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CHEMICAL TECHNOLOGY DIVISION

UNIT OPERATIONS SECTION

MONTHLY PROGRESS REPORT

APRIL 1961

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ORNL-TM 32

UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT

April 1961

CHEMICAL TECHNOLOGY DIVISION

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ABSTRACT

The density of the thoria product particles from Sol-Gel runs seems to increase as the ratio N/Th decreases but this ratio alone does not consistently correlate with sol properties. Seven capsules were prepared for the trial irradiation of thoria in the LITR. The three ion diffusion model gives reasonably accurate predictions of the uranyl sulfate loading rates on fluoride equilibrated anion resins. Back-mixing in the leacher rotary drum was found to be due to openings between the spiral flights and the inner cylinder at both ends. In the leaching of UO_2 it was found that 5.5 molar HNO_3 at a mole ratio of 5 was barely sufficient to completely dissolve the UO_2 in 4 hrs. Lowering the temperature to 10° below boiling reduces the leaching rate and the uranium loading. Runs dissolving 8% U-ZrH indicated that a minimum F/Zr ratio of 7.5 was required for total dissolution. Modified Zirflex runs without nitrate using both 8% U-ZrH and PWR-1 feed materials had dissolution rates comparable to those of the conventional reagent and an apparent increased tendency towards foaming. Experimental determinations of the temperature of spent fuel elements in simulated shipping casts have started. A waste calcination run using a close-coupled evaporator and calciner system operated and controlled very satisfactorily.

CONTENTS

		Page
	Abstract	2
	Previous Reports in this Series for the Years 1960-1961	4
	Summary	5
1.0	Fuel Cycle Development	7
2.0	HR Thoria Blanket Studies	14
3.0	Ion Exchange	15
4.0	Power Reactor Fuel Processing	19
5.0	Reactor Evaluation Studies	33
6.0	Waste Processing	34

Previous Reports in this Series for the Years 1960-1961

January	ORNL CF 60-1-49
February	ORNL CF 60-2-56
March	ORNL CF 60-3-61
April	ORNL CF 60-4-37
May	ORNL CF 60-5-58
June	ORNL CF 60-6-11
July	ORNL CF 60-7-46
August	ORNL CF 60-8-86
September	ORNL CF 60-9-43
October	ORNL CF 60-10-49
November	ORNL CF 60-11-38
December	ORNL CF 60-12-28
January	ORNL CF 61-1-27
February	ORNL CF 61-2-65
March	ORNL CF 61-3-67

All previous reports in this series are listed in CF 60-6-11 from the beginning, December 1954.

SUMMARY

1.0 FUEL CYCLE DEVELOPMENT

Six runs at identical conditions were made in the agitated trough denitrator to prepare product of N/Th mol ratio of 0.05 to 0.10 for sol dispersion-drying-calcining studies. The N/Th ratio alone does not consistently correlate whether dispersion into a sol will occur or what the sol properties will be. The density of the final product particles seemed to increase as the sol N/Th mol ratio decreased. Products of 9.72 to 9.88 g/cc as measured by toluene immersion compacted to 8.4 or 8.5 g/cc in 5/16-in.-dia tubes.

2.0 HR THORIA BLANKET STUDIES

Procedures were approved and seven capsules prepared for dry irradiations of ThO_2 or ThO_2-UO_2 in the LITR. An autoclave was designed and fabricated for irradiation in D_2O in one pressure vessel of six samples separately contained by thin-walled tubes and sintered metal disks.

3.0 ION EXCHANGE

Uranyl sulfate loading rates on chloride equilibrated resin appear to be dependent upon the fractions of the resin occupied by uranyl sulfate and sulfate ions at equilibrium. If one assumes that at equilibrium 0.98 of the resin is occupied with $UO_2(SO_4)_2^{=}$ and 0.02 is occupied with $SO_4^{=}$ (bisulfate ions and other uranyl sulfate complexes are neglected) then the three ion diffusion model gives reasonably accurate predictions of the uranyl sulfate loading rate on chloride resin and of the rate at which chloride ions are eluted from the resin.

4.0 POWER REACTOR FUEL PROCESSING

4.1 Shearing and Leaching

Operation of the rotary drum leacher as a conveyor at an elevation of 20 degrees and 2 rpm using color coded 3 liter batches of stainless steel rods (1/2-in.-OD x 1-in.-long) resulted in backmixing by as much as 4 to 6 flights. The leacher rotary drum was operated independent of the outer shell and it was found that the backmixing was due primarily to an opening between the spiral flights and the inner cylinder at both the feed and discharge ends.

It was found that 4 M HNO_3 at a mole ratio (g mol HNO_3/g mol UO_2) of 4.06 was insufficient to completely dissolve the UO_2 in a 4 hr dissolution time whereas 5.5 M HNO_3 at a mole ratio of 5 was borderline for the same dissolution time.

When maintaining the stage temperature at approximately 10 degrees below boiling, the maximum uranium loading is 300 g/liter compared to 350 g/liter at boiling and the dissolution time is ~2 to 2-1/2 hrs compared to ~1-1/2 to 2 hrs.

The dissolution of crushed UO_2 pellets results in a slightly greater spread between the maximum and minimum uranium loading in the product at apparently steady state and there is a reduction in the dissolution time of ~25%.

4.2 U-C Fuel Processing

In continuing work on a preliminary cost comparison of processing Pebble Bed Reactor fuel by fuming nitric acid disintegration-leaching vs oxygen combustion-acid leaching indicated the rate-limiting step for the former is probably the wash cycle.

A mixture of disintegrated graphite and fresh 90% HNO_3 failed to detonate when primed by a No. 6 cap and a 5 g PETN booster, suggesting that no explosion hazard exists for this combination.

4.3 Modified Zirflex

Modified Zirflex is a batch process for the dissolution of U-Zr-Sn fuels in NH_4F-NH_4NO_3-H_2O_2 solutions with a continuous addition of H_2O_2 to oxidize U^{IV} to the more soluble U^{VI}. Runs dissolving 8% U-ZrH in a 1-in. recirculating dissolver indicated that a minimum F/Zr charge ratio of 7.5 is required for total dissolution. This produces a final free fluoride to uranium ratio of 45. Since a surface layer is formed on the fuel if insufficient fluoride is present, this ratio may be dependent on flow conditions within a dissolver.

The use of NH_4F-H_2O_2 dissolvent (eliminating the NO_3^-) in dissolving both 8% U-ZrH and PWR-1 seed material produced comparable dissolution rates (possibly slightly slower) and an apparent increased tendency toward foaming.

5.0 REACTOR EVALUATION STUDIES

5.1 Heat Transfer from Spent Fuels during Shipping

Experimental determinations of temperature of spent reactor fuels in simulated shipping casts have been started. Measurements have been made with bundles containing 4, 8 (4 x 2), and 16 tubes 5/16-in. in diameter and spaced 0.37-in. apart within a 12-in.-ID simulated shipping cast.

The emissivity of untreated 304SS surfaces was determined to be approximately 0.55 by a simple experiment using heat transfer between evacuated concentric tubes.

6.0 WASTE PROCESSING

Test R-36 was the first close-coupled waste evaporator-calciner test to be performed. The feed used was simulated purex waste (40 g/ton of U). There were no additives to the waste to reduce sulfate volatility. The system feed rate was 20.5 liters/hr. The nitrate recovery in the condensate was 103%. The non-condensable off-gas was 0.2 cu ft of gas/liter of feed. The resulting solid had bulk density of 1.3 g/cc. The close-coupled system operated and controlled very satisfactorily.

1.0 FUEL CYCLE DEVELOPMENT

P. A. Haas

Vibratory compaction of high density ThO_2 or ThO_2-UO_2 is a promising method of remote fabrication of fuel elements for recycle of the fertile and fissile materials used in power reactors. The procedures developed in the laboratory for preparation of thoria sols, addition of uranium, drying, and calcining to give high density oxide particles are being scaled up. The present emphasis is on demonstration of procedures and equipment which would be applicable to Th-U-233 fuel element fabrication at a level of about 50 kg/week of oxides.

1.1 Thorium Nitrate Steam Stripping Studies - J. W. Snider, R. D. Arthur

Ten denitration runs were made in the agitated trough calciner with conditions intended to produce relatively undispersable, low nitrate products. This material is needed as feed for the planned dispersion-drying-calcining studies. The product of run 18 showed less than 2% dispersion during agitation of a 2 m slurry in water at 80°C for one hour. Five additional runs were made with identical conditions to produce 15 kg of product for drying and firing studies (Table 1.1). Analysis of these products is shown in Table 1.2, Runs 18 through 23.

The operating conditions to produce this product consisted of operating for 3 hrs at a steam flow rate of 7.8 lb/hr. The steam temperature was held at 425°C for 2 hrs, then increased to 450°C for the final hour. The skin temperature was held at 400°C for 1 hr and increased to 425°C for the final 2 hrs.

The products of the four initial runs (14, 15, 16, 17) intended to prepare low nitrate materials did not have the properties expected. For run 14, the steam temperature was increased to 425°C from the previous 400°C level and the trough skin temperature was increased after 1 hr of operation from 375°C to 425°C. The run time was extended from 2 hrs to 2-1/2 hrs. The material quite unexpectedly (for analysis see Table 1.2) produced a stable gel after agitating for 1 hr at 80°C in approximately a 3 m concentration. Gelation previously occurred at high nitrogen concentrations, not at the low concentration found in this material. This gel was stable enough to retain its surface shape for 3 days while inclined at ~30 degrees. Nitric acid was added to break the gel for material transfer.

Run 15 was made using an air-steam mixture at 425°C. The product formed a thixotropic sol upon water addition.

Runs 16 and 17 were made again as an attempt to produce material too low in nitrate for dispersion. Run 16 was made with the skin temperature at 400°C and the steam at 360°C while run 17 was made with the skin temperature unchanged but with the steam temperature increased to 450°C. The product from run 17 is approximately twice as high in nitrate as that from run 16 (Table 1.2).

Table 1.1. Operating Conditions for Denitration of $Th(NO_3)_4 \cdot 5H_2O$ in the Agitated Trough Calciner

Run Number	14	15	16	17	18	19	20	21	22	23
Steam Temperature, °C	425	425	360	450	(425-450)[a]	(425-450)[a]	(425-450)[a]	(425-450)[a]	(425-450)[a]	(425-450)[a]
Steam Rate, lb/hr	7.8	7.8[b]	6.6	11.8	7.8	7.8	7.8	7.8	7.8	7.8
Skin Temperature, °C	(375-425)[c]	400	400	400	(400-425)[d]	(400-425)[d]	(400-425)[d]	(400-425)[d]	(400-425)[d]	(400-425)[d]
Time, min	150	150	180	120	180	180	180	180	180	180

[a] 425°C for 2 hrs, then 450°C for 1 hr

[b] Air added with the steam (~20 vol % air)

[c] 375°C for 1 hr, then 425°C for 1.5 hrs

[d] 400°C for 1 hr, then 425°C for 2 hrs

Table 1.2. Analysis of Product from Steam Denitrated $Th(NO_3)_4 \cdot 5H_2O$

Run Number	14	15	16	17	18	19	20	21	22	23
LOI-1000°C, %	2.67	4.82	3.77	5.64	2.50	2.18	3.46	3.66	3.84	4.40
% Total N	0.55	0.77	0.55	1.02	0.28	0.42	0.29	0.28	0.26	0.26
Fe, ppm	15	15	25	50	85	60	40	30	<25	85
Crystallite Size, A°	62	54	60	62	61	65	61	58	65	70
N/Th	0.108	0.152	0.107	0.205	0.054	0.082	0.057	0.055	0.051	0.051

1.2 Sol Dispersion, Drying, and Calcining - C. C. Haws, Jr., F. N. McLain

Product from the trough calciner steam stripping studies was used to study the effects of varying conditions for dispersion into a sol, drying, and calcining. The density of the final product particles seemed to increase as the nitrogen content of the sol decreased. Dispersion into sols and the sol properties showed anomalous behavior with respect to the N/Th ratios. All of the sols prepared gave products which could be vibratorily compacted to 8.4 or 8.5 g/cc in 5/16-in.-dia tubes.

The highest particle densities and the highest vibrated densities were obtained from trough calciner products (Batch Nos. 4 and 5) low in nitrogen. The low nitrogen content appears consistent with the small amount (~5 wt %) of these materials which could disperse in 80°C water. After decanting off the dispersed phase and drying the residual powder from these batches, the dried powder dispersed readily with additional nitric acid. A small sample of the dried powder (from Batch 5) was withheld from this nitric acid dispersion and stored for about 2 weeks. Sixty-eight per cent of this sample (N/Th = 0.096) could then be dispersed in 80°C water. This indicates that absolute nitrogen content alone is not a sufficient criteria for whether dispersion will occur.

