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CHEMICAL PROCESSING TECHNOLOGY QUARTERLY PROGRESS REPORT

July - September, 1962

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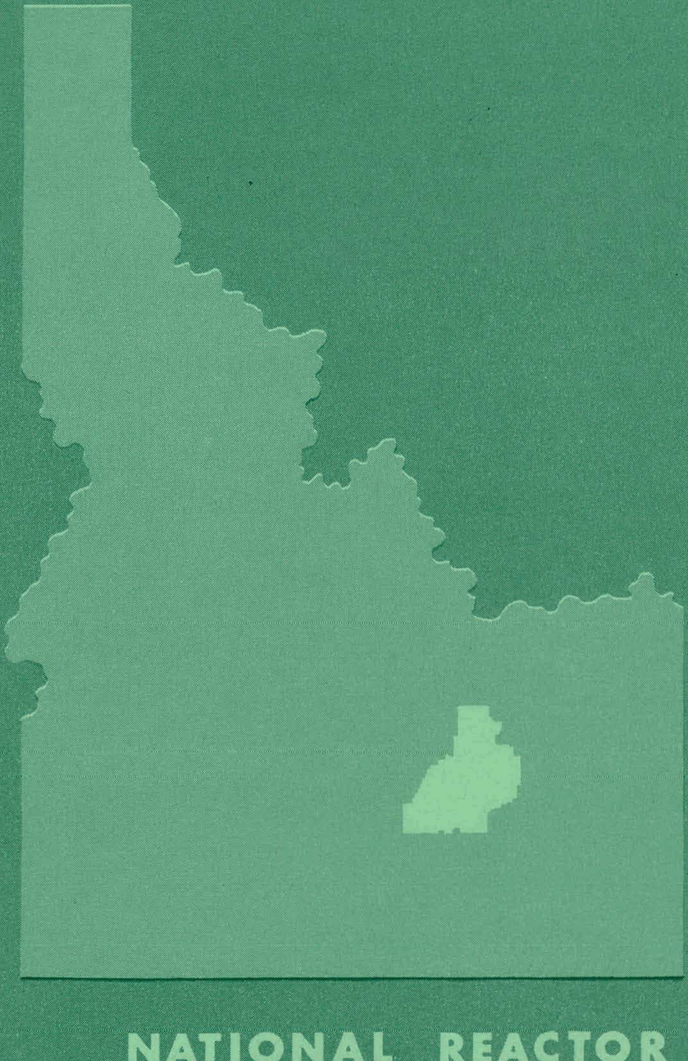

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CHEMICAL PROCESSING TECHNOLOGY
QUARTERLY PROGRESS REPORT
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CHEMICAL PROCESSING TECHNOLOGY
QUARTERLY PROGRESS REPORT
JULY - SEPTEMBER, 1962

SUMMARY

Aqueous zirconium fuel processing studies, directed at adapting the hydrofluoric acid process to continuous dissolution-complexing in order to increase the capacity of the ICPP process, have resulted in two successful approaches to the complexing-feed adjustment step. Continuous in-line adjustment (conversion of uranium IV to uranium VI necessary for extraction) was accomplished in one minute or less at approximately 90°C; surges of dissolver product from the operating dissolver up to 1.9 times the flow sheet rate did not inhibit the oxidation of the uranium at this temperature. Batchwise mixing in air of dissolver product solution with complexer solution oxidized the uranium within two minutes at 23°C or higher. Further studies of continuous zirconium dissolution indicate that precipitation of uranium at the acid inlet can be a problem, probably because of local concentration gradients of free HF which result in conditions of low uranium solubility. Control of dissolver acid composition by electrical conductance measurement appears possible due to the linear relationship of conductance with acid concentration.

Aluminum alloy dissolution rates in nitric acid were found to vary significantly, depending on the type and amount of alloying agent. Silicon, nickel, and copper in the alloy significantly decreased the dissolution rate. Batch dissolution times for standard test coupons ranged from 14 minutes for a high purity aluminum to 1400 minutes for an alloy containing 2.9 percent silicon.

In the electrolytic dissolution of Nichrome in a bench-scale basket dissolver, the substitution of titanium for niobium as the anode basket material significantly reduced the contact resistance. Current interruption due to contact failure was essentially eliminated, and contact resistance on the titanium was sufficiently low that increasing solution resistance due to acid depletion became a major contributor to current decline as dissolution progressed. The indirect solution-contact electrolytic dissolution principle was further studied, producing data on electrode corrosion, power consumption, and gas generation on noble metal electrodes using both direct and alternating current. A second dual component analyzer, making use of density-conductivity measurements on the dissolver effluent, was shown to give an accurate measure of the acid and dissolved metal concentrations. Chemical-irradiation tests of insulating materials for use in electrolytic dissolvers have been completed. Alumina ceramic was the only material tested which showed little or no change at dose levels of 10^{10}r; plastic materials with varying degrees of resistance are reported.

Studies on new waste treatment methods indicate the successful application of either ion exchange resins or locally available soil material to the removal of low concentrations of cesium-137 and strontium-90 from ICPP fuel storage basin effluent. The workability of a melt-freeze process for separation of aluminum nitrate from fission products, aimed at a 200-fold reduction in

volume of ICPP generated wastes, was demonstrated in a single-stage laboratory unit. Pertinent solubility and density measurments were made and the operating diagram applicable to a multistage process is presented. Preliminary experiments on impregnation of calcined alumina with molten sulfur appear to be favorable from the standpoints of leach resistance, particle immobilization, and heat transfer.

