised to 150°C. The results of three tests were 57 ± 9 mg I_2/g AgZ. The 95% confidence interval is based on pooling the variance of this set of tests with those in Table 1. The results indicate that the effect of pretest purge can also be removed by raising the test temperature to 150°C in the absence of H_2 pretreatment.

Based on the data we have hypothesized that an equilibrium similar to:

$$Ag_2O(s) \rightleftarrows 2\,Ag(s) + 1/2\,O_2(g)$$

exists in the silver-exchanged substrate. The oxygen involved is part of the alumino-silicate structure. Hydrogen pretreatment would protonate the oxygen anion, reduce the Ag to the metallic state and block the return of the Ag to the oxide. This mechanism would predict the absence of a pretest purge effect; the high loading in the H_2-pretreated material would indicate that the metallic state is more active for iodine recovery. The same mechanism can be used to explain the temperature effect in the untreated AgZ. In the ideal state, the equilibrium has a zero free energy at 180°C, with the oxide being favored at lower temperatures and the metal at higher temperatures. When the AgZ is prepared, part of the procedure is to bring it to constant weight at 150°C. This would establish an equilibrium mixture of Ag_2O/Ag. Running the iodine-loading test at 100°C would upset the equilibrium, causing more oxide formation during testing. Running the iodine-loading test at 150°C would not upset the equilibrium, and no pretest-purge effect would be noted as was the case. The low loading at 100°C would indicate that the silver oxide is less reactive for iodine recovery than the metal.

Using a face velocity of 15 m/min, a bed temperature of 100°C, and a dew point of 23°C, the effect of contact time and H_2 pretreatment on the iodine-loading of AgZ was examined. The results, along with the distribution of the iodine from the top to the bottom of the bed, are shown in Table 2.

TABLE 2

Effect of Contact Time and H_2 Pretreatment on the I_2 Loading of AgZ

Bed Depth (cm)	mg I_2/g Ag in each 2.5 cm segment 1	2	3	4	5	6	Avg Loading (mg I_2/g AgZ)
5	57	10					33 ± 7[b]
5[a]	60	12					36 ± 7
15	71	70	68	67	47	9	56 ± 7
15[a]	138	136	123	94	34	5	88 ± 7

---

[a] H_2 pretreated

[b] Duplicate tests were run in all cases. The 95% confidence interval is based on a pooled variance.

All the above tests were pretest purged 16 hr with the carrier gas before testing. In the short beds, no effect due to H_2 pretreatment is noted, whereas the effect is quite large in the deeper beds. The same mechanism used to explain the results in Table 1 can be applied here if one considers the kinetics of the Ag_2O/Ag equilibrium to be slower in the presence of water vapor. The deeper beds provided the reaction time needed for conversion to the oxide. Of more importance, data from the 15-cm beds indicate a mass-transfer zone of 7.5 to 10 cm under these conditions. The iodine loadings obtained above the mass-transfer zone are the loadings expected in deep beds. Thus, the data in the first 5 cm of the bed depth indicate loadings of 71 and 137 mg I_2/g AgZ for untreated and H_2 pretreated AgZ respectively could be obtained in deep beds. Again, the oxide is shown to be less reactive for iodine recovery than the metal.

A rough draft of a topical report entitled "Airborne Elemental Iodine Loading Capacities of Metal Zeolites and a Dry Method for Recycling Silver Zeolite", has been written. The topical covers all the laboratory work done between January 1975 and February 1977. It includes a process-flow diagram illustrating full-scale application of AgZ regeneration and recycle to iodine recovery from the dissolver off-gas (DOG) of LWR fuel reprocessing plants. Sufficient engineering details are given to permit cost analysis.

A conceptual design of a pilot plant to simulate DOG test streams and demonstrate the regeneration and recycle concept of AgZ for iodine recovery has been drafted. However, the Iodine Adsorbent and Storage Development program will be stopped at the end of FY 1977. Therefore, no further work on the conceptual design or fabrication of a pilot plant is planned.

Plans for Next Quarter

The effect of dew point, NO_2 and NO concentration on the iodine loading of 15-cm-deep beds of AgZ will be studied. Particular attention will be paid to the length of the mass-transfer zone and the iodine loadings in the saturation zone.

A 15-cm bed of AgZ will be loaded, regenerated, and recycled under conditions expected in the DOG to determine its loading capacity vs the number of times recycled. The stripped iodine will be chemisorbed on load-exchanged zeolite (PbX) downstream, and loading capacities at breakthrough will be determined.

The physical properties of the iodine on the PbX for storage will be determined. The iodine vapor pressure of the PbX vs temperature will be measured, and solubility of the adsorbed iodine in hexane and water evaluated.

The topical report will be published.

III. WASTE MANAGEMENT

(B. E. Paige)

Liquid waste from the reprocessing of spent nuclear reactor fuels must be concentrated prior to and/or during interim storage to increase storage capacity and thereby reduce the cost of chemical reprocessing. The light water reactor liquid waste contains high concentrations of fission products; thus, it requires greater heat transfer capability than has previously been required in the management of radioactive liquid waste. The primary purpose of the waste evaporation and storage program is to study factors which affect the rate of heat transfer as well as the service life of the equipment. This includes: (1) investigation of solids formation, fouling tendencies, and off-gas behavior during evaporation and storage, and (2) evaluation of materials of construction.

Simulated high-level liquid waste (HLLW) solutions are being used for current investigations in order to avoid the difficulties and expenses of experimenting extensively with actual radioactive LWR waste. Considerable attention is being given to the composition and preparation of the simulated wastes in order to produce solutions which resemble the actual wastes as closely as possible.

Three types of simulated HLLW solutions which have been used for laboratory evaporations and waste storage studies were described previously.[1] In current work, HLLW solutions with a composition similar to that of the Barnwell Nuclear Fuel Plant (BNFP) waste, designated HLLW-BNFP, have also been prepared and investigated. Data obtained are compared to data from the three previous waste compositions. Simulated wastes are being evaluated to determine the effects of fission product substitutions and concentrations of process contaminants upon solids formation and materials behavior. This information will make future tests in the small-scale evaporators and storage tanks more meaningful. Results from these studies should finally be verified with actual LWR waste, for limited process conditions, using the experimental techniques developed in these studies with simulated waste.

1.0 Evaporation

Laboratory tests and evaporations of simulated HLLW have been performed to obtain data (boiling point rise, density, viscosity, and percent solids) for use in the design and operation of commercial HLLW evaporators and storage tanks and to provide criteria for construction of small-scale units for program studies. Precipitates have been characterized at various levels of evaporation. Current laboratory work primarily has been performed using a waste composition expected at the BNFP; this HLLW is considered more typical for currently planned LWR reprocessing plants than the three general HLLW compositions previously studied. The HLLW-BNFP waste contains lower corrosion product concentrations to reflect the use of a titanium waste evaporator and dissolver, and the phosphate concentration has been lowered to reflect more effective solvent cleanup systems. The HLLW-BNFP contains gadolinium as a nuclear poison. The HLLW-BNFP solution will be used for future small-scale evaporator studies and for laboratory waste storage tank studies.