The advantages of carrying a dried sol to a high drying temperature (150°C), re-dispersing the solids and then processing them through the regular procedure were investigated. Duplicate samples were processed from four calciner batches, i.e., 7, 8, 9 and 10. One series of samples (7A, 8A, 9A and 10A) followed the standard procedure, while the other (B Series) was dried and then re-dispersed before passing through the standard procedure. There was no detectable difference between the sample pairs with respect to density or vibratory compaction density. The re-dispersed samples, however, yielded a larger percentage of the desirable large (+16 mesh) particles in all cases. This factor will become important when the recycle of excess fines is studied.

An increase in vibratory compaction density is obtained by tumbling the 10/16 fraction of the sintered product (Table 1.3). None of the samples vibrated, beginning with sample 7A, showed satisfactory packing. Tumbling allowed an increase in the packed density in all cases to the desired minimum of 85%. In 1/2-in. tubes a composite sample made up of all of samples 7, 8, 9 and 10 (before ball milling) achieved a density of 85.3%. This latter fact shows that some bridging occurred in the small 5/16-in. tubes.

The product of run 18 was treated with hot water to test its dispersion characteristics, and then allowed to settle. Three-fourths of one per cent of the solids dispersed in 80°C water. Four distinct layers were observed after completion of the settling. A clear water layer was on top, followed successively by a sol layer, a flocculated layer and a sedimentary layer. A sample of each layer was taken and the quantity of each layer was measured. The results of this sampling-measuring procedure are given in Table 1.4. It is noted that some 1% of thoria, i.e., all layers other than the sediment, has 2-1/2% of the total nitrogen. The N/Th ratio of the upper two layers is extremely high, possibly indicating nitrogen "free" of the thoria. As flocs are usually encountered above N/Th = 0.3, this is an unusually high value

Table 1.3. Results of Dispersion and Firing Tests

Batch No.	N/Th Atomic Ratio	Screen Analysis (wt %) +16	+100	-100	Toluene Density g/cc	Vibratory Compaction Density g/cc
4	-	-	-	-	9.83	8.4[a]
5	-	-	-	-	9.88	8.4[a]
7A	0.193	68	31.3	0.7	9.78	~8.0[a]
7B		77.2	22.4	0.4	9.77	8.53[b]
8A	0.242	83.5	16.1	0.4	9.77	~8.0[a]
8B		87.0	12.3	0.7	9.75	8.53[b]
9A	0.172	71.7	28.0	0.3	9.76	~8.0[a]
9B		83.6	15.7	0.7	9.73	8.53[b]
10A	0.187	78.3	21.4	0.3	9.80	~8.0[a]
10B		84.2	14.6	1.2	9.72	8.53[b]
7910	0.178	75.2	>99	-	9.81	8.54[b]

[a] 5/16-in. tube

[b] 5/16-in. tube; 10/16 fraction tumbled

Table 1.4. Nitrogen-Thorium Balance for Four Layered Sample

Layer Description	Nitrogen Present g	Thorium Present g	N/Th Atomic Ratio
Water, clear	0.09	0.124	12.5
Sol	0.47	1.975	3.96
Flocculated	0.06	9.86	0.106
Sedimentary	1.14	1264	0.018
Total	1.76	1276	

to obtain a stable sol. The floc which was obtained is about the minimum N/Th ratio at which sols are obtained. The sedimentary layer could not be expected to disperse at a N/Th ratio as low as that given; so its behavior is considered normal.

The above results further illustrate the conclusion that, while the presence of nitrogen is a necessary condition to obtaining dispersion, its concentration within specific limits per se is not a sufficient condition to obtaining a predictable result.

2.0 HR THORIA BLANKET STUDIES

P. A. Haas

Engineering assistance and development are being supplied for the irradiation of thoria or thoria-urania slurries or pellets as fabricated for reactor blankets. The principal objective is to study the mechanisms which cause particle degradation during irradiation of the oxide slurries or pellets in water.

2.1 HR Irradiation Engineering - S. D. Clinton

Seven capsules were loaded with oxides, welded, inspected, and scheduled for insertion into the LITR on May 2, 1961. The oxide preparations are as follows: sixteen ThO_2-UO_2 pellets (2 wt % fully-enriched UO_2), sixteen P-82 ThO_2 pellets, five g of arc-fused ThO_2 (10-12 mesh), five g of gel ThO_2 (10-12 mesh), and two g of classified DT-22 ThO_2-UO_2 powder (0.5 wt % fully-enriched UO_2). A Co wire for monitoring the thermal neutron flux and a 0.1 g of silvered Yorkmesh for absorbing iodine-131 were inserted in each capsule. The maximum temperature in the experiment should occur at the center of the ThO_2-UO_2 pellets. At a thermal neutron flux of 2×10^{13} and with He in the capsule, the calculated maximum temperature is 275°C. The thermal gradient (center to surface) within a ThO_2-UO_2 pellet is expected to be approximately 600°C/in. The maximum temperatures in the pure ThO_2 samples should not exceed 100 to 150°C. Since the initial "dry irradiation" is scheduled for only four weeks; the ThO_2 preparations will be exposed to relatively few fission fragments due to the 27 day half-life of Pa-233.

A 347-SS autoclave (Dwg. C-34593) was designed and fabricated for irradiating multiple samples of "wet ThO_2" in the C-43 air-cooled facility of the LITR. The autoclave, which is sealed at one end by a threaded fitting, has a cavity dimension of 7/8-in.-ID by 7-1/4-in.-long and a wall thickness of 1/16-in. Twenty-four longitudinal, triangular shapped fins were machined into the autoclave bomb increasing the effective heat transfer area by a factor of four. With an autoclave surface temperature of 250°C and an air velocity of 55 ft/sec (38 scfm), approximately 475 watts of gamma and fission heating can be removed from the bomb ($h = 10$ Btu/hr-ft^2-°F). The weight of a loaded autoclave may be as follows: 330 g SS (less than 60 g in the fins); 100 g of ThO_2, and 40 g of D_2O. At a thermal neutron flux of 2×10^{13} in the LITR, gamma heating will contribute 235 watts leaving 240 watts of allowable fission heat. This quantity of fission heat is equivalent to 0.3 wt % U-233 in 100 g of ThO_2 which would be present after five months in the LITR.

An autoclave of the preceeding design is scheduled for reactor insertion on May 23, 1961, and will be loaded with the following: pressed ThO_2 pellets, sol-gel ThO_2 pellets, arc-fused ThO_2 pellets, arc-fused ThO_2 particles (300 to 500 microns), DT-46 ThO_2 slurry, and single crystals of ThO_2 (prepared by fused salt process). The pellet preparations will be contained separately in thin-walled, annular tubes (maximum OD = 11/32-in.), designed to permit thermal convection of D_2O past the pellets; whereas, the slurry or particle-type ThO_2 materials will be enclosed in single, thin-walled tubes. Each sample will be exposed to common gas and liquid phases by sintered stainless steel disks (5 micron mean pore size).

3.0 ION EXCHANGE

J. C. Suddath

3.1 Predictions of Uranyl Sulfate Loading Rates on Chloride Equilibrated Dowex 21K - J. S. Watson

During the past months, considerable data have been obtained and reported which demonstrated that uranyl sulfate loading rates on sulfate equilibrated resin are relatively insentive to the solution uranium and sulfate concentrations over the range of solution concentrations studied. This observation suggested that the loading rates could be predicted by calculating the rate at which a single uranyl sulfate ion would load onto a resin equilibrated with sulfate ions. This was a significant simplification since it assumed that the uranium could be considered to exist as a single specie. Calculations showed that this simplification did allow the loading rates to be predicted reasonably well with only self-diffusion coefficients of the ions involved.

Attempts have now been made to apply this analysis to uranyl sulfate loading rates on chloride equilibrated resin. Here the results have not been so satisfying, but final evaluation of the results will await more data on loading rates from solutions having different uranium and sulfate concentrations. Calculated rates of uranium sulfate loading on chloride equilibrated 960 micron Dowex 21K are shown in Figure 3.1. The data points shown are from a run using a loading solution 0.005 M in uranyl sulfate and 0.025 M in total sulfate (the balance is from sulfuric acid and sodium sulfate). The parameter for each curve, f, is the fraction of the resin capacity occupied by uranium at equilibrium. The upper curve shows the rate predicted by the calculations if a uranium ion (with charge -2) were diffusion into 960 micron resin equilibrated with chloride ions. No free sulfate ions were assumed to take part in the process. Note that the predicted loading rates are higher than those observed experimentally. These are not considered to be the best assumptions to describe the process since the uranyl sulfate complex could not exist in the presence of large quantities of chloride ions if there were no sulfate ions; however, they do present an upper limit on the loading rate. In the experimental cases, significant quantities of sulfate ions are always present. With a loading solution such as that used to obtain Figure 3.1, the resin at equilibrium will have approximately 0.75 of its capacity occupied with the uranyl sulfate complex (assuming the complex carries a charge of -2). Taking this lower uranium loading into account, and assuming the rest of the resin capacity (at equilibrium) occupied with sulfate ions was expected to lower the predicted loading rate, but the degree to which it was lowered came as a surprise (Figure 3.1). The calculated curve was considerably lower than the observed curve. It is difficult to interpret this behavior quantitatively but the data may fall above the lower curve because of either of two reasons, (1) the single uranyl sulfate species which controlled the loading rate on sulfate equilibrated resin does not control the rate on chloride resin (e.g., lower sulfate complexes may be significant), or (2) the assumption that the resin capacity not occupied by uranium is occupied by sulfate ions is not valid. This latter cause appears to be more probable and will be considered first. Some bisulfate ions are always present on the resin when it is loaded from uranyl

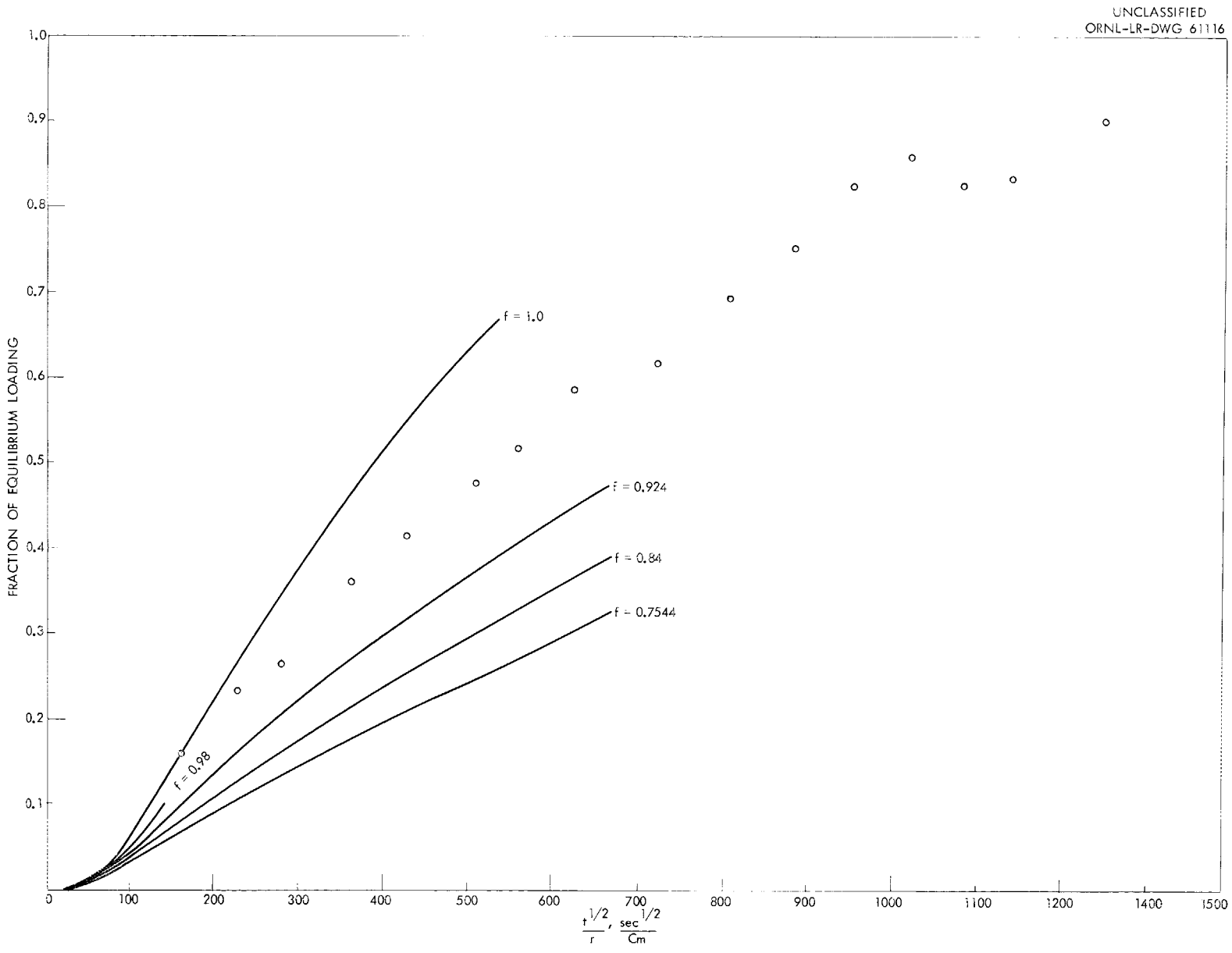

Fig. 3.1. Uranyl sulfate loading rates on chloride equilibrated 960 micron Dowex 21K.

sulfate solutions or acid sulfate solutions. The effects of the bisulfate ion can not be predicted quantitatively with information presently available. Attempts have been made during equilibrium studies to determine the amount of bisulfate ion on the resin by eluting the resin with a neutral chloride or nitrate salt and analyzing for the hydrogen ions present. However, the hydrogen ion concentration in the relatively concentrated eluate is too small to measure accurately although it may represent a significant fraction of the resin capacity.