Operation of the Demonstrational Waste Calcining Facility during this period further confirmed the applicability of process control methods developed in pilot plant operations to the DWCF, and demonstrated that these methods provide an ample degree of control over processing conditions. With this assurance of operability of the unit, plans are being made for a run spiked with radioactive sodium-24 as the next test. Key processing conditions which have been selected for this run include operation at 400°C bed temperature, control to an amorphous bed, and return of the primary cyclone fines directly to storage with the bed product. Supplemental pilot plant and laboratory studies during the reporting period have included tests of a wet spray return to control solids from the primary cyclone, demonstration of the control of particle size by addition of sand nuclei as an alternative to nozzle-air-ratio control, and completion of a study of the products of stainless steel and Nichrome nitrate calcination.

Additional basic process studies made include methods of determining the amplitude and liquid level in an air pulsed column, a new method of securing flooding data for dynamic tests in pulse column control studies, and recommendations for control instrumentation on a uranium salvage evaporator. High absorption efficiency of hydrous zirconium oxide for degradation products of tributyl phosphate was demonstrated.

CHEMICAL PROCESSING TECHNOLOGY
QUARTERLY PROGRESS REPORT
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FIGURES

TABLES

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I. ICPP OPERATIONAL SCHEDULE, PERFORMANCE, AND PROBLEMS

1. ICPP PROCESSING SCHEDULE

No fuels were processed during this period; decontamination operations were in progress in cells E, F, G, and H. Operating crews were largely shifted to the Demonstrational Waste Calcining Facility (DWCF) in accordance with established schedules, leaving only a skeleton crew for cleanup and preparation for certain renovations in the main processing plant.

With the exception of cells E and F, all scheduled process cell decontamination was completed. Certain areas of cells G and H would not yield to decontamination, and lead shielding was installed on lines and equipment which were contributing to high radiation background. The principal trouble spots were the bottoms of the dissolvers, the bottom of the extraction column, and the bottom of the tube bundle on the feed evaporator. It is suspected that the source of the radiation, at least in the dissolvers, is stainless steel fragments which dropped below the crash plates and could not be removed with the larger stainless steel pieces which were removed earlier [1]. Following installation of shielding, background readings were generally below 100 mr/hr with the shielded areas reading 150 to 200 mr/hr. A hot spot reading greater than 500 r/hr is located at the bottom of the coarse feed adjustment vessel in E cell. This has proved to be resistant to all decontamination attempts and it is planned to cut a two-inch vent line at the top of the vessel to inspect the interior.

Two barium-140 runs were made this quarter for a total production of 61,252 curies. The most recent run gave the largest shipment (40,067 curies) made from the Idaho Chemical Processing Plant (ICPP) and resulted from a 65.9 percent recovery of the theoretical yield.

2. MODIFICATION OF ICPP PROCESS SYSTEMS

The uranium rework and recovery cell (J cell) is in the hands of the construction contractor. The non-geometrically safe processing equipment and infinitely safe, but space-wasting, storage tanks have been removed. The new installation will use boron-stainless-steel, neutron-poison inserts in large-sized equipment to assure nuclear safety and eliminate sole dependence on analytical and supervisory control for prevention of critical incidents.

Installation of the new Amsco cleanup process in the solvent recovery cell (K cell) is awaiting receipt of equipment. This process involves steam distillation of the Amsco from plutonium-containing residues which have interfered with disposal of the used Amsco.

A new first cycle extraction column feed system is being designed and will be installed by construction forces before the aluminum fuel process is restarted. Several other modifications are under consideration for completion by plant maintenance forces.

3. PLANT ASSISTANCE PROBLEMS

3.1 Corrosion Evaluation of Boron-Stainless-Steel (T. L. Hoffman)

A preliminary corrosion evaluation was conducted on stainless steel 304 containing 1.13 percent boron* and intended for use in neutron-poison plates to be installed in large-diameter vessels handling concentrated, enriched uranium solutions. Mild general corrosion was observed on the boron-stainless-steel after immersion in ICPP aluminum-process intercycle-evaporator compositions at boiling temperatures. Severe pitting and grain-boundary attack were observed on the alloy in boiling electrolytic dissolver product solution from a proposed stainless steel process.

Procedure

Bench-type corrosion studies were conducted on boron-containing stainless steel 304 in synthetic solutions which are representative of ICPP process solutions. The stainless steel contained 1.13 percent boron, 0.061 percent carbon, 1.58 percent manganese, 0.027 percent phosphorus, 0.010 percent sulfur, 0.068 percent silicon, 18.60 percent chromium, and 9.61 percent nickel*. Two process solutions, II AF and III AF (intercycle evaporator products), were chosen from the aluminum-containing fuel recovery process, and a third solution simulated the dissolver product from a proposed stainless steel electrolytic dissolution process.

The coupons used for this study were made by welding together two strips of steel according to ASTM designation A 371-53T using parent boron-steel wire for welding electrodes. Each coupon was then machined to 1-1/2- x 1- x 1/8-inch size. One-half of the coupons were post-annealed at 1850°F for 15 minutes and furnace-cooled. The remaining coupons were tested in the as-welded metallurgical condition.

The coupons were exposed in the three different synthetic solutions for five 48-hour boiling periods. Each coupon was positioned at the liquid-air interface of the boiling solutions so that about one-half of each coupon was in the liquid and one-half in the vapor. At the end of each 48-hour boiling period, the coupons were withdrawn from the boiling solution, cleaned, weighed, and examined microscopically. The coupons were then returned to the flasks, and the test repeated four times with the same solutions.