1.1 Simulation of HLLW from BNFP (P. A. Anderson)

Early laboratory tests were performed on three types of waste solutions which were selected as representative of HLLW expected from future reprocessing plants. The three original solutions are designated HLLW-O (containing minimal process additives), HLLW-Fe (containing high iron concentrations from dissolved basket liners), and HLLW-UP (containing high uranium and phosphate concentrations from extractant degradation).[1] The compositions of solutions currently being studied and designated HLLW-BNFP are shown in Table 3. The composition of wastes expected during early operation of the BNFP is based on longer-term cooling of stored fuel. The steady-state composition represents processing of short-term-cooled fuel. Simulated waste solutions were prepared from a series of stock solutions by a procedure previously reported.[1] For the present studies, waste having the composition of the early operation was used. Manganese, cobalt, and nickel were substituted as less expensive simulants for the fission products technetium, rhodium, and palladium, respectively.

TABLE 3

Composition of HLLW-BNFP Test Solutions

	Early Operation[a]	Steady State[b] Operation
Evaporated Volume	336 l/MTU[d]	1375 l/MTU
Total Fission Product Conc.	65 g/l	22.4 g/l
Uranium at 1% Process Loss	29.8 g/l	7.3 g/l
Soluble Poison (Gd)	66.7 g/l	24.9 g/l
Phosphate	0.50 g/l	0.12 g/l
Free HNO_3	4-7 M	4-7 M
Total NO_3^-	10 M	8 M
Corrosion Products[c]	0.22 g/l	0.083 g/l

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[a] Based upon an estimated cooling period of 6.25 yr

[b] Based upon a cooling period of 1.8 yr

[c] Fe = 74%, Cr = 18%, Ni = 8%

[d] Liters per metric ton of uranium

Previous studies have shown that these substitutions do not affect solids formation or physical properties of the slurries.[2] Ruthenium was omitted from laboratory studies because of its high cost; no known simulant is considered satisfactory with respect to volatility and formation of solids.

1.2 Laboratory Evaporation of HLLW-BNFP (P. A. Anderson)

HLLW-BNFP solutions for laboratory evaporations were adjusted to 4918 l/MTU in 2.5M HNO_3 to approximate the expected concentration of first-cycle extraction raffinate at the BNFP prior to evaporation.

1.21 Acidity and Undissolved Solids Formation During Evaporations

HLLW-BNFP solutions were batch evaporated essentially without reflux from 4918 l/MTU at 2.5M HNO_3 to 336 l/MTU. As shown in Figure 1, the nitric acid concentration increased during evaporation to a concentration of approximately 12.8M which is considerably higher than predicted by most flowsheets and is also higher than waste compositions used in most solidification programs. Figure 2 illustrates that the quantity of undissolved solids in HLLW-0 decreases in higher concentrations of nitric acid regardless of the degree of evaporation. This shows that higher acid concentrations in the stored waste offer a possible process advantage of smaller quantities of undissolved solids.