One method of treatment would be too simply ignore the resin capacity occupied by the bisulfate ion and consider the predicted loading rate of only uranyl sulfate and the sulfate loading on chloride resin where the $SO_4^{=}$ concentrate actually present at equilibrium (rather than sulfate +2 bisulfate) is used. The problem is that the equilibrium sulfate concentration is not known. However, as shown in Figure 3.1, one can fit the experimental data by assuming values for the fraction of available resin capacity (neglecting bisulfate) occupied by uranium at equilibrium. The fact that a value of 0.98 for the fraction fits the data means little since it is an empirical fit. However, these calculations also predict the rate at which chloride leaves the resin as well as the rate at which uranyl sulfate loads the resin. It is interesting to note that the predicted rate at which chloride is being eluted from the resin appears to be essentially the measured rate when the equilibrium loading fraction is assumed to be 0.98 (Figure 3.2).

Currently measurements of uranyl sulfate loading rates are being made with a wide range of solution concentrations. The initial single bead experiments covered a rather wide range of solution concentrations only for loading studies on sulfate equilibrated resin. It has just been shown that variations in the fractions of the resin capacity occupied by uranyl sulfate and sulfate ions at equilibrium should affect the observed loading rates.

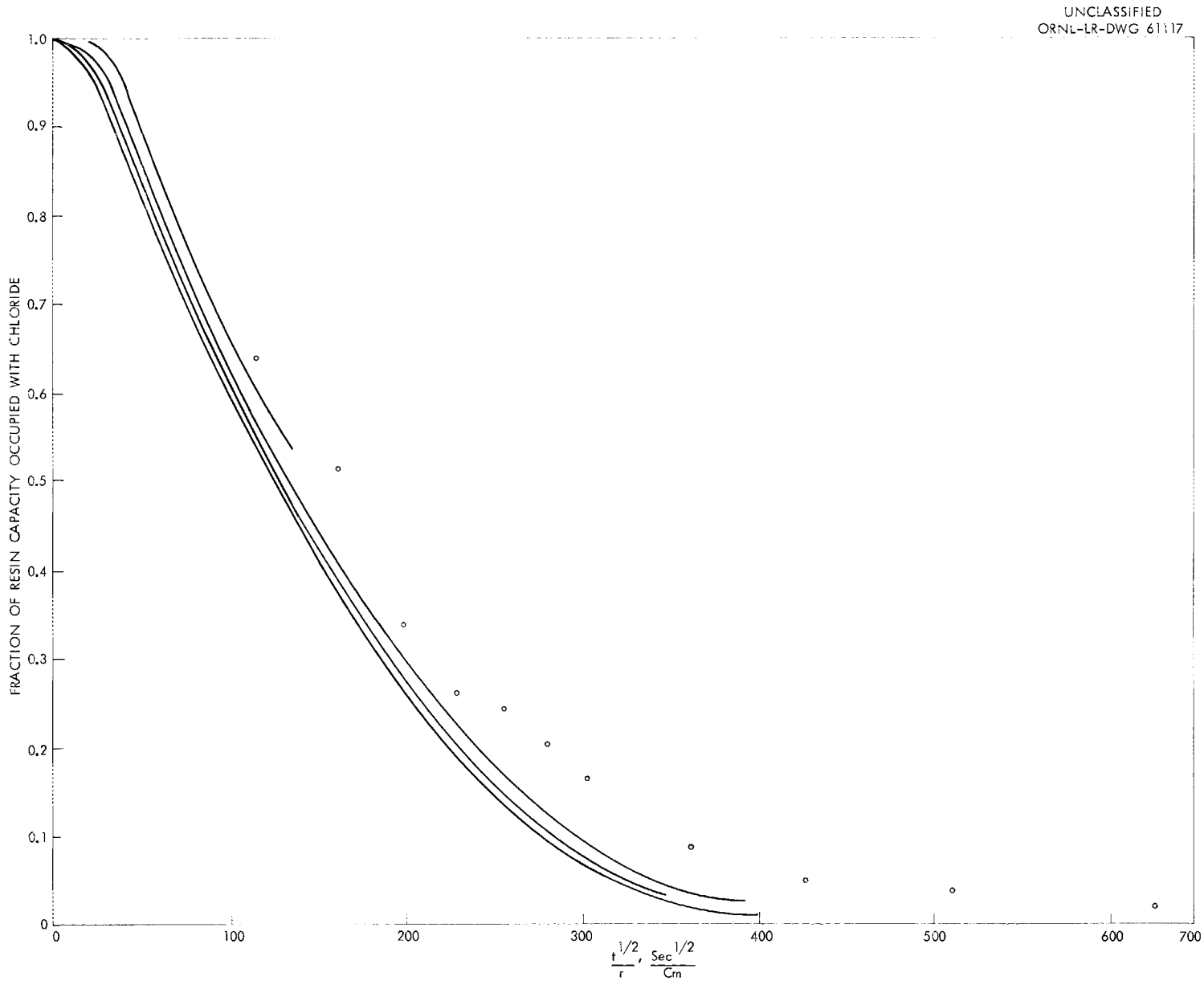

Fig. 3.2. Chloride elution rates from 960 Ø micron Dowex 21K during uranyl sulfate loading.

4.0 POWER REACTOR FUEL PROCESSING

C. D. Watson

4.1 Shearing and Leaching - B. C. Finney

A chop and leach program to determine the economic and technological feasibility of continuously leaching the core material (UO_2 or UO_2-ThO_2) from relatively short sections (1-in. long) of fuel elements produced by shearing is continuing. This processing method enjoys the apparent advantage of recovering fissile and fertile material from spent power reactor fuel elements without dissolution of the inert jacketing material and end adapters. These unfueled portions are stored directly in a minimum volume as solid waste. A "cold" chop-leach complex consisting of a shear, conveyor, leacher, and compactor is being evaluated prior to "hot" runs.

Conveyor. The leacher spiral rotary drum was operated on the test rack independent of the outer shell at a 20 degree angle of inclination and ~2 rpm to determine the reason for the severe backmixing encountered when the leacher was operated as a conveyor. It was found that the backmixing was the result of the open gaps between the flights and the inner cylinder at both the feed and discharge ends of the leacher. The open gaps allowed the chopped sections of stainless steel rods to fall back from one flight to the next.

Modifications to the leacher will be made to eliminate the gaps and further tests will be made to determine the optimum batch size. Previous tests have been made using a 3 liter batch but there is some question as to whether this is the optimum batch size.

Leaching. A total of six glassware leacher model dissolution runs (Run-19 through 24, Table 4.1) using various HNO_3 concentrations and flow rates were made to further investigate the operating characteristics of the 4 stage leacher model.

It was found that 4 M HNO_3 at a HNO_3/UO_2 mole ratio of 4 (37.5 ml/min, Table 4.1) was inadequate to completely dissolve the UO_2 pellets in a 4 hr dissolution time. The run (Run-19) was terminated as the result of a successive stagewise heel buildup.

Complete dissolution of the UO_2 pellets was accomplished when using 5.5 M HNO_3 at a HNO_3/UO_2 mole ratio of 5 (Run-20). A plot of the incremental uranium loading and acidity for nine batch charges of UO_2 pellets is presented in Figure 4.1. Steady-stage operation was attained in 3-4 batches and the composite product (section of curves above line A-B) uranium concentration and acidity was 275-300 g/liter and 2.2 - 2.5 M HNO_3; respectively. It is estimated that there is approximately a 25% increase in the time for complete dissolution when using 5.5 M HNO_3 as the dissolvent as compared to 7 M HNO_3 at comparable operating conditions.

Figure 4.2 is a plot of the incremental uranium loading and acidity for a nine batch dissolution run (Run-21) using 7 M HNO_3 at a HNO_3/UO_2 mole ratio

Table 4.1. Leacher Model Dissolution Data UO_2-HNO_3 System

Pellets: PWR Rejects (0.360-in.-OD x 0.370-in.-long, edges chipped) $\rho \cong 10.1$ g/cc

Run No.	UO_2 Batches Used	Dissolution Time, min	Temp. °C	Dissolvent (HNO_3) M	Dissolvent (HNO_3) Flow Rate ml/min	Dissolvent (HNO_3) Vol liters (total)	UO_2 Pellets Wt Charged g	UO_2 Pellets % Dissolved	Product (Composite) Loading g U/liter	Product (Composite) H^+ M	Product (Composite) Vol liters	Off-gas Nitrogen g-mol	Off-gas % of HNO_3 feed	Acid Consumption g-mol HNO_3 / g-mol UO_2
R-19	1	240	101-103	4	37.5	12.75	600.3	98.3	Run was discontinued because stagewise heel build up was indication that chosen run conditions were inadequate for complete dissolution in 4 hrs.					
	2	240	101-103				602.5	97.6						
	3	240	101-103				603.1	96						
	4	220	101-103				601.7	83.1						
	5	100	101-103				602.1	43.3						
R-20	1	240	100-105	5.5	33.4	16.4	602.0	100	264	2.58	17.1	9.2	10	2.55
	2	240	100-105				600.0	100						
	3	240	100-105				602.2	100						
	4	240	100-105				600.1	99.5						
	5	240	100-105				600.5	99.8						
	6	240	100-105				600.3	100						
	7	130	100-105				604.1	100						
	8	70	100-105				600.9	50.5						
R-21	1	240	103-109	7.0	30.3	18.5	601.2	100	257	4.14	18.5	12.9	10	2.64
	2	240	103-109				600.0	100						
	3	240	103-109				600.3	100						
	4	240	103-109				600.0	100						
	5	240	103-109				600.8	100						
	6	240	103-109				600.6	100						
	7	240	103-109				600.0	100						
	8	240	103-109				600.4	100						
	9	240	103-109				603.6	100						
R-22*	1	160	92-94	7	19.8	3.2	601.5	100	170	5.04	3.17	1.42	6.3	2.64
R-23	1	240	101-108	7	22.9	15.4	600.3	100	297	3.69	16.2	11.8	10.5	2.58
	2	240	101-108				600.5	100						
	3	240	101-108				599.5	100						
	4	240	101-108				600.0	100						
	5	240	101-108				600.0	100						
	6	240	101-108				601.0	100						
	7	240	101-108				601.9	100						
	8	240	101-108				600.3	100						
	9	240	101-108				600.8	100						
R-24**	1	240	101-109	7	26.3	17.6	601.1	100	247	4.18	19.3	11.1	9.0	2.55
	2	240	101-109				601.2	100						
	3	240	101-109				601.3	100						
	4	240	101-109				601.4	100						
	5	240	101-109				601.4	100						
	6	240	101-109				603.5	100						
	7	240	101-109				602.3	100						
	8	240	101-109				597.8	100						
	9	240	101-109				599.8	100						

* Temperature of stage was maintained at ~10°C below boiling to determine effect of lower temperature.
** Crushed UO_2 of following size distribution was used in each stage: 62.5% - 1/4-in. + 4760μ; 22.7% - 4760μ + 1680μ; 11.5% - 1680μ + 297μ; 1.5% - 297μ + 149μ; 1.9% - 149μ.