Results

The experimental data are shown in Table I; each value is the average of duplicate samples. Only the results for the first, third, and fifth test periods and a cumulative rate representing all five test periods are shown.

Microscopic examination of the coupons which were exposed in II AF or III AF process solutions indicated that pitting and localized corrosion attack were absent. In specimens exposed to the boiling electrolytic dissolver product solution, severe pitting and grain-boundary attack were observed. Grain-boundary attack was deeper on the as-welded coupons than on the annealed coupons, and corrosion rates were higher for the as-welded coupons.

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* Analysis by Superior Steel Co., the supplier.

TABLE I

CORROSION OF BORON-STAINLESS-STEEL-304 IN SYNTHETIC ICPP PROCESS SOLUTIONS

Process Solution	Heat Treatment	48-hr Corrosion Rate (mils/mo) First	Third	Fifth	Cumulative Rate (mils/mo)
Electrolytic Dissolver Product (75 g/l SS 1.0$\underline{M}$ HNO_3)	Annealed	2.1	2.8	4.5	3.3
	As welded	2.9	4.8	5.8	4.7
II AF (164 g/l U 1.5$\underline{M}$ HNO_3)	Annealed	0.2	0.3	0.2	0.3
	As welded	0.4	0.5	0.5	0.4
III AF (353 g/l U 0.1$\underline{M}$ HNO_3)	Annealed	0.1	0.1	0.0	0.0
	As welded	0.1	0.1	0.0	0.0

These tests suggest that boron-stainless-steel-304 may have relatively long service life in II AF and III AF process solutions, but that this alloy may not be suitable for electrolytic dissolver product service. It is planned to continue the testing program by exposing coupons in operating equipment under actual service conditions.

II. AQUEOUS PROCESS STUDIES

(Section Chiefs: K. L. Rohde, Chemistry; M. E. Weech, Plant Processes)

1. AQUEOUS ZIRCONIUM FUEL PROCESSING

1.1 Continuous Laboratory Dissolution of Zirconium Alloy Fuel with Hydrofluoric Acid (D. W. Rhodes, Problem Leader; B. J. Newby)

Continuous dissolutions, each of several hours duration, of 3 percent uranium-Zircaloy-2 fuel with hydrofluoric acid were made in a 1-inch-diameter Monel dissolver to furnish material for study of the conditions under which complexer solution (aluminum nitrate containing nitric, hydrofluoric, and chromic acids) will oxidize uranium in dissolver product solution. The uranium IV in dissolver product solution must be oxidized to uranium VI before it can be extracted with tributyl phosphate. The effects of irregularities in the flow of product solution from the operating dissolver, and temperature of adjustment on uranium oxidation during continuous in-line adjustment, were investigated. In addition, the effects of adjustment temperature and time on the oxidation during aerated batchwise adjustment were studied.

1.11 Continuous In-line Adjustment of Dissolver Product. Adjustment Temperature The dissolver effluent produced during continuous dissolution of 3 percent uranium-Zircaloy-2 fuel with 4.8M hydrofluoric acid solution was fed continuously into an adjustment vessel where it was mechanically stirred for one minute at various temperatures with complexer solution. The composition of the adjusted dissolver product solution was 3.8M fluoride, 1.3M acid, 2.0M nitrate, 0.58M aluminum, 0.68M zirconium, 1.6 g/l uranium, and 0.015M chromic acid. This solution was cooled and an aliquot immediately extracted with an equal volume of 10 percent tributyl phosphate in Amsco. Results are given in Table II. A control sample was prepared under conditions expected to achieve complete oxidation, in order to provide a comparison standard for the other tests. For this, an aliquot of the adjusted solution was boiled 1/2 hour under total reflux with a small quantity of chromic acid, cooled to room temperature, and extracted with an equal volume of 10 percent tributyl phosphate in Amsco; 100 percent oxidation of the uranium resulted. Comparison of the results indicates that a temperature of about 92°C will achieve the same result under

TABLE II

EFFECT OF TEMPERATURE ON URANIUM OXIDATION
DURING CONTINUOUS IN-LINE ADJUSTMENT OF DISSOLVER PRODUCT

Adjustment Temperature (°C)	Average Extraction Coefficient	Uranium Oxidized (%)
46	6.0	43
62	8.5	61
78	9.0	64
92	15	100
Control	14	100

the conditions of the proposed in-line adjustment. Lower temperatures will not oxidize the uranium rapidly to an extractable species in this environment, ie, an atmosphere of hydrogen and nitrogen.