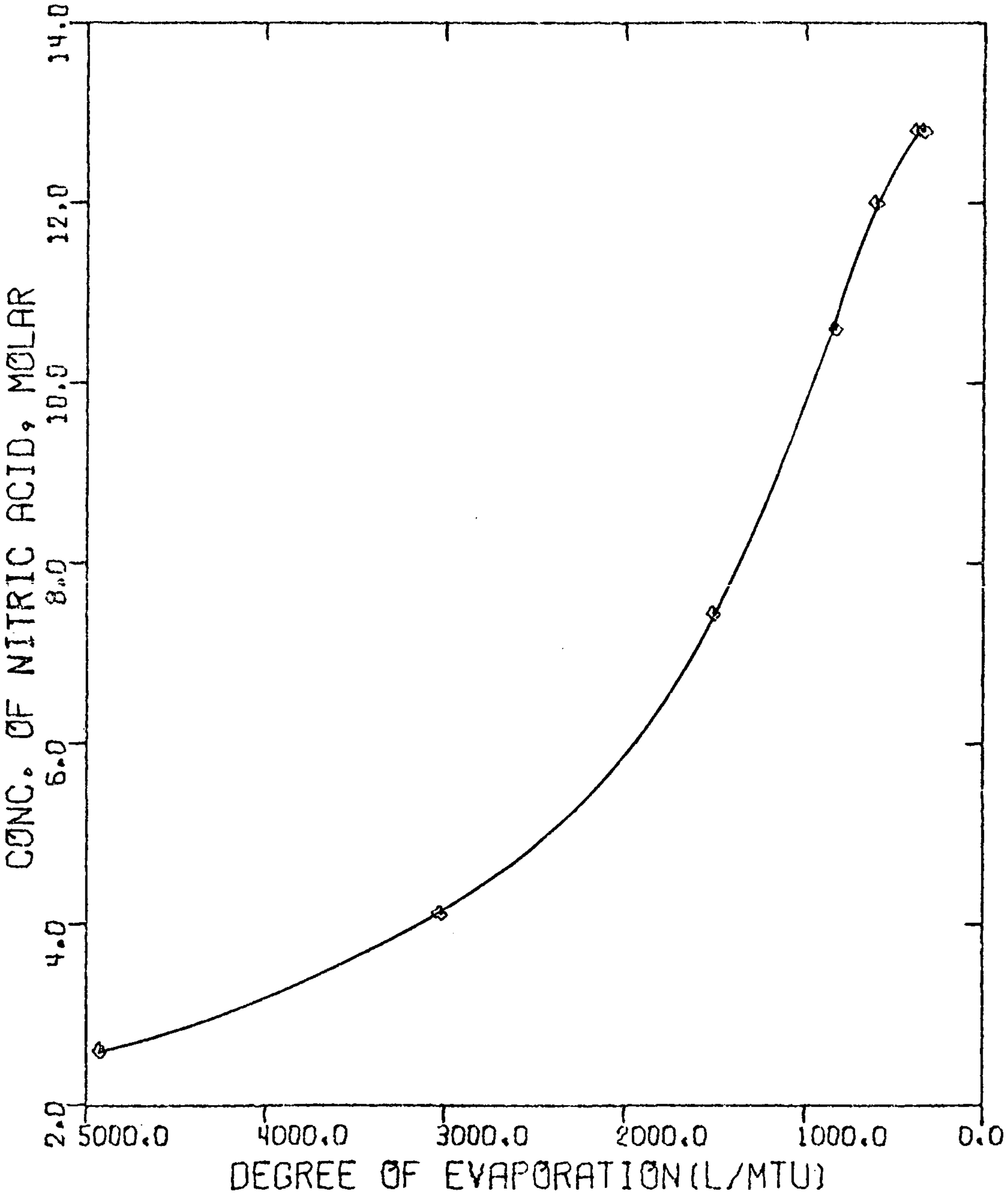

Figure 1. Acid Concentration of Evaporated HLLW-BNFP vs Liters per MTU

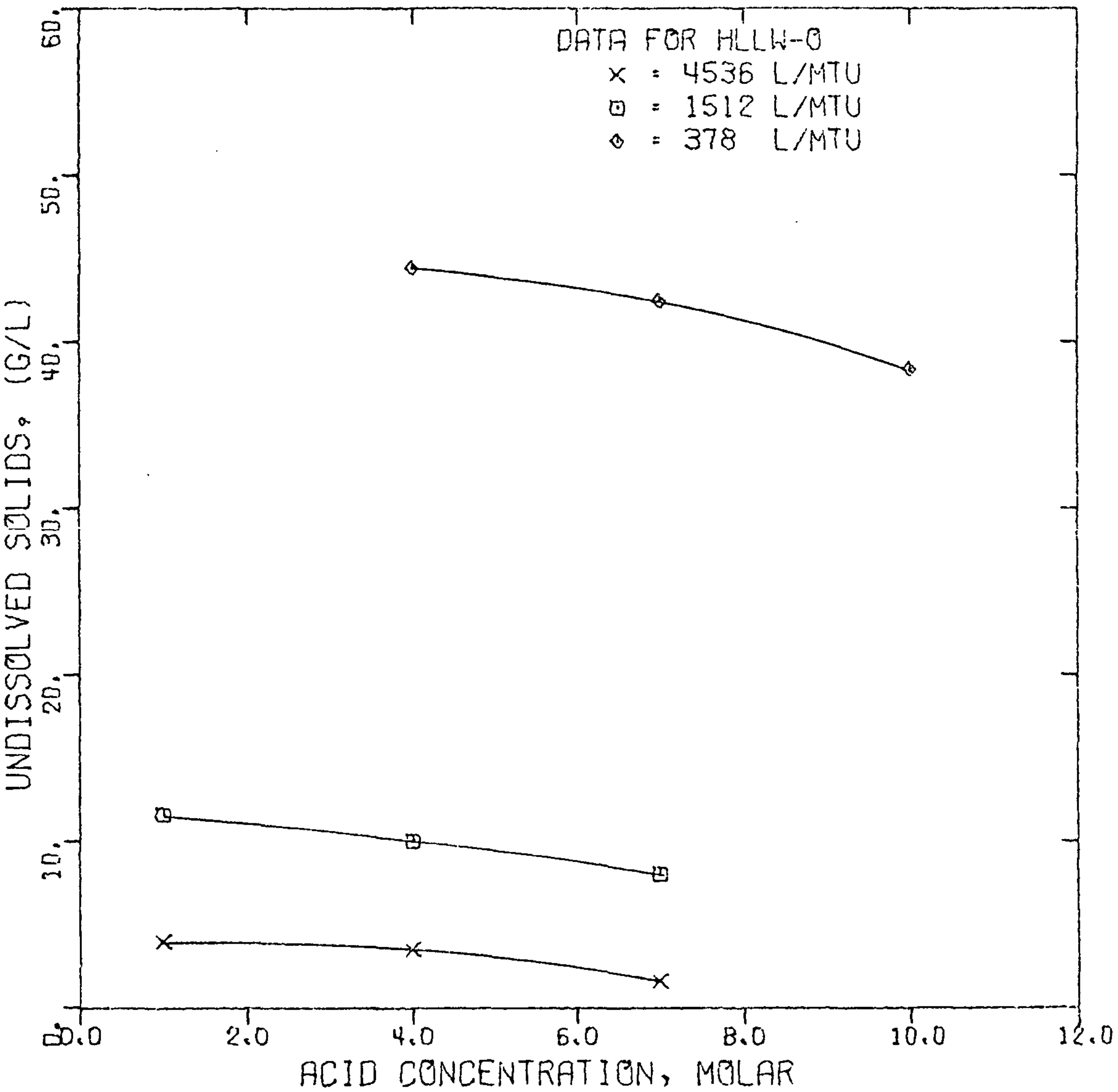

Figure 2. Effect of Nitric Acid Concentration on Undissolved Solids Concentration

Figure 3 illustrates the effect of acid concentration upon the undissolved solids content of two evaporated HLLW solutions. The HLLW-BNFP initially contained 2.5M HNO_3, while HLLW-0 contained 8.3M HNO_3. At the beginning of the evaporation, the undissolved solids content was lower in HLLW-0 solution which had the higher acid concentration. At about 700 l/MTU, the acid concentrations become approximately the same. As the evaporation continued, the undissolved solids contents of both solutions increased rapidly.

A comparison of HLLW-BNFP evaporations to those made previously with HLLW-0, HLLW-Fe, and HLLW-UP[3] showed that smaller amounts of undissolved solids were present in the HLLW-BNFP solutions when the acidity was the same, regardless of the degree of evaporation. The greater solubility of solids in HLLW-BNFP may be attributed either to the reduced phosphate content or to the increased content of soluble gadolinium and uranium.

The undissolved solids from the HLLW-BNFP are easily suspended at all degrees of evaporation. Fewer solids plated on the laboratory evaporator heat transfer surfaces with HLLW-BNFP than with solutions previously studied, whereas higher acid concentrations tend to increase plating in other HLLW solutions.

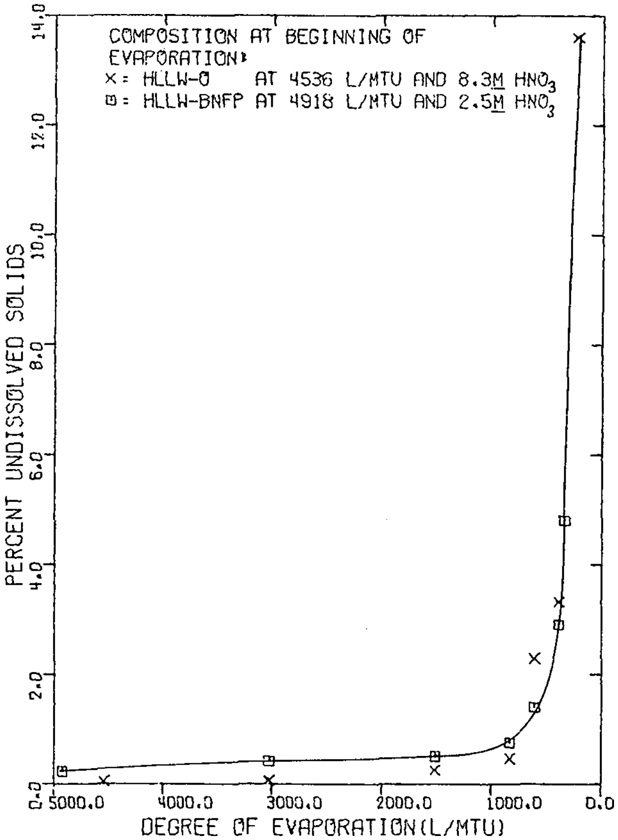

Figure 3. Relative Undissolved Solids in Evaporated HLLW-BNFP

1.22 Physical Properties of Evaporated HLLW-BNFP

Evaporated HLLW-BNFP at 336 l/MTU contains approximately 30% total dissolved and undissolved solids compared to approximately 20% for HLLW-0 at the same degree of evaporation. The density of HLLW-BNFP slurry as it is evaporated is presented in Figure 4. The density of HLLW-BNFP is higher than for HLLW-0 because of higher dissolved solids concentrations. The boiling point rise is presented in Figure 5 for use in design and operation of waste evaporators. The boiling point rise, with respect to dissolved solids content, is approximately the same for HLLW-BNFP as for HLLW-0. However, the temperatures encountered with HLLW-BNFP waste in a thrmosiphon evaporator will be about 10°C higher at the 336 l/MTU level due to the higher levels of dissolved solids. A boiling point increase of approximately 25°C (the maximum expected for evaporation to 336 l/MTU) should not greatly affect evaporator design.