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Conditions:

5.5 *M* HNO_3 33.4 ml/min
UO_2 pellets (PWR rejects, 0.360 in. O.D. x 0.370 in. long, $\rho \cong 10.1$ gms/cc) ~600 gms/batch
HNO_3/UO_2 mole ratio = 5

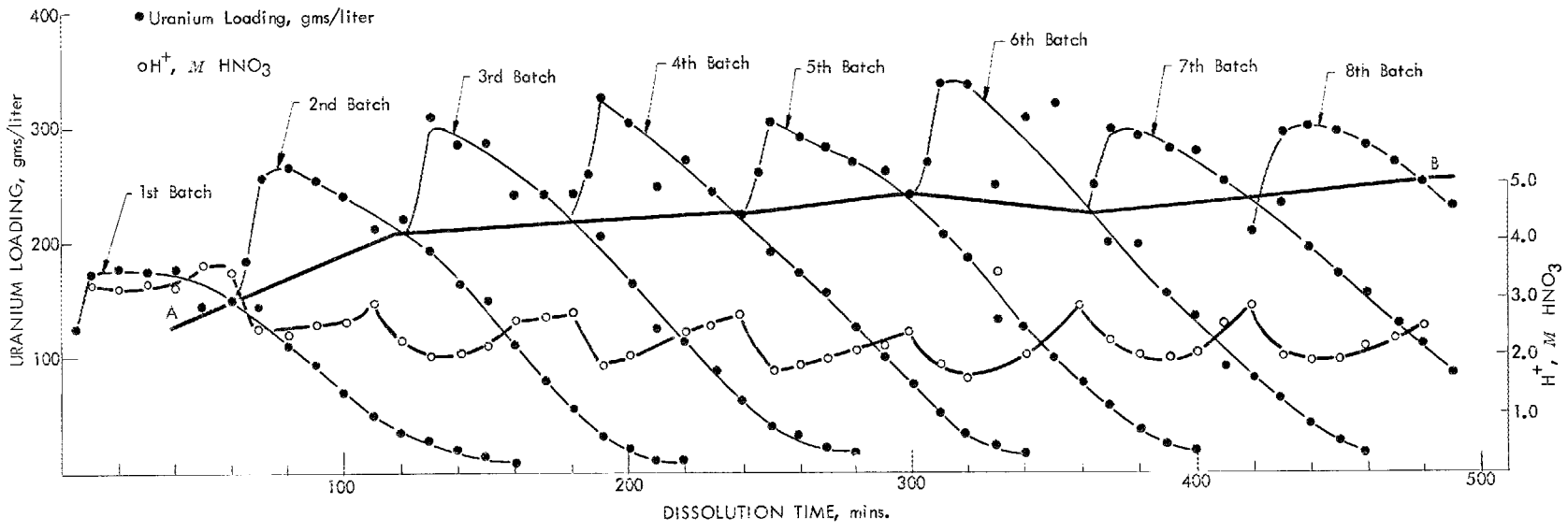

Fig. 4.1. Uranium loading and H^+ as a function of dissolution time for 4 stage leacher model dissolution (Run-20) of eight batches of UO_2 pellets based on a 4 hour dissolution time.

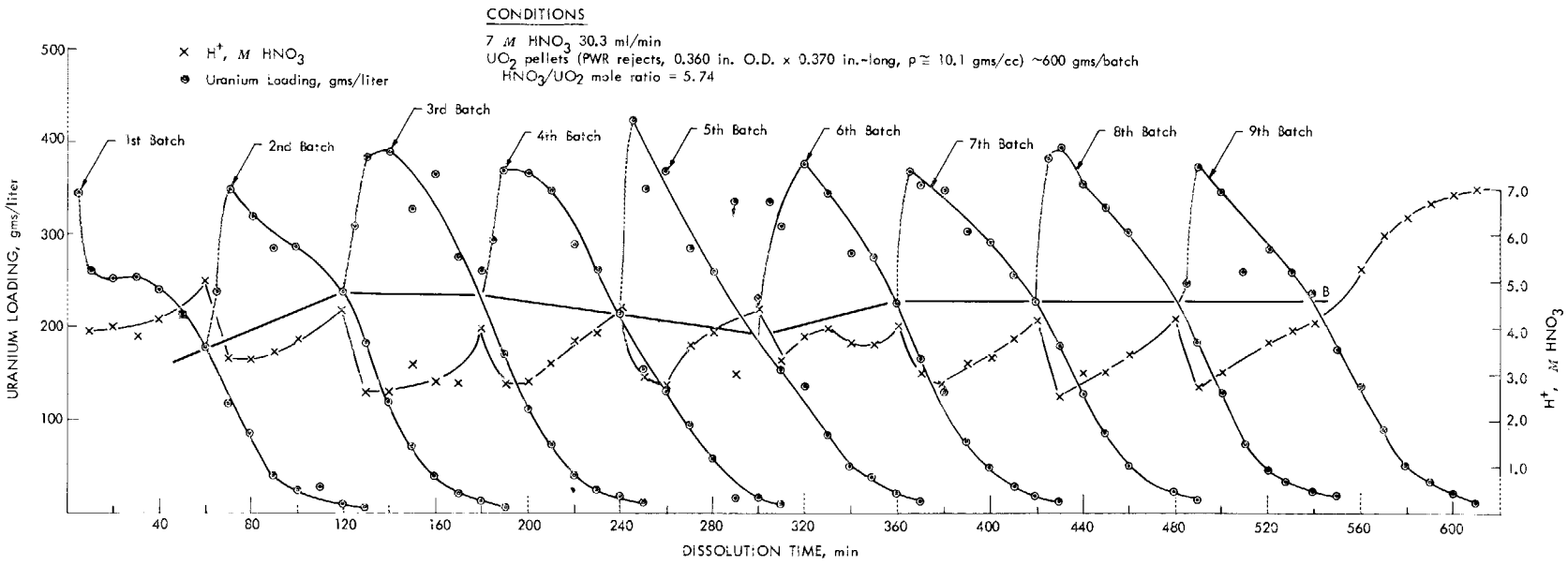

Fig. 4.2. Uranium loading and H^+ as a function of dissolution time for 4 stage leacher model dissolution (Run-21) of 9 batches of UO_2 pellets based on a 4 hour dissolution time.

of 5.74. Again steady state was attained in approximately 3-4 batches. The uranium concentration varied from 215 - 235 g/liter minimum to 375 - 400 g/liter maximum and the acidity varied from a minimum of 2.6 M to 4.4 M HNO_3. The composite product was 300 - 325 g/liter uranium and 3.3 - 3.5 M HNO_3.

A single batch scouting run (Run-22) was made using 7 M HNO_3 at a HNO_3/UO_2 mole ratio of 3.75 to investigate the effect of maintaining the dissolvent temperature approximately 10°C below boiling (~92°C). A comparison of the incremental uranium loading and acidity for Run-22 and Run-17 in which the dissolvent temperature was maintained at boiling (~101°C) is presented in Figure 4.3. Although the effluent uranium concentration was the same at the conclusion of the first hour dissolution, 79.5% of the UO_2 pellets had been dissolved in Run-17 as compared to 66.1% in Run-22.

Run-23 was a nine batch run using 7 M HNO_3 at a HNO_3/UO_2 mole ratio of 4.33 as the dissolvent (Figure 4.4). In comparing Run-23 (Figure 4.4) and Run-21 (Figure 4.2), the lower HNO_3/UO_2 mole ratio of Run-23 resulted in a higher minimum and maximum uranium loading and lower acidity at apparent steady state. The uranium loading varied from 300 - 500 g/liter for Run-23 as compared to ~225 - 375 g/liter for Run-21. The composite product uranium loading and acidity was 415 g/liter and 2.3 M HNO_3 for Run-23 as compared to ~310 g/liter and 3.4 M HNO_3 for Run-21. The effect of a lower HNO_3/UO_2 mole ratio is to produce a product of a higher uranium loading and lower acidity with some increase in dissolution time.

Run-24 was a nine batch run using 7 M HNO_3 at a HNO_3/UO_2 mole ratio of 4.95 (Figure 4.5). Each pot was charged with ~600 g of crushed UO_2 pellets of the following particle size distribution: 62.5 wt % - 1/4 inch + 4760μ; 22.7 wt % - 4760μ + 1680μ; 11.5% - 1680μ + 297μ; 1.5 wt % - 297μ + 149μ; 1.9 wt % - 149μ. The number of batches required to attain an apparent steady-state operation is not as clearly defined when dissolving crushed UO_2 pellets as compared to whole UO_2 pellets as evident by the continuing change in line AB. The maximum uranium loading was fairly constant at ~400 g/liter whereas there appears to be a decreasing trend in the minimum uranium loading and the acidity varied from ~2 M HNO_3 to ~4.6 M HNO_3. The composite product was ~320 g/liter uranium and ~3.1 M HNO_3.

4.2 U-C Fuel Processing - B. A. Hannaford

Proposed reactor fuels of the uranium-graphite type contain particulate compounds (UO_2, UO_2-ThO_2, UC_2, UC_2-ThC_2) dispersed in a graphite matrix. Fuel particles may be uncoated or coated with a refractory (Al_2O_3, pyrolytic carbon); fuel elements may be coated with SiC or associated with unfueled graphite.

As the basis for a preliminary estimate of the cost of processing a uranium-graphite fuel, a continuously-loaded 350 MWT Pebble Bed Reactor[1] was chosen. Processing load, assuming plant operation 300 days per year,

[1] NYO-2373, Progress Report, Pebble Bed Reactor Program.

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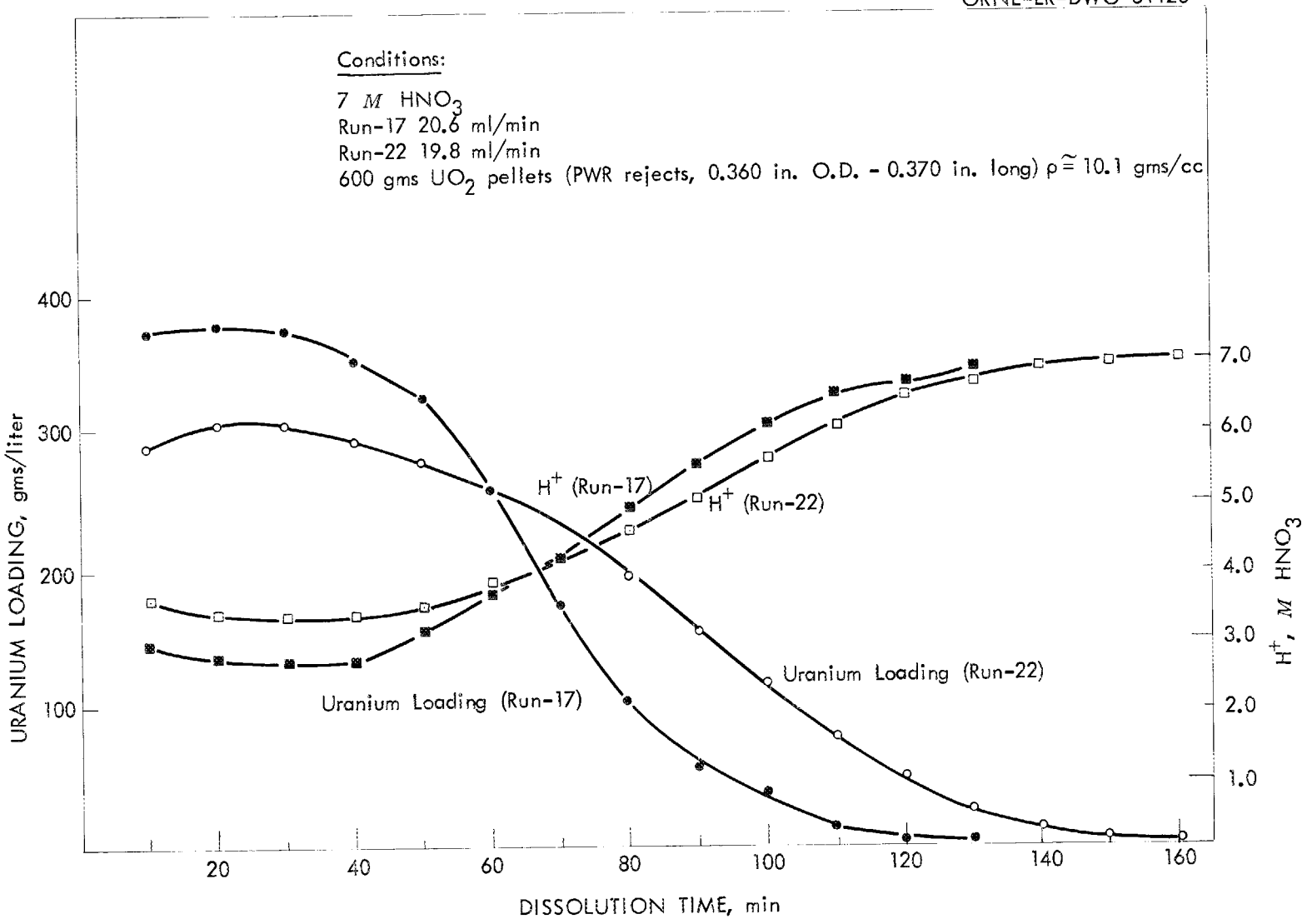

Fig. 4.3. Comparison of uranium loading and H^+ for four stage leacher model dissolution of single batch of UO_2 pellets when operating at boiling (~ 101°C, Run-17) and approximately 10°C below boiling (92°C, Run-22).