Surges From an Operating Dissolver. During adjustment of dissolver product solution prior to extraction, complexer solution will be pumped continuously into the adjustment vessel at a constant rate. Although the dissolver product also should enter the adjustment vessel from the operating dissolver at a steady rate, the vigorous dissolution process may create surges. Accordingly, laboratory experiments were performed to indicate the effect of surges on the oxidation of the uranium. Complexer solution (1.41M aluminum nitrate, 1.73M hydrofluoric acid, 0.66M nitric acid, and 0.036M chromic acid) was fed into an adjustment vessel at a rate of 7.5 ml/min. Dissolver product solution, prepared by continuously dissolving 3 percent uranium-Zircaloy-2 fuel in 4.8M hydrofluoric acid - 0.03M nitric acid was fed into the adjustment vessel at rates of 19.0, 13.9, and 10.0 (specified flow sheet rate) ml/min. The temperature within the adjustment vessel was maintained at 94°C and the solution was mechanically stirred. Retention time in the adjustment vessel varied from 0.66 to 1.0 minute under the flow conditions studied. The dissolver and adjustment vessel were held at equilibrium conditions for one hour while several samples were taken from the adjustment vessel overflow. Sufficient complexer solution without chromic acid was added to samples to bring their salting strength up to flow sheet specifications, the samples were cooled, and an aliquot immediately extracted with an equal volume of 10 percent tributyl phosphate in Amsco. Another aliquot was boiled with a small amount of chromic acid prior to extraction to determine the value of the extraction coefficient for the control which represented 100 percent uranium oxidation. The information, which is tabulated in Table III, shows that simulated surges of dissolver product from the operating dissolver up to 1.9 times the volume specified by the flow sheet did not affect oxidation of the uranium at 94°C even though the mixing time in the in-line adjustment vessel was reduced from 1 to about 0.7 minute. The adjusted dissolver product solution resulting from these surges was stable for several days.

TABLE III

EFFECT OF DISSOLVER PRODUCT SURGES ON URANIUM OXIDATION DURING ADJUSTMENT AT 94°C

Flow Rate to Adjustment Vessel				
Dissolver Product (ml/min)	Complexer Solution (ml/min)	Contact Time (min)	Average E_o/E_a for Uranium	Uranium Oxidized (%)
10.0	7.5	1	30	100
13.9	7.5	0.82	31	100
19.0	7.5	0.66	36	100
Control	—	—	26	100

1.12 Batch Adjustment of Dissolver Product. A vessel used for continuous in-line adjustment of dissolver product as discussed above would have to be constructed of some highly resistant metal, such as platinum, because of the highly corrosive conditions existing at the high temperatures ($\approx 90°C$) required. If the adjustment could be accomplished at lower temperatures, corrosion rates might be reduced to the point where use of more common construction materials would be possible. With this in mind, a study of adjustment under batch conditions was undertaken; batch adjustment could allow long holding times at low temperatures. At the same time, the reducing environment of the fresh dissolver solution in the in-line adjustment vessel could be eliminated by using an open tank in contact with air; this might permit completion of the oxidation reaction under much milder conditions.

Ten volumes of dissolver product solution were mechanically stirred at various temperatures for 5 hours with 7 volumes of complexer solution. Samples were taken after 2, 5, 30, 60, and 300 minutes of stirring. They were cooled rapidly and immediately extracted with an equal volume of 10 percent tributyl phosphate in Amsco. A sample to serve as a control was taken after 5 hours of stirring and boiled with a small amount of chromic acid prior to extraction, to determine the value of the extraction coefficient representing 100 percent uranium oxidation in the dissolver solution. Table IV shows that batchwise adjustment of dissolver product for 2 minutes at 23°C in an open vessel was sufficient to oxidize all uranium present. Apparently, removing the dissolver product to an aerated vessel virtually eliminated the inhibiting factors existing in the earlier in-line adjustment, which required high temperature for complete oxidation. With this knowledge, design of cooled, aerated in-line adjustment equipment probably could accomplish the same result.

1.2 Continuous Zirconium Fuel Dissolution in the Pilot Plant (A. P. Roeh)

Dissolution of Zircaloy-uranium alloy in small scale continuous dissolvers has been under investigation for some time. The last pilot plant test reported was a 300-hour test with periodic dissolver inspection revealing precipitate buildup on the dissolver wall [1]. It was subsequently determined, through individual fuel rod analysis, that the fuel charge to this dissolver contained 3.0 percent uranium rather than 2.3 percent stated by the metal suppliers. Since the amount of uranium in a 3 percent fuel exceeds the uranium solubility limits of the dissolver solution, a definite increase in the rate and amount of precipitate formation in the dissolver would be expected. Precipitate buildup for this and earlier runs is reported in previous quarterly reports [1, 2]. A new source of Zircaloy-uranium alloy containing 2.0 percent uranium was located and two additional tests were made to study the precipitate buildup in the dissolver.

These tests of 152-hour duration each were made in 1-inch-diameter Monel dissolvers [2] using a $4.8\underline{M}$ HF-$0.03\underline{M}$ HNO_3 dissolvent. The acid feed inlet line was located flush with the bottom of the dissolver in the first test and approximately one inch above the bottom in the second test.

At the conclusion of the first test, a heavy deposit of $UF_4 \cdot 3/4\ H_2O$ which partially plugged the acid feed inlet was found in the bottom of the dissolver. This deposit was localized around the feed inlet. The side of the dissolver opposite the feed inlet was free of deposit.

These results suggested incomplete mixing and, if the feed were introduced into the dissolver a short distance above the bottom, that more favorable

TABLE IV

BATCHWISE ADJUSTMENT OF DISSOLVER SOLUTION AT VARIOUS TEMPERATURES IN A VESSEL EXPOSED TO AIR

Adjustment Temperature (°C)	Stirring Time (min)	Average Uranium Extraction Coefficient (E_o/E_a)
23	2	30
23	5	22
23	30	25
23	60	24
23	300	25
—	—	25(a)
54	2	16
54	5	18
54	30	21
54	60	15
54	300	18
—	—	19(a)
71	2	24
71	5	23
71	30	25
71	60	21
71	300	23
—	—	28(a)

(a) Control (100% uranium oxidation).

conditions might be established. However, accumulations of precipitate were again found in the acid feed inlet line and the bottom of the dissolver, indicating that non-equilibrium solubility conditions still existed.