1.23 Characterization of Solids

Freshly prepared simulated solutions of HLLW-BNFP at 4918 l/MTU contain essentially no visible solids, but increasing cloudiness appears within 10 minutes at room temperature. The rate of formation of visible solids also increases with temperature. Freshly prepared (<5 minutes) HLLW-BNFP at 4918 l/MTU contained <0.1 g/l undissolved solids at room temperature. The same solution held at 70°C contained 2.2 g/l after 68 hours and 2.4 g/l after an additional 22 hours. Freshly prepared solution which was heated to boiling over a two-hour period, also contained 2.4 g/l undissolved solids. This indicates that the undissolved solids content should not increase in the BNFP-type first-cycle raffinate, which is boiled in the dissolver, even if the solution is stored for several days before it is evaporated.

When stored at 60°C, the undissolved solids in HLLW-BNFP concentrated to 336 l/MTU are easily suspended with gentle agitation. Most of the solids settle again within 5 to 10 minutes when agitation ceases, which is considerably faster than in HLLW-0. HLLW-BNFP slurries at 336 l/MTU form copious amounts of crystalline solids when stored at room temperature; therefore, solutions should not be cooled below 60°C during storage.

The elements contained in the undissolved solids in HLLW-BNFP are identical to those in HLLW-0. X-ray diffraction data show the presence of a distinct crystalline compound with its most intense lines at d=5.70, 4.20, 3.62, and 3.11 angstroms. It appears to be a hydrated form of $ZrMo_2O_8$. Slurries at 336 l/MTU also contain small amounts of the nitrates of cesium, barium, and strontium which salt out in high concentrations of nitric acid.

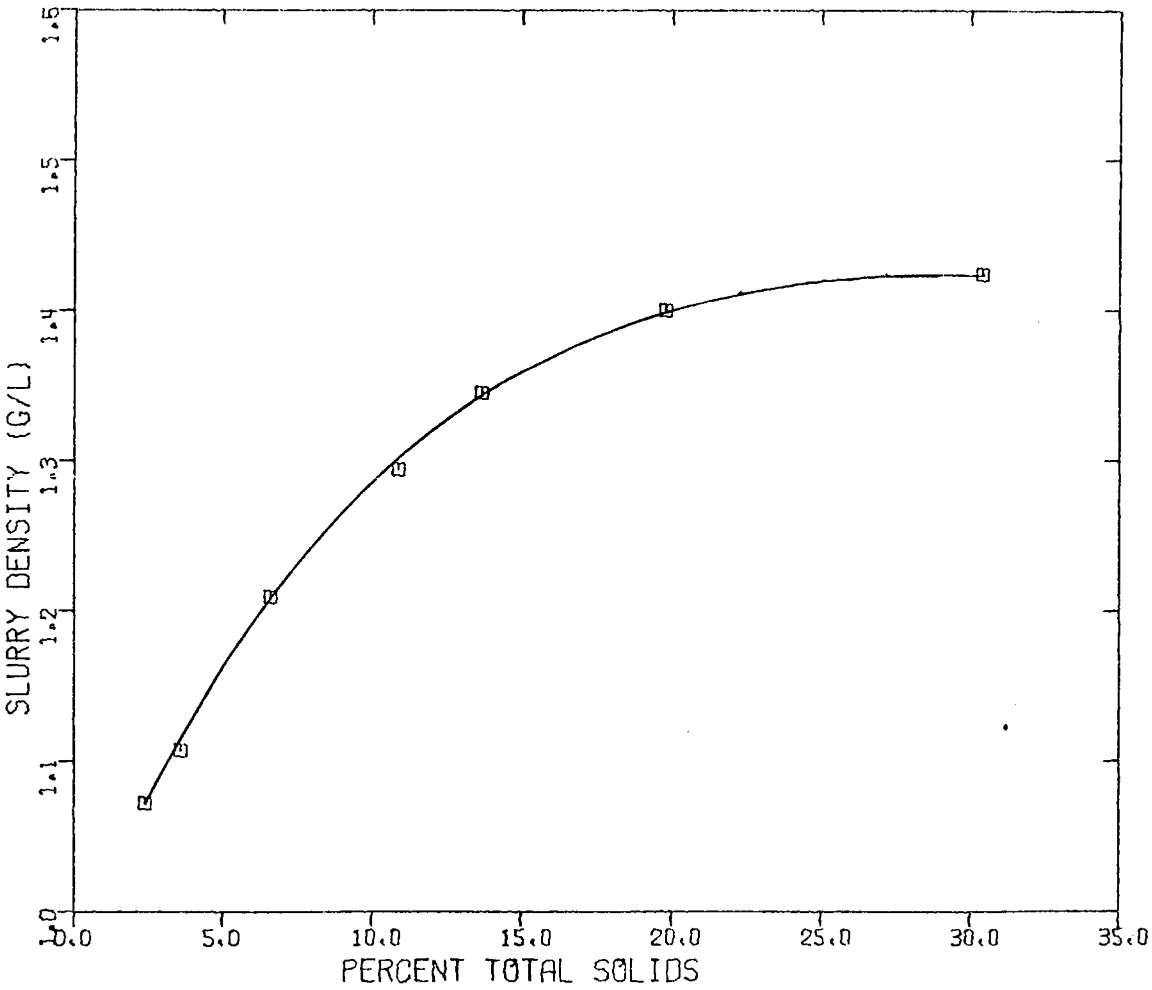

Figure 4. Slurry Density of HLLW-BNFP Relative to Total Solids (Dissolved plus Undissolved)