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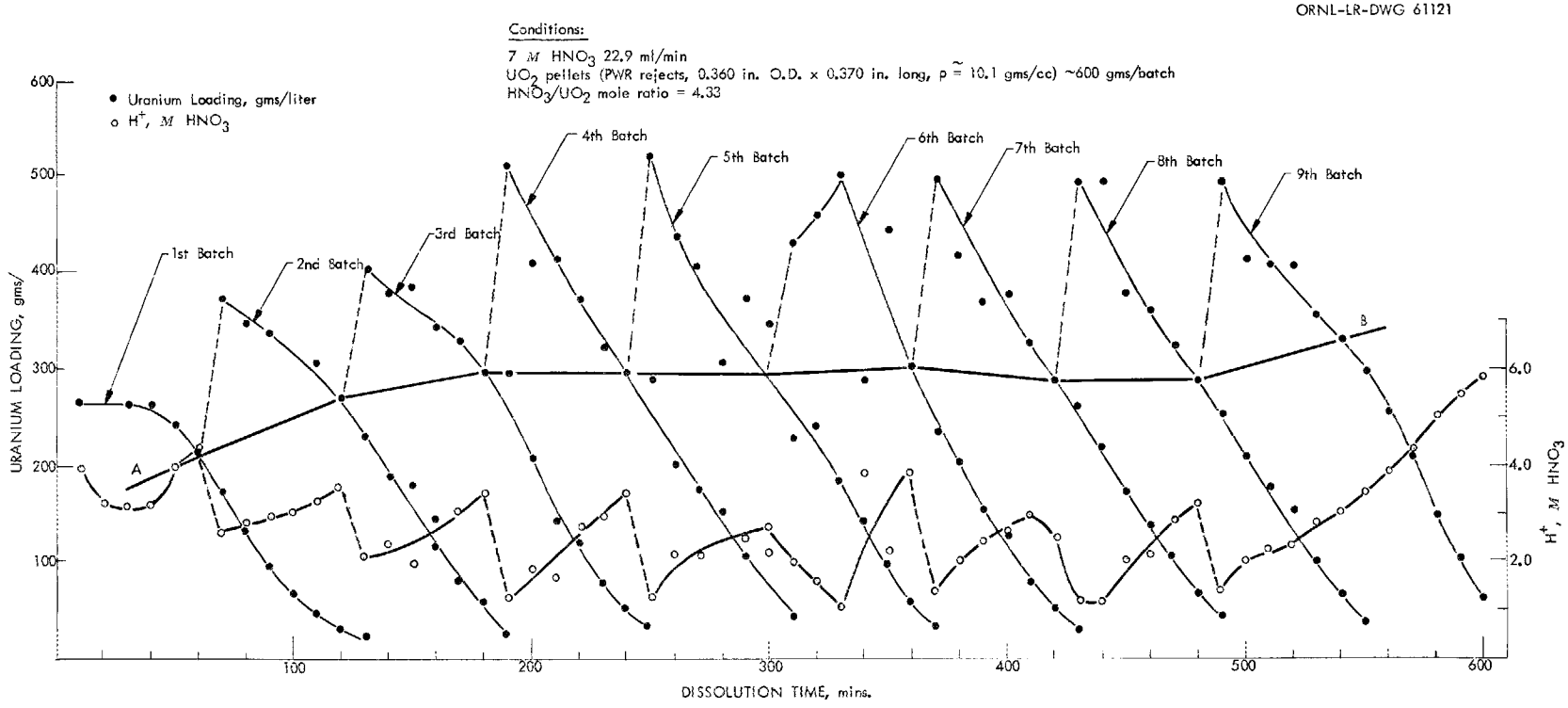

Fig. 4.4. Uranium loading and H^+ as a function of dissolution time for 4 stage leacher model dissolution (Run-23) of nine batches of UO_2 pellets based on a 4 hour dissolution time.

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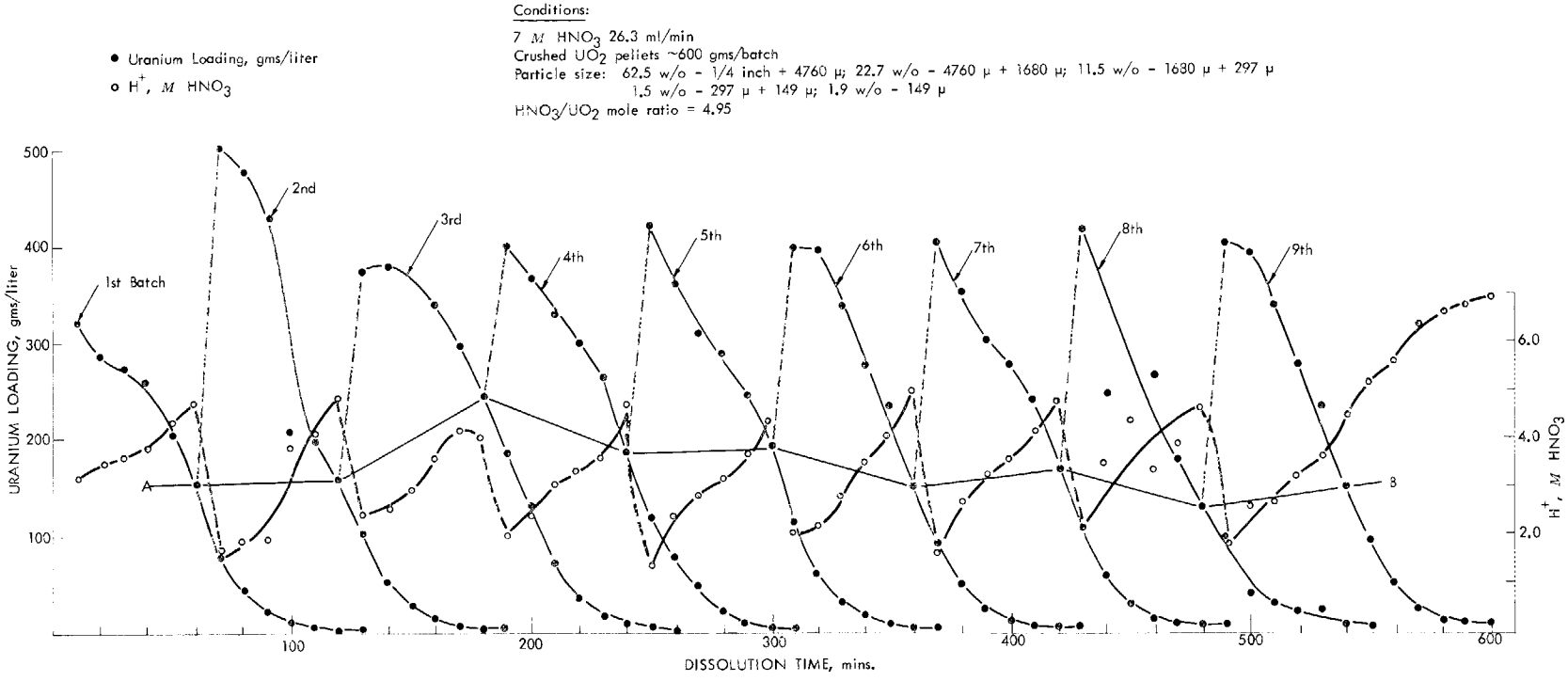

Fig. 4.5. Uranium loading and H^+ as a function of dissolution time for 4 stage leacher model dissolution (Run-24) of nine batches of crushed UO_2 pellets based on a 4 hour dissolution time.

would be 100 kg/day. Fuel was assumed to be UC_2-ThC_2 particles coated with pyrolytic carbon, dispersed in 1-1/2-in. spheres covered with Si-SiC.

The low permeability of disintegrated 3% U-graphite fuel to the flow of water[2] (or acid) indicates that the time required to separate the acid and water from the reference (PBR) fuel will determine the total cycle time, assuming that the irradiated reference fuel behaves in the same way as that used in laboratory tests. Leaching experiments on the 3% U fuel showed that extended leaching with a single batch of acid was less effective than several successive leaches covering the same total time.[3] Both these factors - low permeability and the advantage of countercurrent extraction - suggest that continuous flow of solution is desirable.

On the basis of many assumptions, a critically-safe slab dissolver was sized, having a thickness of 4-in., width of ~24-in., and height of ~15 ft. The assumptions were:

1. Mass of fuel = 100 kg
2. Volume of disintegrated fuel = ~150 liter
3. Pore volume = ~90 liter
4. Volume of leach and wash required = ~420 liter
5. Permeability = ~60 gal $ft^{-2}hr^{-1}$ per ft thickness
6. Dissolver Cycle
   a. 1.0 hr Pour new sand filter; add 60°C HNO_3
   b. 0.5 hr Crack and load fuel
   c. 2.0 hr Soak time
   d. 15.8 hr Leach with continuous flow of acid
   e. 4.2 hr Wash with continuous flow of water
   f. 0.5 hr Transfer slurry waste of sand, graphite, Si-SiC

Additional experimental data are required for a fuel similar to the chosen reference fuel in order to determine a more reliable value for the volume of acid and water required for a 1.0% and 0.1% U loss.

The possibility of a spontaneous explosion of graphite and fuming HNO_3 has been raised from time to time. An empirical test of this possibility gave negative results. A 100 cc mixture of acid-disintegrated U-graphite and fresh 90% HNO_3 failed to detonate when primed by a No. 6 cap and a 5 g PETN booster. This conclusion was based on a comparison of the sound and crater size of the sample with a blank (using water instead of HNO_3) and of an equal volume of 40% extra dynamite.

4.3 Modified Zirflex - F. G. Kitts

Modified Zirflex denotes a process for the recovery of uranium from U-Zr-Sn fuels by batchwise dissolution in NH_4F-NH_4NO_3-H_2O_2 solutions. During dissolution a small, continuous addition of hydrogen peroxide is made to oxidize U^{IV} to the more soluble U^{VI}. Such a process is desirable for processing zirconium fuels containing higher per centages of U

[2] Unit Operations Section Monthly Report, February 1961.

[3] Chemical Development Section B Monthly Progress Report, April, 1961.

(up to 10%) without the intermediate precipitation of UF_4 which would occur if no oxidant were added. Dissolutions of unirradiated zirconium fuels are being carried out both on a laboratory scale and in engineering-scale equipment.

Run CZr-4 was made in the engineering-scale equipment using dissolvent initially 6.65 M NH_4F-0.67 M NH_4NO_3-0.01 M H_2O_2 (Table 4.2). The unoxidized PWR-1 prototype weighing 1738 g was 98.2% dissolved (portions of the thicker, inert Zr-2 side plates remained) in 4 hrs of refluxing. Although 140% of the NO_3^- required to oxidize the H_2 to NH_3 was present, the off-gas after HNO_3 scrubbing (total volume only 0.94 ft^3 at 1 atm and 78°F) contained 27 - 42% hydrogen. Ammonia evolution was 4.86 moles/mole Zr dissolved. The off-gas was sampled by flowing the entire stream through the sampler for the period indicated. Off-gas data are shown in Table 4.3. The N_2/O_2 ratio of ~4 in sample No. 2 suggests air contamination but the ratio of 2.7 in sample No. 1 indicates that some oxygen was evolved in the dissolution.

Table 4.3. Off-gas Data for Run CZr-4

Sample No.	Volume Passed (ft^3)	% of Dissolution Time	Composition (%)		
			H_2	O_2	N_2
1	0.32	9 - 25	42	14	38
2	0.12	25 - 52	27	14	54

Before run CZr-4 was made the equipment had been modified by the addition of a sight glass in the top of the dissolver, for observing foaming characteristics, and a sampler and rotameter in the line returning overhead condensate to the dissolver. In this run a boil-up of 0.07 cc/cm^2-min (based on initial fuel surface) was sustained by external heat; this was more than doubled at the peak dissolution rate by heat of reaction; no stable foam was observed. The condensate (boil-up) rate and NH_4OH concentration in the condensate are plotted in Figure 4.6. The shapes of the curves are as would be predicted for unoxided fuel, tailing off from the initial high boil-up and NH_4OH concentration. Ammonia and scrubber off-gas evolution behaved as described for a previous run with unoxided fuel (Unit Operations Monthly Progress Report, March 1961).

The dissolution product from run CZr-4 was stabilized with thirteen different combinations of HNO_3-$Al(NO_3)_3$ to produce solutions for corrosion and stability tests. Two levels of nitric acid (0.75 and 1.5 M) and three levels of $Al(NO_3)_3$ (0.6, 0.8 and 1.0 M) were evaluated with variable Zr concentrations from 0.36 - 0.58 M at a constant F/Zr ratio of 6.8. Table 4.4 shows approximate compositions and relative fluoride complexing for these solutions. No precipitates formed in any of the solution in the first 24 hrs but after 16 days a coarse, white, crystalline precipitate was observed in solutions No. 1 and 8; these contained the highest Zr concentrations and the lowest Al concentrations at both acid levels. All the other compositions were stable after 16 days at room temperature.