Existing solubility relationships indicate that uranium should be soluble up to and slightly above a dissolver product composition resulting from dissolution of a 2 percent by weight uranium fuel. The uranium precipitation problems observed in the above experiments are attributed to local concentration gradients existing within the dissolver, forming a UF_4 precipitate that redissolves very slowly. Because of an inverse solubility relationship, operation of the dissolver at lower temperatures (≈60°C) should increase the UF_4 solubility; dissolution rates would be decreased by the lower temperature but would still be more than ample to meet the projected plant rates. The next series of runs will provide, by dissolver modification, means for rapidly circulating the dissolvent in the dissolver, and the mean dissolver temperatures will be kept at approximately 60°C. These steps should eliminate the concentration gradients and the UF_4 precipitation problems.

Experiments discussed in the preceding section, in which laboratory dissolution of 3 percent uranium-Zircaloy-2 is reported in connection with feed adjustment and complexing studies, should not be regarded as in conflict with the above reported solubility information. Individual experiments were of a few hours duration and the dissolver was cleaned out between runs. Dissolver deposits were observed but did not accumulate sufficiently to cause concern in the few hours of operation required to obtain the other data desired.

1.3 In-line Analysis of Hydrofluoric Acid - Nitric Acid Dissolver Reagents (H. T. Hahn, Problem Leader; D. P. Pearson)

A sensitive method is required for composition control during the makeup of hydrofluoric acid-nitric acid solutions. The measurement of electrical conductance potentially affords a basis for this instrumentation.

Electrical conductances at 25°C were studied for solutions of the composition 3.0-7.5$\underline{M}$ HF, 0.00-0.05$\underline{M}$ HNO_3. In this range the conductance conforms within ± 0.3 percent to the equation

$$10^3 L = -2.1 + 24.51\,[HF] + 184\,[HNO_3]$$

where the brackets refer to molar concentrations. The linearity of the relationship indicates that conductance would be a suitable parameter for this application.

2. AQUEOUS ALUMINUM FUEL PROCESSING

2.1 Aluminum Dissolution Rate Studies (R. D. Fletcher, Problem Leader; H. R. Beard)

Phase 2 of the four-part program to study the causes of variable dissolution rates for aluminum has been initiated. Phase 1, which was reported in the previous quarterly report [1] covered the catalytic or retarding effects of the ions in solution derived from constituents of the alloys. From this study it was concluded that iron was catalytic, and nickel and copper had a retarding effect on the dissolution. Phase 2 consists of determining batch dissolution rates with standard-sized (1.00- x 1.26- x 0.176-inch) aluminum alloy coupons of various compositions in 6.6$\underline{M}$ nitric acid - 0.005$\underline{M}$ mercuric nitrate at 90°C.

The aluminum alloy coupons were fabricated from Alcoa spectrochemical standards. The compositions and batch dissolution times required to reach a solution concentration of 30 g/l are given in Table V.

The compositions chosen for all except SS 6061 were based as nearly as possible on one or two of the apparently catalytic or retarding constituents

TABLE V

ALUMINUM ALLOY COMPOSITIONS AND BATCH DISSOLUTION TIMES

Conditions: 6.6M nitric acid, 0.005M mercuric nitrate at 90°C.

Standard No.	Retarding Constituents (%)			Catalytic Constituent (%)	Other Constituents (%)							Batch Dissolution Time to 30 g/l (min)		
	Cu	Si	Ni	Fe	Mg	Mn	Cr	Ti	Zn	Sn	Be	Run 1	Run 2	Run 3
SAC 1091	4.80	1.19	0.06	0.42	0.008	0.034	—	0.15	0.04	0.001	—	320	340	—
SAC 1033	3.54	0.24	2.09	0.43	1.79	0.025	—	0.072	0.033	—	—	690	720	—
SS 2618	2.29	0.18	1.14	1.08	1.60	0.062	0.002	0.078	0.060	—	—	165	170	—
SS 6061	0.31	0.59	0.05	0.36	0.99	0.054	0.26	0.080	0.081	—	—	290	595	660
SS 5456	0.06	0.14	0.01	0.16	5.12	0.082	0.10	0.025	0.055	—	0.0008	13	14	—
SA 1617	0.01	0.10	—	2.14	—	—	—	—	—	—	—	36	38	—
SA 1673	0.01	0.10	—	0.60	—	—	—	—	—	—	—	14	8	—
SAC 774	—	2.91	—	0.5	—	—	—	—	—	—	—	1400	1700	—
SAC 1022	—	1.55	—	0.5	—	—	—	—	—	—	—	960	8	1190

being present as a significant percentage. The SS 6061 composition falls within the limits of commercial grade 6061 aluminum alloy.

Duplicate dissolutions were carried out with each coupon. However, because a considerable difference in dissolution time occurred with SS 6061 and SAC 1022, a third coupon was run for each of these. The dissolution time for the third coupon in each case agreed reasonably well with one of the original two and it was then assumed that a marginal active or passive condition might exist with some or all of the alloys. Possible passivity was investigated by assuming that the aluminum in the alloy must amalgamate with the mercury present as a first step in the alloy dissolution. The first approach was to attach a piece of 99.999 percent alluminum to a coupon of SAC 774 which had a previous average dissolution time of 1550 minutes. In the presence of high purity aluminum the SAC 774 alloy dissolved in approximately 80 minutes. A similar approach was taken with several other apparently slow-dissolving alloys with improvement noted in some cases. An increase of mercury concentration from 0.005M to 0.05M also was investigated with improvement in dissolution time resulting in all except one alloy.