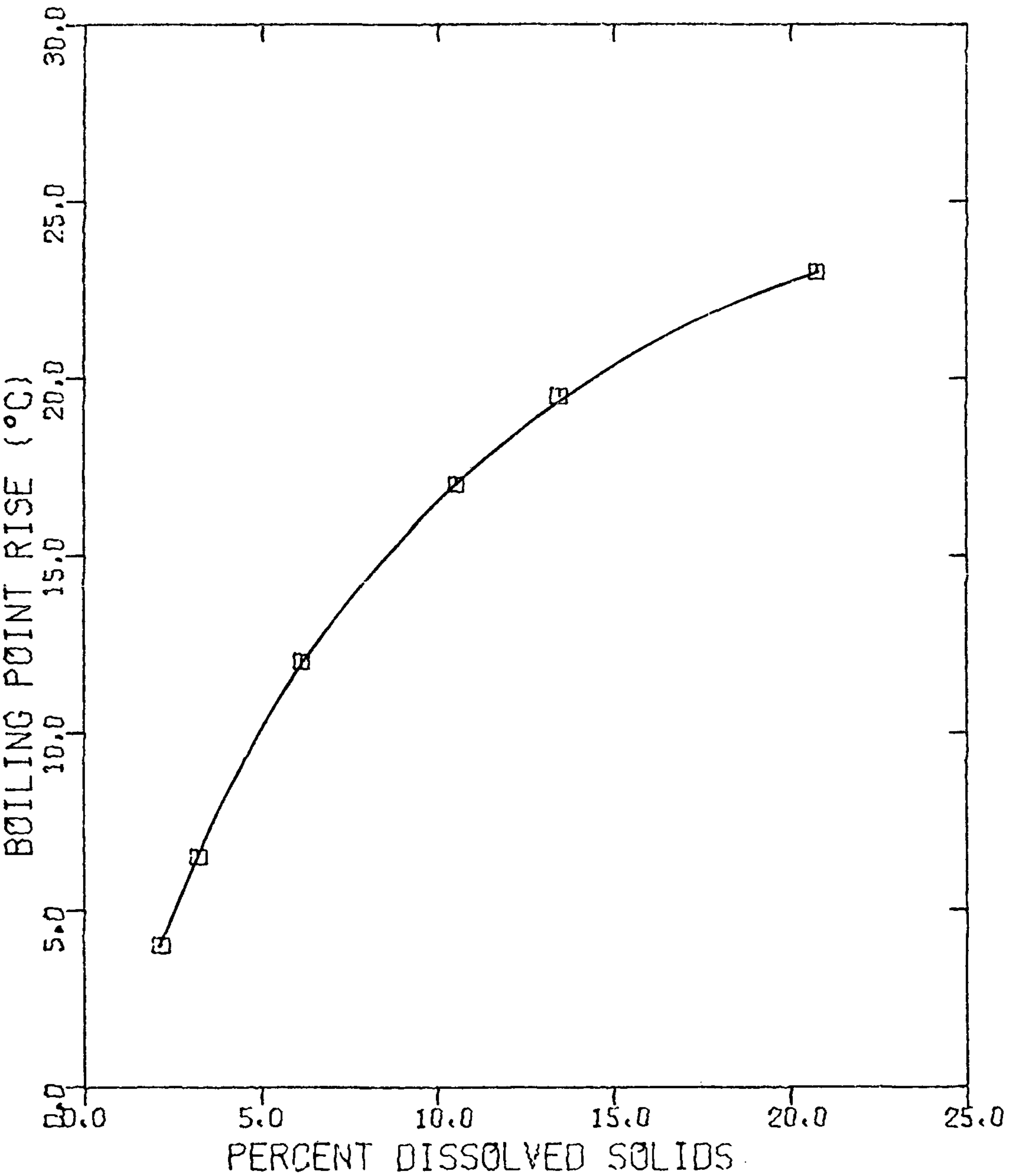

Figure 5. Boiling Point Rise During Evaporation of HLLW-BNFP (Based on 95.0 ± 0.5°C, The Boiling Point of water at approx. 630 mm local pressure.

1.3 Small-Scale Evaporator (G. R. Villemez)

The construction of the small-scale thermosiphon evaporator was completed. The unit will be operated to evaporate simulated HLLW from LWR fuel reprocessing waste to evaluate the effects of fouling, corrosion, contamination, and fission product entrainment in the off-gases.

The small-scale evaporator unit was checked out with water at two vapor rates in the reboiler tube. The overall heat transfer coefficient was 105 Btu/hr/ft^2/^{o}F with a vapor rate of 1.0 ft/sec and 290 Btu/hr/ft^2/^{o}F at a vapor rate of 2.9 ft/sec.

1.31 Evaporation of Nitric Acid

The evaporator was operated continuously for 30 hours with a 2.5$\underline{M}$ nitric acid feed. The product was 8.6$\underline{M}$ nitric acid and the vapor condensate was 1.28$\underline{M}$ nitric acid. During this preliminary run, the overall heat transfer coefficient was 377 Btu/hr/ft^2/^{o}F with a vapor rate of 1.25 ft/sec in the reboiler tube. A complete run will be made with nitric acid to establish the baseline for each reboiler tube test material.

1.32 Operating Criteria for HLLW

The operation of the small-scale thermosiphon evaporator will be directed toward the study of variables related to the evaporation of HLLW-BNFP solutions. The same dependent variables will be used for Type 304L stainless steel and titanium reboiler tube materials. Each reboiler material will be inspected after 158 hours of operating time for the effects of exposure to the HLLW-BNFP solutions. Each run includes three operating conditions during the total of 158 hours operating evaporation time as follows:

(1) Evaporate 20 liters of HLLW-BNFP solution at 2.5$\underline{M}$ nitric acid from 4918 l/MTU to 1375 l/MTU in 48 hr.

(2) Evaporate 20 liters of reconstituted HLLW solutions from Run 1 from 4918 l/MTU to 336 l/MTU in 62 hr.

(3) Recirculate vapor condensate together with a HLLW-BNFP solution from Run 2 at 336 l/MTU for 48 hr. The solution will be 12.5$\underline{M}$ nitric acid at 336 l/MTU according to laboratory nitric acid data.

The independent variables to be studied include the waste feed compositions. Initially, HLLW-BNFP in 2.5$\underline{M}$ nitric acid, which represents raffinate from the extraction cycle, will be used. Changes in composition which may be investigated in the future include the concentration level (l/MTU), corrosion product level, acid concentration, and the phosphate content. The maximum reboiler temperature difference will be 25^{o}F based upon the boiling point rise of the HLLW solution and the safety limit of 27^{o}F for Purex waste evaporations. The reboiler tube materials used in these tests will be Type 304L stainless steel and titanium metal. The dependent variables will be fouling, scaling, heat transfer, corrosion rate of reboiler material, and contamination of solution with corrosion products. In addition, the effects of corrosion and fission products entrainment in the off-gas system will be investigated. Later tests will investigate other materials.

2.0 WASTE STORAGE

Storage studies will determine the behavior of stored HLLW and provide design and operational data for efficient and economical storage of commercial LWR liquid waste until it is solidified. In the initial studies, three types of evaporated HLLW are being tested over an extended period for solution stability, undissolved solids formation, and corrosion of Type 304L stainless steel. Viscosities of evaporated HLLW slurries and supernates have been measured and are reported for use in heat transfer calculations for liquid waste storage tanks.

A laboratory storage tank is being designed and constructed for preliminary studies to determine the effect of solution mixing, solids suspension, scaling, and other phenomena on heat transfer to the cooling coils. The glass equipment is patterned after the BNFP waste tanks for interim liquid waste storage.[2] Preliminary data and operational experience obtained with this laboratory unit will be applied to the design of a small-scale stainless steel storage tank. This will provide criteria for the operation of existing waste tanks, the design of future waste tanks, and can serve as a prototype for any future studies with actual LWR waste.