Table 4.2. Data for Modified Zirflex Runs

Run No.	Dissolvent Vol ℓ	Dissolvent NH_4F M	Dissolvent NH_4NO_3 M	Dissolvent H_2O_2 M	Fuel Specimen Type	Fuel Specimen Wt, g	Fuel Specimen Diss. %	H_2O_2[a] Add. Rate moles/cm²-min	Diss. Time, hrs
CZr-4	18.9	6.65	0.67	0.01	PWR-1	1738	98.2	0.4×10^{-5}	4.0
MZr-11	0.220	6.6	0.32	0.01	TRIGA	17.158	100	0.6×10^{-5}	2.5
MZr-12	0.280	6.6	0.32	0.01	TRIGA	27.512	94.1	0.6×10^{-5}	3.5
MZr-13	0.260	6.54	0.00	0.01	PWR-1	23.973	95.1	0.4×10^{-5}	4.0
MZr-14	0.290	6.5	0.00	0.01	TRIGA	27.063	94.6	0.5×10^{-5}	3.25
MZr-15	0.285	6.65	0.67	0.01	PWR-1	26.764	96.3	0.5×10^{-5}	3.0
MZr-16	0.316	6.79	0.00	0.01	8%U-Zr	27.136	100	0.6×10^{-5}	3.7

Run No.	Stabilizer Vol, cc	Stabilizer HNO_3 M	Stabilizer $Al(NO_3)_3$ M	Solvent Extraction Feed[d] Vol, cc	Zr g/ℓ	U g/ℓ	Sn g/ℓ	F M	H_2O_2 M	F^-/U	U-Zr-Sn Matl. Bal., %
CZr-4	Variable			Corrosion Test Solutions							-
MZr-11	260	1.8	1.8	473	33.3	2.6	0.04	2.94	0.004	70	99.0
MZr-12	330	1.8	1.8	602	38.3	2.47[b]	0.02	2.93	0.007	40	95.0
MZr-13	350	1.8	1.8	627	33.1	0.94	0.47	2.24	0.002	NL[c]	95.2
MZr-14	360	1.8	1.8	660	34.5	2.72	-	2.70	0.001	38	96.1
MZr-15	350	1.8	1.8	645	38.1	0.95	0.50	2.83	0.001	NL[c]	99.1
MZr-16	277[e]	-	-	608	35.5	2.12	0.02	3.10	0.002	(55)[f]	84.3

[a]As 3% solution (~0.9 M)

[b]Also a small amount of UF_4 ppt

[c]Not limiting at low U per centages

[d]Also ~1 M HNO_3, ~1 M $Al(NO_3)_3$

[e]H_2O

[f]Calculated (some precipitation); in supernate $F^-/U = 86$

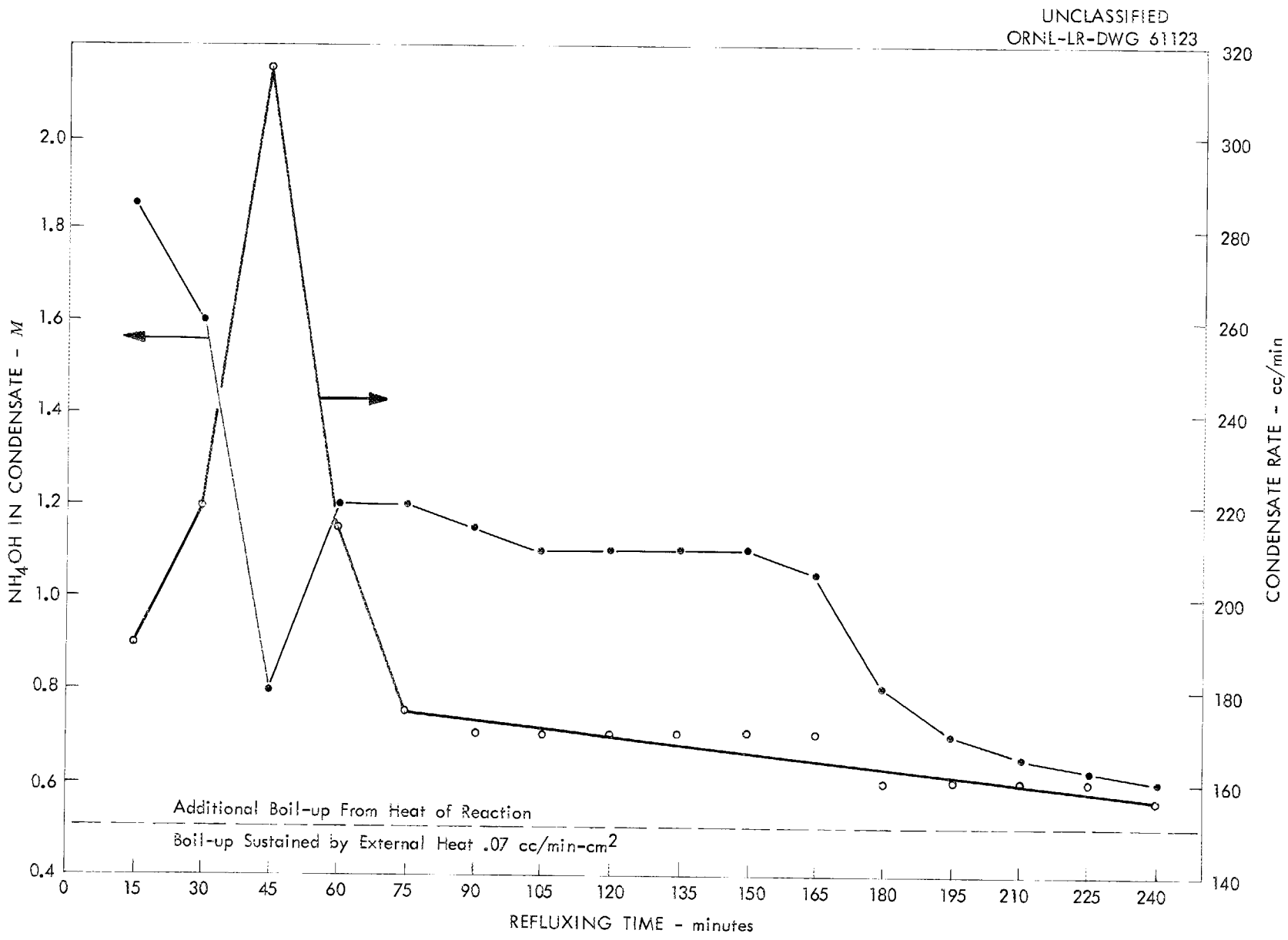

Fig. 4.6. Condensate rate and NH_4OH concentration as functions of refluxing time.

Table 4.4. Compositions and Relative Complexing of Solutions

Solution No.	HNO_3 M	Al M	Zr M	F^- M	C 4Zr + Al	C/F^-	X $F^- = 4Zr + XAl$
1	0.75	0.6	0.58	3.9	2.91	0.74	2.70
2	0.75	0.6	0.49	3.3	2.56	0.77	2.28
3	0.75	0.6	0.40	2.7	2.20	0.81	1.87
4	0.75	0.8	0.49	3.3	2.76	0.83	1.71
5	0.75	0.8	0.40	2.7	2.40	0.88	1.40
6	0.75	1.0	0.40	2.7	2.60	0.96	1.12
7	0.75	1.0	0.36	2.4	2.44	1.00	1.00
8	1.5	0.6	0.54	3.6	2.74	0.75	2.50
9	1.5	0.6	0.45	3.0	2.39	0.79	2.09
10	1.5	0.6	0.36	2.4	2.04	0.84	1.67
11	1.5	0.8	0.45	3.0	2.59	0.85	1.56
12	1.5	0.8	0.36	2.4	2.24	0.92	1.25
13	1.5	1.0	0.36	2.4	2.44	1.00	1.00

Six runs were made in the 1 in. dia recirculating batch dissolver (Table 4.2). Runs MZr-11 and 12 made with 8% U - Zr H alloy showed that dissolution could be accomplished to free fluoride to uranium (F^-/U) ratios of < 70 with a probable lower limit of ~40. Run 13 showed that dissolution rates were comparable with no NO_3^- present; more foaming was evident due to the increased H_2 evolution. Run 14 showed the same H_2O_2 rate would oxidize U when present in higher per centages. Run 16 showed very little difference between 8% U-Zr and 8% U-ZrH. Slightly higher dissolution rates were observed in run 15 with less foaming due to a smaller volume of H_2 evolved.

5.0 REACTOR EVALUATION STUDIES

J. C. Suddath

5.1 Heat Transfer from Spent Fuels during Shipping - J. S. Watson

Experimental determinations of spent reactor fuel temperatures in simulated shipping casts have been started. Measurements have been made with 5/16-in. 304 SS tubes spaced 0.37-in. apart and supported horizontally within a 12-in.-ID SS container as described in the March Unit Operations Monthly Progress Report. Bundles have been assembled containing 4, 8 (4 x 2), and 16 tubes, and heat generation rates up to 0.28 watts/cm-tube employed. The 1/4-in. thick SS container was insulated for most of the runs, but two different insulation thicknesses were employed with the 16 tube bundle to simulate different carrier thicknesses. The temperature rises obtained have corresponded to overall heat transfer coefficients of up to 2 Btu/hr-°F. An overall value such as this is not alone very informative and does not aid much in predicting temperature rises from other tubes or other bundles. Efforts are being made to separate the effects of the various methods of heat transfer and obtain reasonably reliable correlations.

In these experiments the apparatus described in the March Unit Operations Monthly Progress Report has generally performed well, but some modifications are warranted. Angular temperature variations are a problem in the simulated cast. At the top of the cast where most of the convection heat is carried, the surface temperature is considerably higher. Although the relatively thin (1/4-in.) SS shell and asbestos insulation covering does adequately simulate the radial resistanct to heat conduction, it does not simulate the angular or axial heat conduction of several inches of lead (although with a relatively long apparatus axial gradiants are no problem). In an actual cast one would not expect as much angular temperature variation.

Since approximately one-third of the heat transferred in some of the early experiments was by radiation, a reasonably accurate value of the emissivity for the tubes and cast wall was needed. The emissivity of SS is known to vary between 0.18 and 0.8 depending upon the degree of polish or weathering. Since a more accurate value than this was needed, a simple experiment was made to measure the emissivity of new 304 SS tubing without polish or weathering. Two foot lengths of 1-in. and 5/16-in. tubing were assembled concentrically with transite plugs at their ends. The center tube (5/16-in.) was heated at a known rate, and temperatures of both tubes were measured. The configuration factor for this geometry is unity so the emissivity can be readily calculated from the heat flux and surface temperatures. A near vacuum was pulled in the annular space to reduce the effects of conduction and convection. The results were not consistent until the pressure in the annular space was reduced to below 200 microns of Hg. Below this value there was no apparent variation in the measured value of emissivity with pressure. The average value obtained under these conditions was approximately 0.55. This is considered a reasonable value for these tubes.

6.0 WASTE PROCESSING

J. C. Suddath

The purpose of the waste processing studies is to procure design information necessary for the design of waste calciner pilot plant. This report will describe an evaporator-calciner test (R-36), which was the first combined evaporator-calciner test.

6.1 Evaporator-Calciner Test R-36 - C. W. Hancher

The purpose of evaporator-calciner test R-36 (E-C, R-36) was to demonstrate the operability of a close-coupled waste evaporator and calciner, Figure 6.1. This system was described in the Unit Operations Monthly Progress Report, March 1961. In brief, the evaporator (~25 liter capacity) prepares feed for the ~60 liter calciner. The condensate from the calciner returns to the evaporator, where it is steam stripped by water added to the evaporator. Acid is removed from the evaporator to keep the acid concentration below 6 molar to reduce Ru volatility when the system is used on actual high level waste. The evaporator condensate goes to condensate catch tank. The entire system operates under a reduced atmosphere of about minus one pound, by employing a water jet which is operated by a closed loop filled with water and pumped with a turbine pump (10 GPM at 50 psig).

The end result of the test (E-C, R-36) was to produce a calciner pot of solid purex waste and to treat the calciner off-gas with the evaporator in a controlled manner.

The feed used was simulated 1WW waste (40 gal/ton of U)(Table 6.1) without additives to reduce the sulfate volatility during the calcination step. Calcium or Mg may be used to decrease SO_4 volatility. There was no tendency of this feed to foam at any time during this test. The test operated 28 hours, 22 hours to fill the calciner, and 6 hours more to finish the calcination (Table 6.2). The calcination step was stopped when all of the thermocouples in the calcining solid were above 850°C except the top two which were 620°C and 755°C. The average feed rate for the test was 20.5 liter/hour (Table 6.3). The bulk density of the calciner solid was 1.29 g/cc.

Calciner Operation. The calciner pot used was 84-in. long x 8-in.-dia equipped with 18 thermocouples. This is the "standard" calciner pot and described in detail in the Unit Operations Monthly Progress Report, September 1960. This calciner pot was equipped with two liquid level probes in case one plugged. Four hours after the test started the calciner liquid-level probe plugged showing a false high level. The probe was blown out with water, but plugged again only after 10 minutes of operation. The purge air rate was 0.6 CFH. After the probe plugged the second time the water clean-out line was left on at 25 cc/min rate for the remainder of the test. The probe did not plug again until the calciner was full of solid near the end of the test. Outside of two times the liquid level probe plugged the calciner liquid level controlled very good, Table 6.4.