It is generally concluded that silicon, nickel, and copper, as alloying constituents, exert a retarding effect on the dissolution rate of aluminum alloys. The effect of silicon appears to be most significant. The catalytic effect of ferric ion in solution, observed earlier, was not verified in the present tests. The range in batch dissolution times from 14 minutes for the higher purity alloys to 1400 minutes for the alloy containing 2.9 percent silicon is indicative of the extra processing time and cost associated with highly alloyed materials.

III. ELECTROLYTIC DISSOLUTION SYSTEMS
(Section Chief: K. L. Rohde, Chemistry)

1. FUEL-ELECTRODE DIRECT CONTACT PRINCIPLE
(H. T. Hahn, Problem Leader)

A bench-scale basket-type continuous dissolver, capable of operating at 500 amperes, has been placed in operation. Experiments this quarter were designed to improve the contact between the dissolving fuel pieces and the anodic metal basket. Two modifications to the basket, which essentially eliminate complete current failure, have been tested successfully and have permitted sustained operation at the 200-ampere level. One modification is the use of a titanium basket. The second involves the use of a platinum cup containing mercury and a protective organic layer at the bottom of the basket.

Concurrently with these experiments another dual component solution analyzer has been developed for in-line use. In this, measurements of specific conductance and density determine uniquely the nitric acid and salt concentrations. Measurement also was made of the particle size range of silica generated during Nichrome rod dissolution.

1.1 Bench-Scale Dissolver Operation (M. R. Bomar, J. R. Aylward)

1.11 Mercury Pool Contact Anode. The basic test dissolver was described in the previous quarterly progress report [1]. A platinum cup (5/8 inch deep) was fastened to the bottom of the niobium basket with a niobium screw. Six Nichrome rods (3/8 inch diameter x 11 inches long) were placed in the basket with one end of each resting in the platinum cup. Four cc of mercury and four cc of tetrabromoethane were introduced to the platinum cup by means of a tube. The mercury was added to provide electrical contact with the rods, while the tetrabromoethane was present to prevent the mercury from dissolving. This arrangement permitted long Nichrome rods, most of which protruded above the tetrabromoethane, to be essentially dissolved, although at a steadily declining current. The decline was due to a combination of an increasing solution resistance and a decreasing rod surface area as the dissolution proceeded. Both conditions probably could be corrected by maintaining a constant solution composition and a basket full of fuel. However, the portions of the rods which were below the surface of the tetrabromoethane were not attacked. When the dissolver with the mercury pool was charged with short Nichrome rods (3/8 inch diameter x 1 inch long) the current decayed to zero within a one-hour period as the lower pieces contacting the mercury dropped below the surface of the organic layer. In an effort to reduce or eliminate the undissolved heel, attempts have been made to produce a very thin layer of mercury by amalgamation of a copper-plated platinum surface. However, the protective organic layer was lost, and the mercury dissolved.

The problem of maintaining a protected liquid metal layer sufficiently thin to prevent the accumulation of a heel does not seem insurmountable. However, further study of this approach has been stopped, at least for the present, since results obtained with a titanium basket (vide infra), in which the contact problem is minimized, seem to offer a more encouraging and simplier application of the basket direct contact principle.

1.12 Titanium Basket Anode. A titanium basket was fabricated to the same specifications as the preceding niobium basket [1]. The basket size was 12 inches long by 1-1/2 inches diameter with 3/32-inch holes on 5/32-inch centers. The free area was 32 percent. This basket was tested with the dissolver vertical, 10 degrees from vertical, and 45 degrees from vertical. In some experiments either a solid titanium wedge or cone was fastened to the base inside the basket in order to promote dissolution from the bottom and at the same time to maintain contact. Perforation of the basket base also was investigated. The results of dissolution experiments with these modifications are given in Table VI.

TABLE VI

ELECTROLYTIC DISSOLVER PERFORMANCE WITH TITANIUM BASKET MODIFICATIONS

Modification	Cant (degrees)	Cell Potential (volts)	Duration (hr)	Current (amp) Maximum	Current (amp) Final	Current Failure Frequency (hr^{-1})
Ti basket	0	5.0 to 5.2	4.9	300	100	0
Ti basket	0	5.8 to 6.1	2.2	520	280	0
Ti basket	45	6.3 to 6.5	5.8	525	200	0
Ti basket + cone	0	5.5 to 6.0	2.0	515	320	0
Ti basket + cone	45	5.9 to 6.1	4.0	405	185	0
Ti basket with holes in base	45	6.2 to 7.0	5.5	180	150	0
Ti basket + wedge	45	6.3 to 6.5	2.1	360	235	0
Ti basket + wedge	10	6.6 to 7.2	5.0	535	200	0
Ti basket + cone + tapered annulus	10	5.9 to 6.0	6.0	445	200	0.17

All runs were made with the dissolver solution initially 8N nitric acid. An upper limit of 7 volts was imposed on operation of the unit. Part of the overall current decline was due to the declining acid and increasing salt concentrations. Only in the latter runs was acid added intermittently to maintain the solution in the 2-4N HNO_3 range. The contact resistance was sufficiently low in many of the runs with a titanium basket that the solution resistance was controlling. For example, the current was increased from 200 to 390 amp in the third experiment in Table VI by draining the product solution and replacing with fresh 8N nitric acid. Only one current failure has been observed to date, and that was corrected by lightly twisting a Teflon plunger which maintained pressure on the dissolving elements.