2.1 Storage of Evaporated HLLW (P. A. Anderson)

Long-term storage studies, with three types of HLLE slurries at constant temperature and without agitation, are continuing. HLLW-BNFP has also been stored at 60°C and will be evaluated for stability with respect to undissolved solids. The physical changes to date are small in the slurries which have been stored up to 8 months.

2.2 Viscosity of HLLW (C. B. Millet)

Viscosity values, which are required for calculation of heat transfer and flow characteristics, have been obtained for HLLW solutions. The viscosity has been measured for both slurries and supernates at various temperatures and degrees of evaporation. Both HLLW-0 and HLLW-BNFP solutions were investigated.

The viscosity of the HLLW-BNFP at 25°C is 0.97 centipoise (cp) at 4918 l/MTU and increases as the waste is evaporated to 1.86 cp at 336 l/MTU. The viscosity begins to increase rapidly as the solution is evaporated to less than 1512 l/MTU as shown in Figure 6.

Temperature has a very pronounced effect on the viscosity of a liquid. For nonassociated liquids, the logarithm of the viscosity is an almost linear function of the reciprocal of the absolute temperature. Figure 7 shows almost a linear relationship of the log of viscosity to the reciprocal of the absolute temperature for water; the values

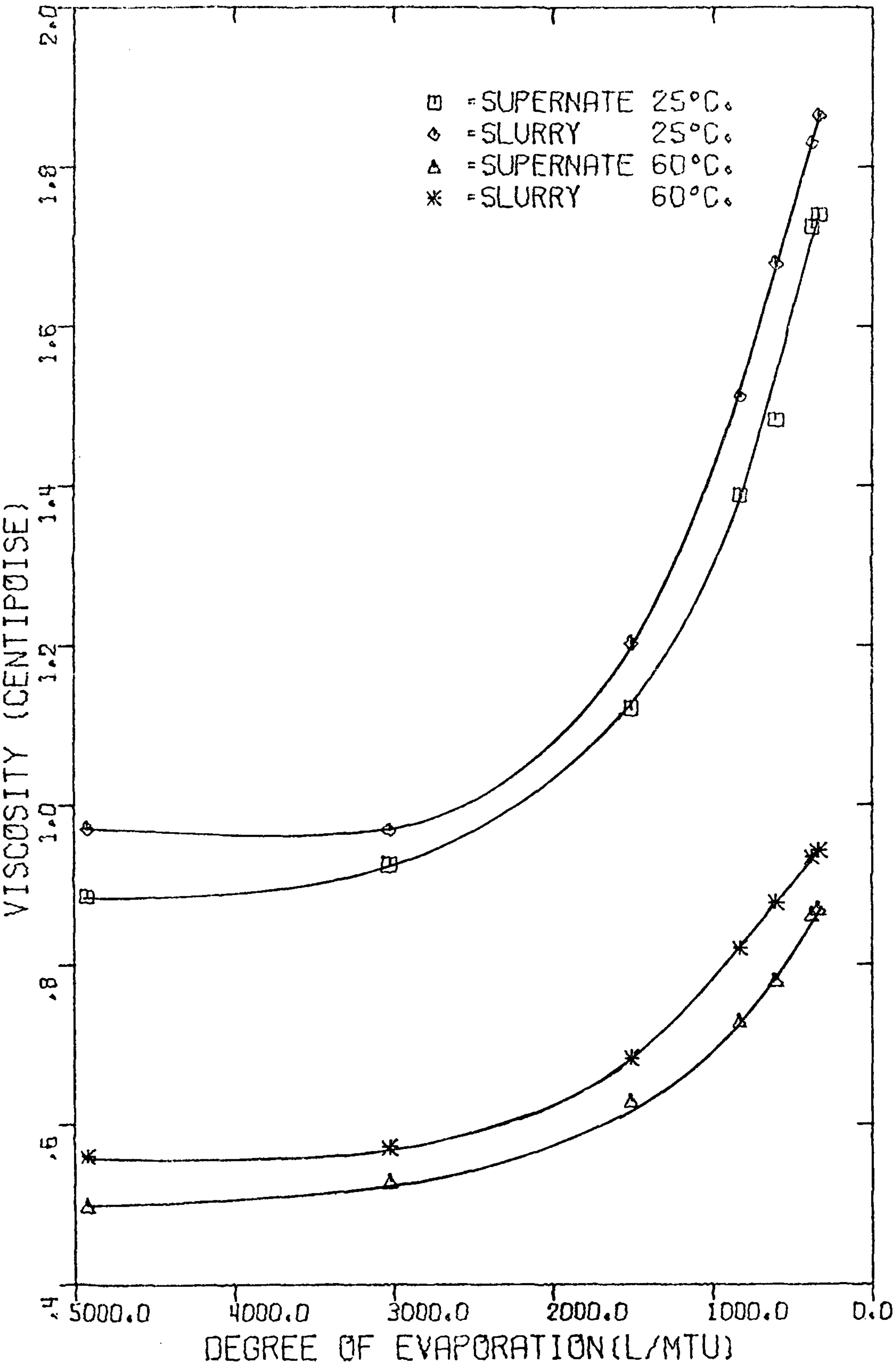

Figure 6. Viscosity of Evaporated HLLW-BNFP

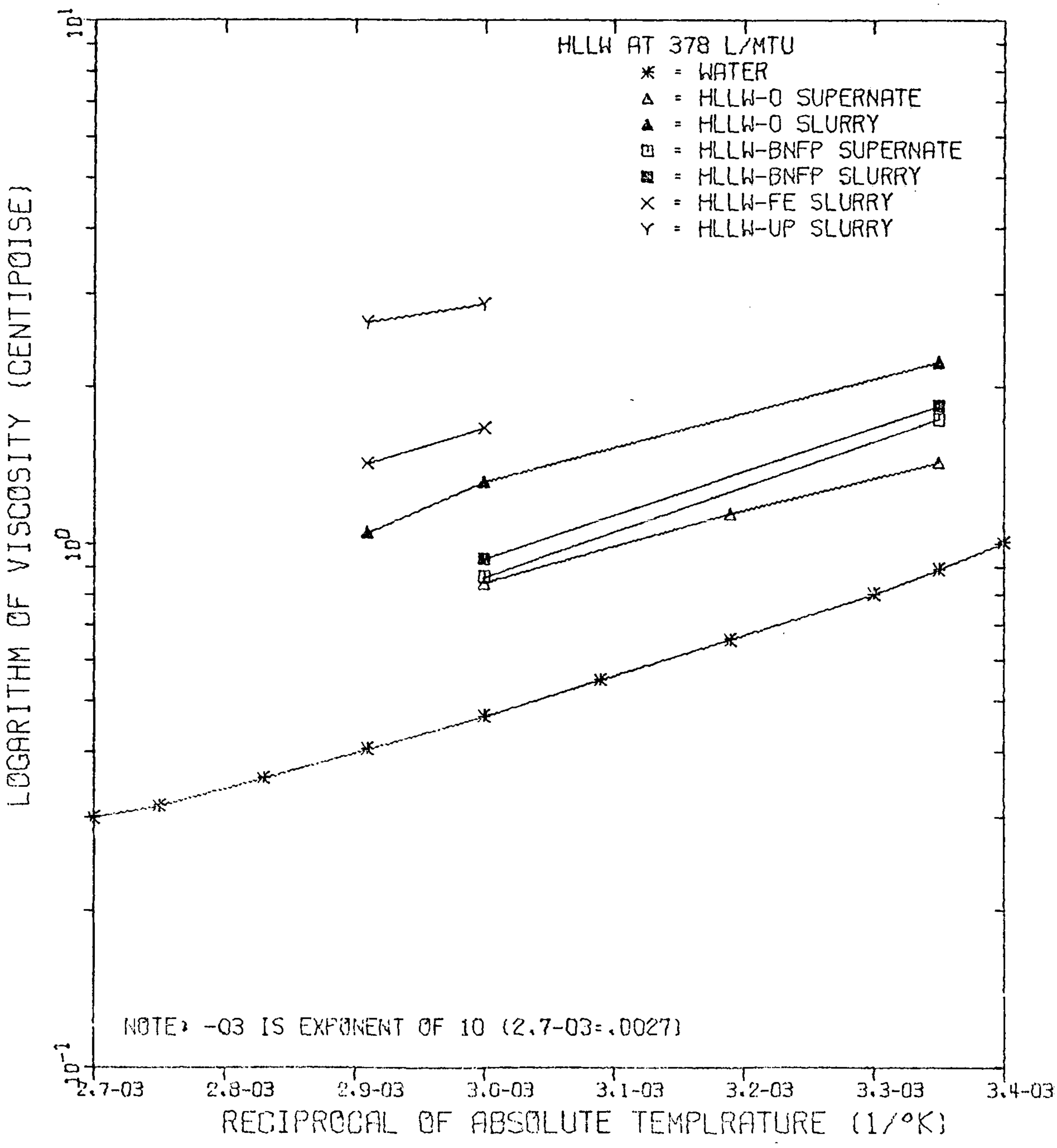

Figure 7. Effect of Temperature on Viscosity

for water plotted were obtained from the Lange Handbook of Chemistry.[4] The viscosity of HLLW-O and HLLW-BNFP solutions was measured at several temperatures; the relationship plotted in Figure 7 is also nearly linear. This plot may be used to approximate viscosities of HLLW solutions at other temperatures. The viscosity of HLLW-Fe slurry at 378 l/MTU was measured at 60 and 70°C and found to be 1.66 and 1.42 cp, respectively. The viscosity of HLLW-UP slurry under the same conditions was 2.86 and 2.64 cp, respectively.

The viscosity of supernates of centrifuged HLLW solutions at 378 l/MTU were measured to determine the effect of suspended solids. The viscosity of the supernate was 1.43 cp at 25°C and 0.84 cp at 60°C. As shown in Figure 7, the slurry solutions containing the precipitated solids exhibited a viscosity 1.55 times that of the supernate both at 25 and 60°C. Figure 7 also shows that for each HLLW-O and HLLW-BNFP solution, the slope of the supernate line is the same as that of the slurry.

2.3 Bench-Scale Storage Tank (P. A. Anderson, C. B. Millet)

Assembly of the laboratory storage tank is complete. The experimental unit consists of a 12-inch-diameter glass tank with a 3.6 gallon capacity. It is designed to model selected conditions in a large HLLW storage tank[2] and will establish operational and design criteria for future experimental storage equipment. The primary emphasis of the present equipment design is to obtain preliminary heat transfer data and to establish criteria for the small-scale stainless steel storage tank. The glass tank is enclosed in a constant temperature Plexiglas cubicle to minimize heat loss from the tank and to allow visibility during mixing and to observe behavior of the undissolved solids. Mixing of the solution and suspension of the solids will be accomplished with two glass ballast tank agitators and two glass air-lift circulators. The tank geometry is not intended to model the exact mixing conditions in a large HLLW storage tank, but it will serve to verify the adaptability of the mixers to small-scale experimental storage equipment. The tank is vented through a total reflux condenser to minimize evaporation losses via air from the ballast tank agitators or air-lift circulators.