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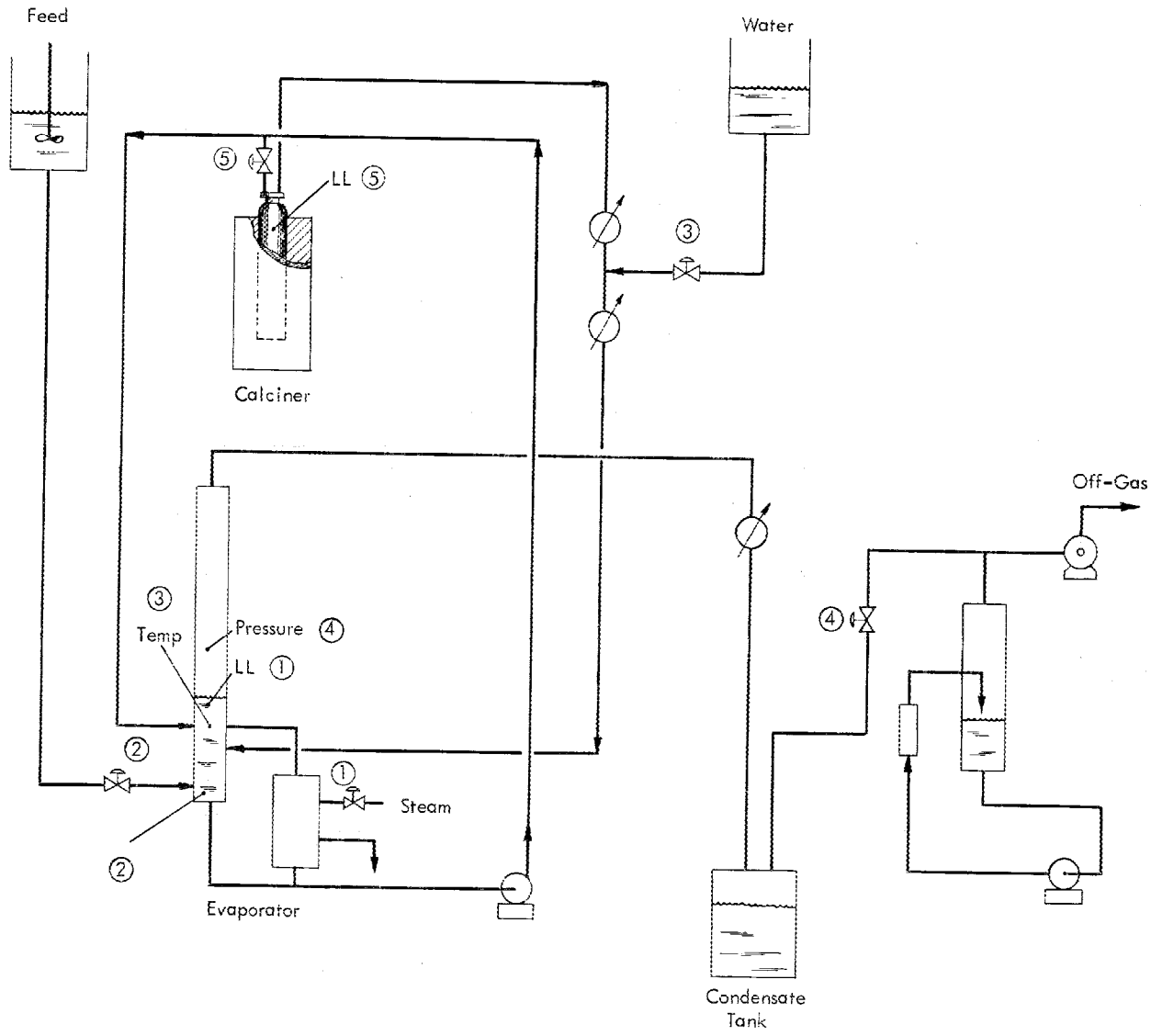

Fig. 6.1. Flowsheet for evaporator-calciner test R-36 using Purex waste.

Table 6.1. Purex Wasted used for Test - R-36

	Molar		Molar
H	5.5	Fe	0.5
NO_3	6.1	Cr	0.01
SO_4	1.0	Ni	0.01
Na	0.6	Al	0.1

(No Additives)

Table 6.2. Log for Evaporator-Calciner Test - R-36

Time	Run, Hour	
8:00 A	0	1. Fill Evaporator with waste feed and sample ~ 25 liters. 2. Calciner with water heel of about ~ 10 liters.
8:30 A	0.5 (start)	1. Start heating calciner furnaces. 2. Start heating evaporator contents. 3. Start filling calciner from evaporator.
9:00 A	1.0	1. Calciner was filled ~50 liters.
12:00 P	4.0	1. Had trouble with calciner liquid level probe plugging.
5:00 A	21.0	1. Stopped feed calciner because level stayed above control point.
6:00 A	22.0	1. Stopped evaporator, switched calciner condensate directly to the condensate tank. 2. Jet pump for system pressure control failed.
12:00 P	28.0	1. Stopped calcination because all thermocouples in the calcining solid were above 850°C except the top two which were 620 and 755°C.

Table 6.3. Test R-36 Results

Nitrate Balance (HNO_3)

System input - 2390 g mols)
System output - 2467 s mols) 103% Balance

Off-Gas

304 ft^3 - 225 ft^3 (system leakage + gas bubbler) = 79 cu ft
79 ft^3/432 liter of calciner feed = 0.18 cu ft gas/liter of calciner feed

Feed Rate

432 liter/21 hrs = 20.5 liter/hr

Calcined Solid

Weight = 136 lb
Volume = 48 liter to level set point
Bulk density = 1.29 g/cc

Table 6.4. Control Settings for Test R-36

Control Variable	Control Range 0-100%	Prob. Band %	Reset min	Set Point %	Dev. From Set Point %	Control Valves No. (see Fig. 6.1)
Evap. Liquid level	7.4-35.0 liter	100	10	50	26-58	1
Evap. Density	1.0-1.5 g/cc	200	10	60	20-74	2
Evap. Temp.	101-123°C	100	10	113	104-120	3
Evap. Pressure	-5 to +5 psig	50	0.3	40	35-45	4
Cal. Liquid level	44-52 liter	25	3.0	50	45-63	5

Evaporator Operation. The major component to be tested in this test (R-36) was the operation and control of the evaporator. The evaporator has four (4) control operations: (Table 6.4)

1. Liquid Level controlled by steam heating
2. Liquid Density controlled by feed addition
3. Liquid Temperature controlled by water addition
4. Evaporator Pressure controlled by off-gas jet by-pass

After the evaporator was initially filled the system feed rate is approximately equal to the calciner feed rate, Table 6.5.

The evaporator liquid level control, Table 6.4, performed very satisfactory. The control set point was 22.0 liters (50%)(Table 6.6). The desired limits of operation were $\pm$ 4.0 liters (18 to 26 or 35% to 65%). If the evaporator level goes too low, there is a chance that the contents may boil dry or the heat exchange tube may become excessively fouled. If the evaporator goes too high the chance of boil over or foam over to the condensate tank is possible. The evaporator went through a minimum liquid level while the calciner was filling. During the rest of the test the level control was good except near the end of the test when the calciner feed demand was low.

The evaporator density which controls the feed addition to the system also performed good, Figure 6.2. The metal salts concentration of feed solutions is a strong function of the density, and it is desired to keep the concentration between two limits: (1) lower limit, the calciner has to boil off more liquid per amount of solid deposited than is optimum, and (2) upper limit, it may plug the evaporator of feed lines if it is allowed to cool. On Figure 6.2 and Figure 6.3 and Table 6.6, four limit terms appear:

A and D "Upper Operational Limit," and "Lower Operational Limit," above or below these limits the operation is in a hazardous area or uneconomical and should be avoided.

B and C "Upper and Lower Desired Limits", between these limits the operation should run. However the operation can drift between B and A or C and D for short periods of time without greatly upsetting the whole system.

The density only exceeded the "C" limit once while the calciner was filling and the "B" limit once when the evaporator level was high and boiled down rapidly, Figure 6.2, it never exceeded the "A" or "D" limits. The external density probe was used for control, as the interior density probe always read low because of steam bubbles or foam. The exterior density probe checked closely with hourly samples taken from the evaporator. The density readings followed the iron concentration sufficiently close to used density a measure of metal salt concentration.

The evaporator temperature is a function of the nitric acid concentration mainly, at a controlled metal salt concentration. The operating set-point was 113°C, this is equal to 6 M HNO_3 at 25 g/liter Fe and -1.0 psig pressure. This temperature is extremely sensitive to the evaporator pressure.

Table 6.5. Evaporator-Calciner Test R-36

Purex 1WW Waste (No Additives)

Run Time hr	System Feed Purex liter	System Water Feed liter	Feed Ratio Water to Feed ratio	System Condensate liter	System Off-gas *-A cu ft	Mols HNO_3 Input g mol	Mols HNO_3 Output g mol	Evap. Density g/cc	Evap. Temp. °C	Evap. Fe Conc. g/ℓ	Evap. Acid mol	Evap. Steam Temp. Input °C	Calciner Heat Input KWH	Calciner Temp. at Feed Point °C	Calciner Temp. Midsection One Inch from Wall °C	
1	0	10	0	0	0	0	0	1.00	40	0	0	0	0	200	70	Start feed
2	48.0	10.7	0.43	0	9	264	0	1.27	106	19.0	4.6	112	16	200	113	
3	96.0	107	1.77	140	18	528	140	1.30	110	24.5	4.5	132	80	113	120	
4	136	192	2.12	265	28	748	378	1.32	113	24.0	6.0	131	123	120	122	Start calcination
5	208	276	1.17	405	41	1118	646	1.37	116	33.0	6.7	142	170	122	630	
6	258	373	1.94	560	56	1382	1141	1.34	120	29.5	6.6	132	219	110	775	
7	321	415	0.68	665	73	1715	1488	1.39	114	27.0	5.7	134	265	115	865	
8	353	479	1.97	760	86	1875	1602	1.28	109	23.0	4.9	123	391	115	890	
9	363	521	4.69	815	98	1920	1700	1.32	112	29.0	6.6	127	425	115	905	
10	370	578	7.18	880	111	1960	1798	1.28	111	27.5	5.4	118	449	130	910	
11	383	642	4.91	958	122	2025	1922	1.32	113	39.0	6.3	125	473	120	915	
12	409	729	3.36	1073	133	2155	2046	1.34	110	37.0	5.8	121	495	125	915	
13	419	762	3.30	1115	144	2205	2172	1.30	112	33.0	5.2	124	512	130	920	
14	429	820	5.79	1181	157	2255	2210	1.28	110	28.0	5.1	121	532	150	925	
15	440	867	4.22	1240	171	2310	2269	1.30	110	31.0	5.3	124	550	150	925	
16	446	925	9.77	1304	184	2340	2304	1.30	107	31.0	5.3	120	564	150	920	
17	448	938	6.2	1322	196	2350	2381	1.31	109	22.5	6.7	114	577	155	920	
18	448	945	-	1354	200	2350	2417	1.37	111	31.0	6.4	116	589	180	920	
19	453	970	5.08	1420	216	2375	2432	1.35	113	26.0	7.3	130	604	160	920	
20	453	1035	-	1443	231	2375	2441	1.34	110	32.0	7.0	121	614	175	920	
21	453	1060	-	1497	255	2375	2467	1.33	110	21.0	6.8	119	626	145	920	
22	456	1111	8.6	1543	271	2375	2467	1.20	104	18.5	3.9	95	641	120	925	End feed
23	-	1137	-	1547	282	2390	2467						656	375	920	
24	-	1138	-	1549	296	2390	2467						667	520	920	
25					304								676	535	920	
													682	560	920	
Total	456	1138		1549	304-225								690	570	920	
					79								699	620	920	End calcination
Average			2.5		0.18 ft^3/liter of waste											

*-A System leakage + gas bubbles for instruments ≅ 9 cu ft/hour

Table 6.6. Operational Limits for Test R-36

		A Upper Operational Limit	B Upper Desired Limit	Set Point	C Lower Desired Limit	D Lower Operational Limit
Evap. Liquid Level	Scale %	90	65	50	35	25
	liters	33	26	22	18	15
Evap. Density	Scale %	80	70	60	40	30
	g/cc	1.40	1.35	1.30	1.20	1.15
				25		
Evap. Temperature	Scale %	81	60	50	0	Off-Scale
	°C	120	115	113	100	90
				6 M		
Evap. Pressure	Scale %	45	42	40	35	35
	psig	-0.5	-0.75	-1.0	-1.5	-1.5
Cal. Liquid Level	Scale %	30	40	50	60	70
	liters	46	47	48	49	50