The conclusions drawn from these experiments may be summarized as follows:

(1) The contact resistance on titanium is sufficiently low that solution resistance is frequently a major contributor to current decline.

(2) Canting the dissolver 45 degrees does not create the same advantage as with a niobium basket [1]. This follows logically as a result of decreased

contact resistance. A cant of 10 degrees has proved helpful for addition of rods during operation.

(3) In the latter stages, the lower ends of the rods tend to round off (as with a platinum base) and the contact deteriorates. Hence, the most desirable situation is one where the lower end dissolves preferentially and new elements are added at the top.

(4) The use of a wedge at the bottom to maintain contact was less promising than a cone.

(5) Tapering the annulus toward the bottom showed considerable promise when used with a cone inside the basket. The rods were shortened and sharpened to points at the bottom, while the current remained in the 200- to 400-amp range for a six-hour run during which fresh acid was added intermittently, and new rods were added to replace those which had dissolved.

(6) The greater access to the cathode afforded by the perforated base is more than offset by the reduced contact area.

(7) Some pits on the wedge, cone, and basket resulted from arcing. However, the titanium components have to date exhibited better-than-anticipated resistance when the dissolver has been operated with fuel in it.

1.2 Silica Sludge (J. R. Aylward)

Particles in the silica sludge resulting from the dissolution of Nichrome rods were examined by microscope. The particles were agglomerated gelatinous spheroids ranging in size from 1 to 100 microns.

1.3 Electrolytic Dissolver Product Analyzer (D. P. Pearson)

A semicontinuous density monitor has been built and installed in the bench-scale electrolytic dissolver circuit. The monitor is shown in Figure 1. The observed solution may flow through stopcocks A and B, as shown by arrows. When B is closed, the solution flows up the overflow tube C and rises into bulb D. Because of increased air pressure in the tube joining bulbs D and E, a reference solution of fixed density

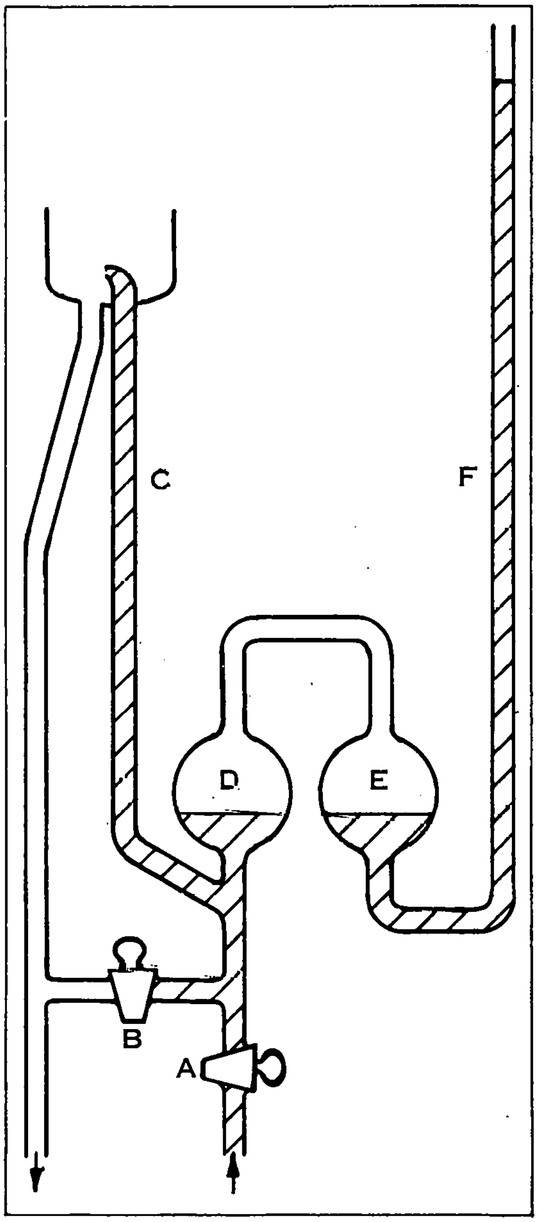

Fig. 1 Solution density monitor.

(saturated potassium nitrate) in bulb E is forced up sight tube F. The height of the air-solution meniscus in F is then read on an attached, calibrated scale, and is a linear function of the density of the observed solution. The reference solution height could be determined by electrical means for remote operation in highly radioactive fields.

The density monitor, in conjunction with a flow type conductance cell, has been applied to the analysis of Nichrome salt-nitric acid solutions, using the conductance-density data given in the previous quarterly report [1]. Limited results to date indicate a precision approximately the same as with the dual component analyzer which is based entirely on conductance measurements [1].

2. FUEL-SOLUTION-ELECTRODE INDIRECT CONTACT PRINCIPLE

(H. T. Hahn, Problem Leader)

The necessity for metal-metal contact may be avoided by designing the dissolver so that the fuel is oriented between the electrodes, and contacts only the solution [3]. Work this quarter has been concerned with a comparison of the corrosion, power consumption, and gas generation on noble metal electrodes in nitric acid using both direct and alternating current.