Based on previous laboratory evaporation studies, initial tests will be made at 60°C using HLLW-BNFP evaporated to 336 l/MTU and containing approximately 12.8<u>M</u> nitric acid. The solution will be monitored for changes in the heat transfer coefficient with respect to changes in acidity, density, viscosity, settling, undissolved solids content, and caking or plating of solids on the heat transfer surfaces.

3.0 MATERIALS AND CORROSION

Materials and corrosion studies are being conducted both in the laboratory and in small-scale equipment to (1) establish the effect of waste composition and components on materials of construction, and (2) to investigate new materials for evaporators and for waste tanks and their auxiliary components. In addition, methods for monitoring corrosion of liquid waste tanks during interim storage of liquid waste are being investigated.

3.1 Laboratory Corrosion Tests (G. R. Villemez, C. B. Millet)

Modified Huey tests are being used to determine corrosion rates for the materials of construction for evaporators, storage tanks, and auxiliary equipment. In current work, unwelded coupons are submerged in boiling solution to determine the corrosion rates. Loss of weight usually is determined for three 24-hr periods and one 96-hr period to complete one week of total exposure. In cases where initial rates were considerably higher, the coupon was exposed for an addition week.

Laboratory corrosion tests are being continued to determine the effects of various fission product substitutions so that simulated HLLW will resemble actual LWR waste as closely as possible in the small-scale evaporator.

3.11 Variation in Corrosion Product Level

The effect of the corrosion products in different HLLW simulated waste solutions has been determined. Tests with Type 304L stainless steel coupons have been performed in HLLW-0 evaporated to 378 l/MTU containing 7M nitric acid. The corrosion product level was varied from zero to 9.15 g/l as shown in Figure 8. The corrosion rate increased from 77 to 130 μ/yr as the corrosion product level increased from 0.62 g/l to 1.83 g/l, respectively; at a corrosion product level of 9.14 g/l, the corrosion rate was accelerated to 1100 μ/yr. The normal corrosion product level of the HLLW-BNFP is 0.88 g/l.

Acceleration of the corrosion rate occurs at a corrosion product level of about 0.6 g/l. Based on these data, the small-scale evaporator operation will be designed to keep the corrosion product concentration in HLLW below this point of accelerated corrosion whenever possible.

The normal corrosion product level of the HLLW-BNFP will be set at 0.002 g/l in the initial feed to the evaporator. This level was determined by calculating the total wetted area of all dissolution and separation vessels having significant residence times and adding 50% of this area for piping and miscellaneous small equipment. The corrosion rate of 0.1 mil/yr was used for stainless steel and 0.1 mil/yr for titanium to compute the corrosion product level in the solution as it enters the evaporator.

The corrosion product level of the HLLW-BNFP solution used for liquid waste studies is 0.88 g/l for early operation with longer-cooled fuel. This level was determined by calculating the total wetted area of the storage tank and using the corrosion rate of 0.3 mil/yr for Type 304L stainless steel to compute the corrosion product level in the liquid waste after five years storage.