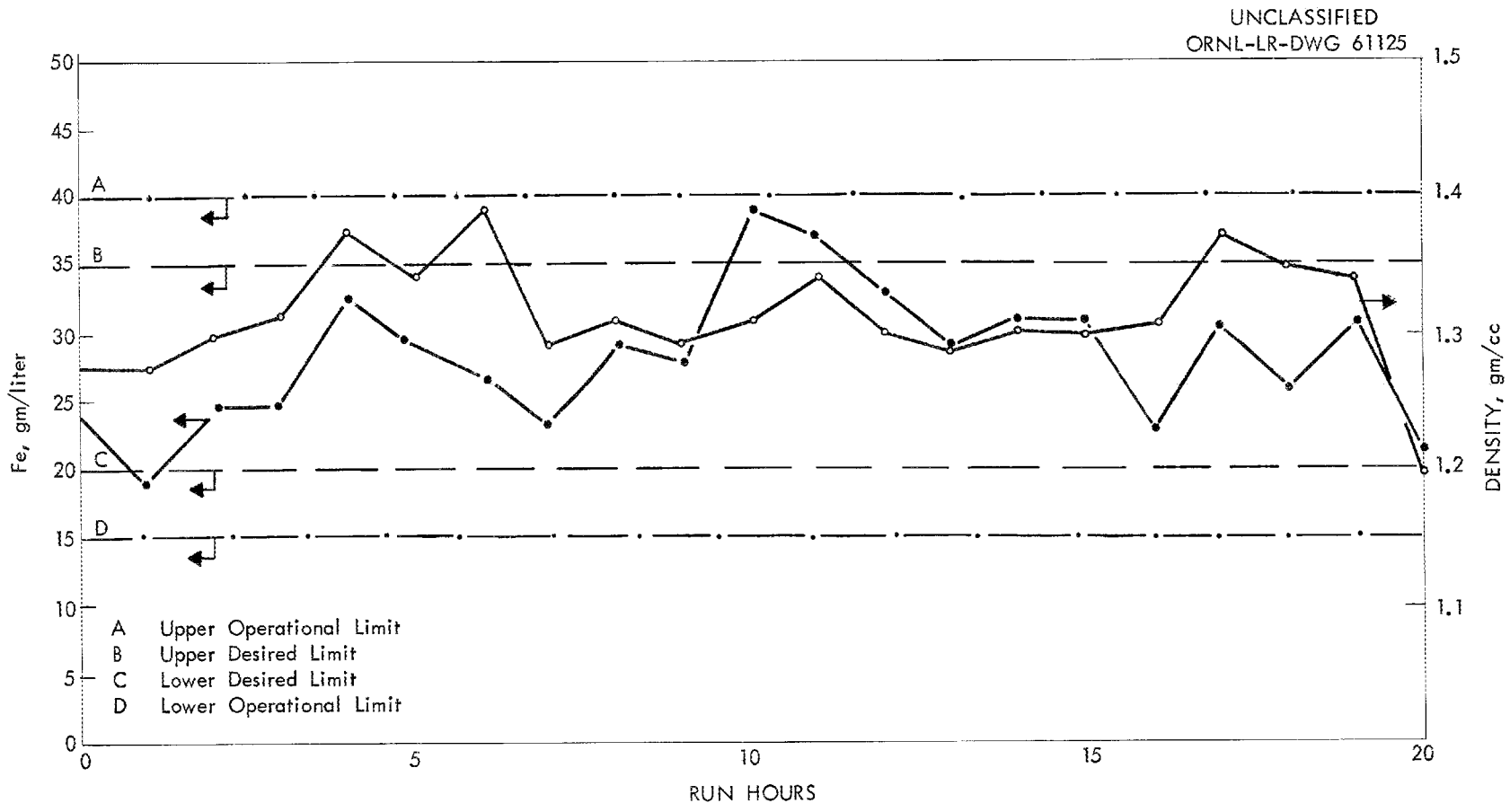

Fig. 6.2. Evaporator densities and iron concentrations for test R-36.

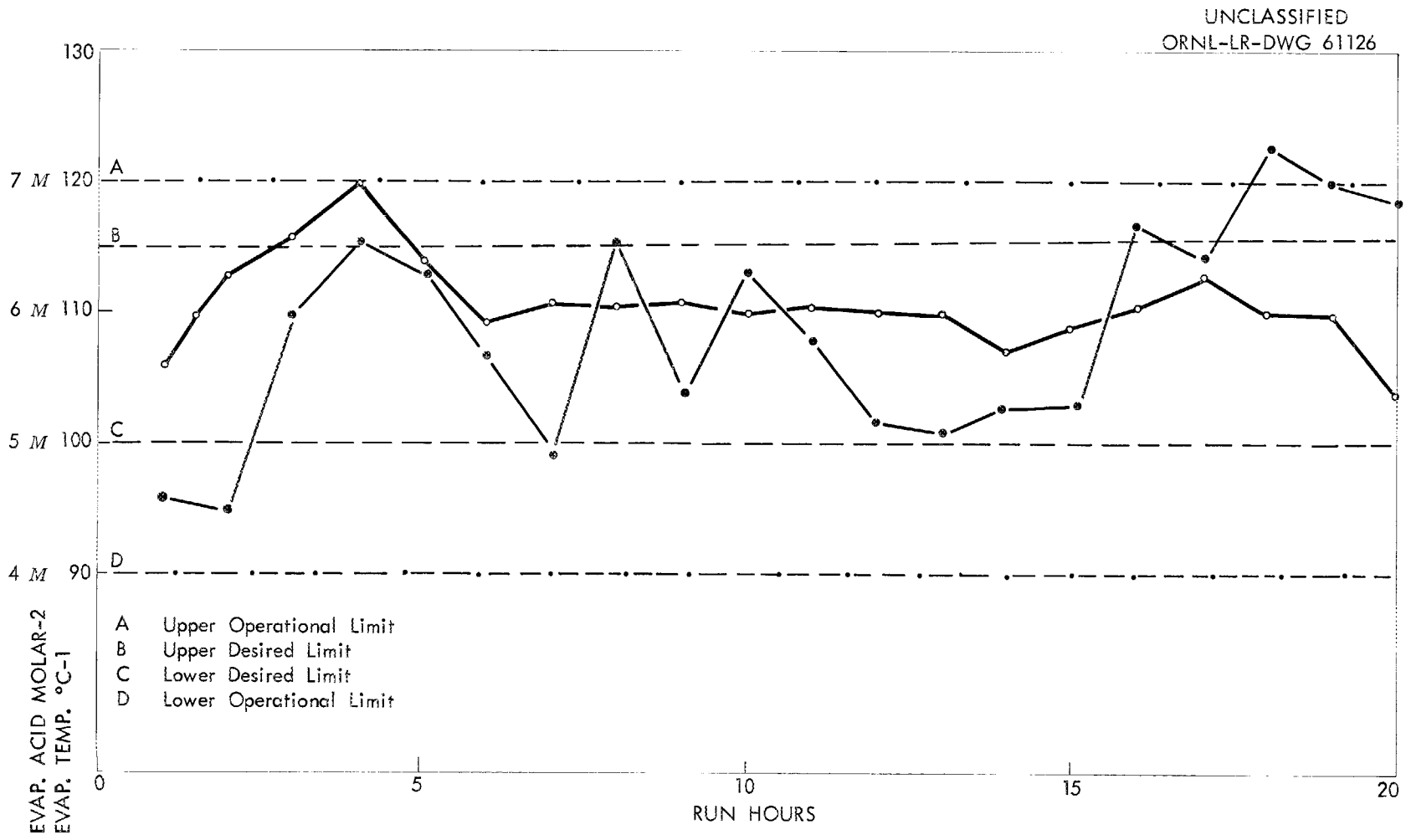

Fig. 6.3. Evaporator temperatures and acid concentration for test R-36.

A good and adequate pressure system is very necessary for the system to operate correctly. The evaporator temperature went to limit "A", Figure 6.3, once during the test. This was partly due to a pressure increase and partially due to the iron concentration going to 37.0 g/liter, however the nitric acid only reached a maximum concentration 6.7 molar. This was during the peak acid return from the calciner to evaporator at 4th to 6th hours. The water addition to steam strip the acid was also at its maximum the 5th hour, Figure 6.4. The maximum water addition rate to the system was 97 liters per hour. The average water addition rate was 46 liters per hour. The average water to feed ratio was 2.5 with maximum of 7.2 one hour when the feed to the calciner was abnormally low and water addition was normal. The water was added to the system partially as steam and partially as cold water.

Of the 2390 g-mol of HNO_3 fed to the system 2467 g-mol was recovered (103%). The total off-gas volume was 304 cu ft. The system had a combined leak and bubble rate of 9.0 cu ft/hour at -1.0 psig evaporator pressure. The non-condensate process off-gas was 79 cu ft or 0.18 cu ft/liter of calciner feed.

The system as a whole operated very well. The control of 5 major variables was satisfactory. The gas purge rate for the calciner liquid level will be increased to 4.0 cu ft/hour, advised T. M. Gayle as a possible solution to liquid level probe plugging.

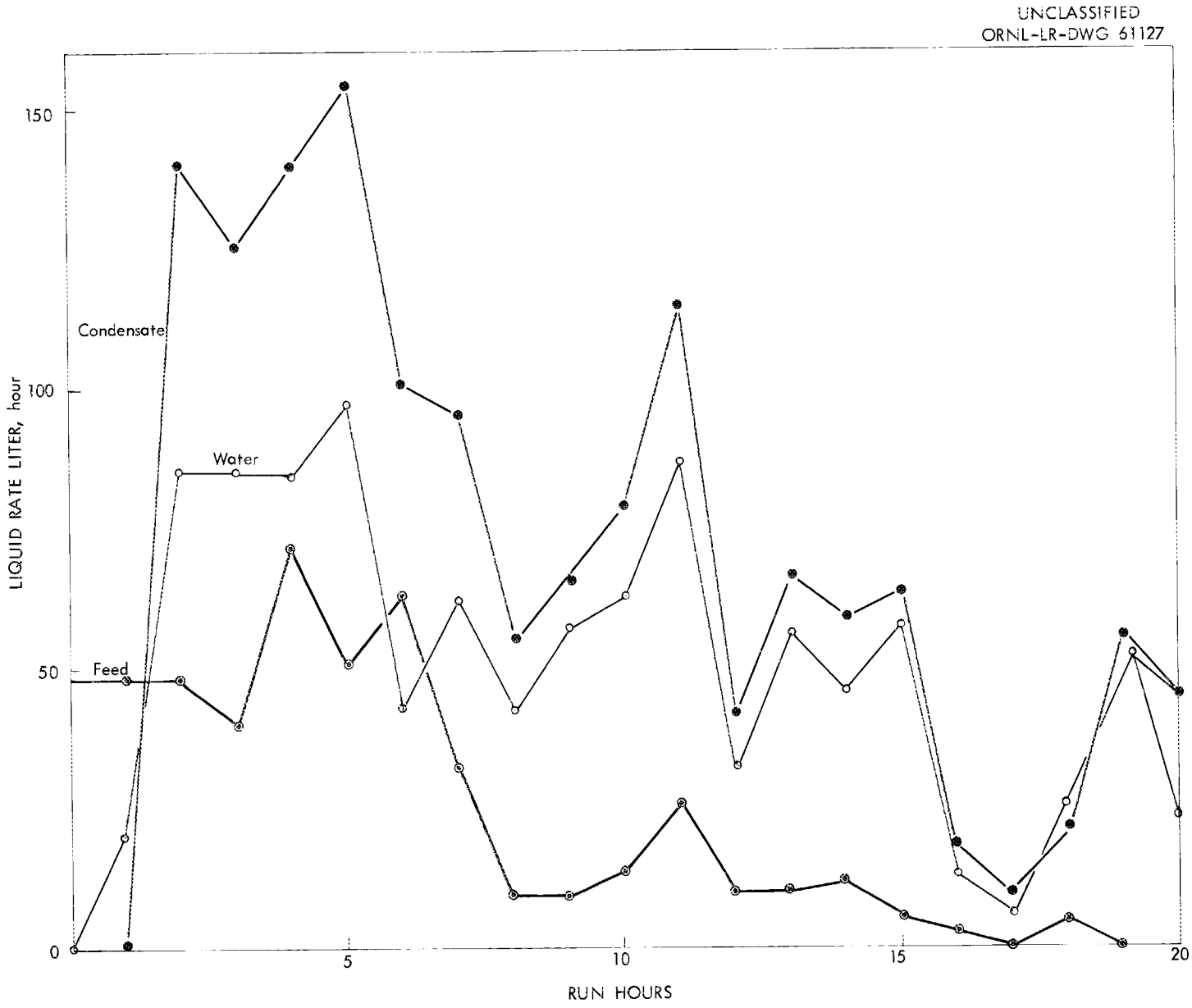

Fig. 6.4. Liquid rates for test R-36.

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