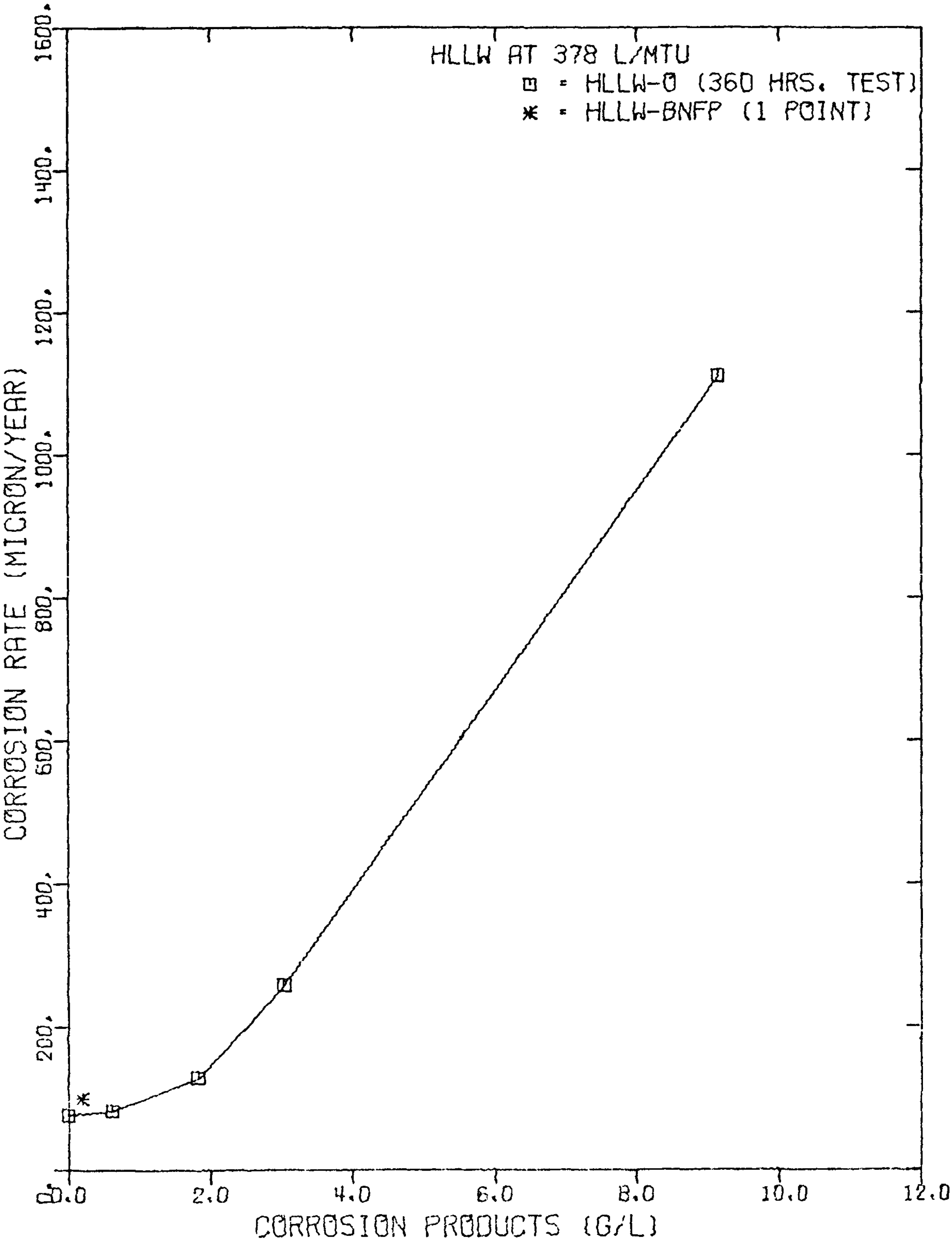

Figure 8. Effect of Corrosion Products Concentration on Corrosion Rate

3.12 Process Variables

Type 304L stainless steel coupons with surfaces as-received in the hot rolled and annealed condition were exposed for 168 hr in boiling solutions of HLLW-BNFP. Corrosion rates were about 100 μ/yr, which was less than half the rate observed in HLLW-0 solution at the same conditions.

The corrosive effect of two potential descaling solutions was also investigated. A 5% solution of Turco Alkaline Rust Remover[a], which was found to corrode Type 304L stainless steel at only 31 μ/yr for a 24-hour test, looks promising. A 2M oxalic acid solution had a corrosion rate of 2640 μ/yr for a 24-hour period and, therefore, will probably receive no further consideration as a descaling agent.

3.2 Monitoring of Storage Tanks

Laboratory tests to evaluate the effectiveness of electronic corrosion monitoring probes are proceeding. The use of electronic corrosion monitoring equipment offers the advantage of remote monitoring without the contamination and personnel exposure problems associated with retrieving metal coupons. Individual Type 304L stainless steel probes are immersed at 60°C in HLLW-0, HLLW-Fe, and HLLW-UP solutions which are stirred at one-hour intervals to suspend the solids. Corrosion readings were made with a corrosometer and probes. Table 4 compares the corrosion rates indicated by the electronic probes to the rates indicated by coupons immersed in the same solutions. Probes in the HLLW-0 and HLLW-Fe solutions showed steady continuous corrosion throughout the test period. Data from the HLLW-UP solution fluctuated, possible because of plate-out of the solids on the electrode.

Remote corrosion monitoring of actual HLLW solutions will require probes constructed of radiation resistant materials. Present probes contain small amounts of Teflon and plastic, chiefly as electrical insulators. These materials could deteriorate when exposed to actual HLLW. The estimated dose rate is 2.6 x 10^6 rad/hr for a probe extending 3.6 inches into a large storage tank containing HLLW at 378 l/MTU with a burnup of 35,000 MWd/MTU and a cooling period of one year. Communications with corrosion probe manufacturers indicate that probe construction can be modified to use electrical insulating materials which will tolerate such exposure.

Two types of electronic corrosion monitoring equipment are generally available. One monitors the amounts of corrosion experienced over an entire exposure period, while the other provides an instantaneous reading of corrosion rate. The latter has not been used for the present studies because long-term corrosion monitoring in large storage tanks does not require instantaneous rate information. However, such instrumentation could be considered for monitoring corrosion in process equipment which is in contact with solutions of varying composition.

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[a] Turco Products, Inc., Division of Purex Corporation, Carson, Calif.

TABLE 4

Corrosion Rates in Stored HLLW Solutions

Type of Solution at 378 l/MTU	Corrosion Rate from Electronic Probe[a], mpy	Corrosion Rate from Coupons mpy[b]
HLLW-0	0.33	0.37
HLLW-Fe	0.84	0.73
HLLW-UP	0.52	0.18

---

[a] Average corrosion rates over time periods of 49 to 73 days at 60°C

[b] Average corrosion rates over time period of 22 days at 60°C

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