2.1 Platinum and Rhodium Electrode Evaluation (J. R. Aylward)

A calculation of the amount of off-gas formed at the inert electrodes of the dc solution contact dissolver was made. In nitric acid solution at 60°C the volume of oxygen formed at the anode is 1.5×10^{-4} ft^3/amp min. The amount of cathode gas will be less than 3×10^{-4} ft^3/amp min. These figures were confirmed experimentally. When 60-cycle ac is used, current densities equivalent to 6 amp/cm^2 dc can be attained without any gas evolution.

The use of 60-cycle ac with platinum electrodes in nitric acid results in the formation of a sponge-like surface of finely divided platinum due to the cyclic formation and reduction of platinum oxides. The depth of surface disintegration was found to be about 5 microns. The platinum surface in this state has a very large active area.

The corrosion rate of platinum electrodes with 60-cycle ac was found to be 1.8 mm/yr penetration and with dc less than 4×10^{-3} mm/yr penetration. Rhodium electrodes were also found to have an excessive corrosion rate with 60-cycle ac. The possibility of using graphite electrodes with ac is being investigated.

Power consumption was found to be less with ac due to depolarization and capacitance effects on the platinum electrodes. At 3 amp/cm^2 the ac-to-dc power consumption ratio was 36 percent, while at 6 amp/cm^2 the ratio increased to 48.5 percent.

3. INSULATOR MATERIALS FOR ELECTROLYTIC DISSOLVERS

(R. D. Fletcher, Problem Leader; L. A. Decker)

Tests on several plastic materials and one ceramic alumina for possible use as insulators and spacers in the electrolytic dissolver are complete. Values were obtained for the impact strength, compressive strength, and electrical resistivity of the four most-resistant materials, Kynar*, Marlex**, G-7 glass fabric silicone resin laminate, and ceramic alumina. Observations of other changes in these materials while undergoing irradiation in a dissolver solution environment were reported earlier [1, 2].

The Marlex retained its compressive strength up to 10^9 r total dose but the impact strength was drastically reduced at that exposure. The impact strength was retained at near its original value up to 10^8 r total dose.

The Kynar specimens possessed greater compressive strength than the Marlex to begin with and, although it dropped to approximately half its original value at 10^9 r, it was still greater than the value for Marlex. The impact strength did not drop off as rapidly for Kynar as it did for Marlex although its initial value was low compared to Marlex. The Kynar samples were completely disintegrated by the time they had received 2.8 x 10^9 r total dose. The Marlex samples became rubbery near 2 x 10^9 r and started to dissolve; they then became hard and brittle at 10^{10} r total dose.

The G-7 laminate had higher impact and compressive strength than the other materials even after an exposure of 10^{10} r total dose. One possible disadvantage of the G-7 laminate is that after long exposure solution penetrates between the laminations. This may or may not present difficulties during decontamination procedures.

The alumina ceramic specimens showed little or no change in any of their properties up to 10^{10} r total dose. All four materials have acceptable electrical resistivity after irradiation to 10^9 r total dose.

Higher acid concentrations will cause more rapid deterioration of G-7 laminate and Marlex. The only immediate effect on the G-7 is a weight loss as shown in Table VII.

TABLE VII

WEIGHT LOSS OF G-7 LAMINATE IN DISSOLVER SOLUTIONS(a)

Time (weeks)	2M HNO_3 (%)	6M HNO_3 (%)
1	5	7
2	9.5	12.5

(a) Solutions of various acidities at 105°C and containing 75 g/l of stainless steel components as nitrates.

A topical report giving the complete results of this program is being issued.

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* Trademark for a vinylidene fluoride resin produced by Pennsalt Chemicals Corp.

** Registered trade mark of Phillips Petroleum Co. for its family of polyolefin resins.

IV. NEW WASTE TREATMENT METHODS
(Section Chiefs: K. L. Rohde, Chemistry; M. E. Weech, Plant Processes)

1. DISPOSAL OF LOW-LEVEL RADIOACTIVE WASTES
(D. W. Rhodes, Problem Leader; M. W. Wilding, R. G. Butzman)

The laboratory study to investigate the use of ion exchange materials, particularly natural earth materials, for the removal of radioactive isotopes from low-level radioactive wastes at the NRTS was continued*. The presence in the ICPP fuel storage basin water of cesium-137 and strontium-90 in concentrations exceeding accepted levels for drinking water (National Bureau of Standards Handbook 59) suggested that experiments be directed toward decontamination of the effluent from this basin. Accordingly, column experiments were conducted using water from the fuel storage basin as feed, and Dowex 50W-X8 cation exchange resin and an earth material high in clinoptilolite as solid ion exchangers. These materials were chosen from among several possible materials because of high equilibrium distribution coefficients obtained in batch experiments.

Fixed bed columns approximately 100 cm long were used for the experiments. Due to the higher flow rate in the ion exchange column [≈ 5 gal/(ft^2)(min)] compared to the mineral column [≈ 0.2 gal/(ft^2)(min)], the experimental work was essentially completed for the resin column during this report period. A comparison of breakthrough values for some of the waste constituents using the resin in the hydrogen and sodium forms is shown in Table VIII.

TABLE VIII

BREAKTHROUGH VALUES (1%) FOR ICPP STORAGE BASIN WASTE CONTAMINANTS CONTACTING DOWEX 50W-X8 RESIN

Waste Constituent	Sodium Form Resin (column volumes)	Hydrogen Form Resin (column volumes)
Cesium	380	500
Total hardness	510	615
Strontium	775	> 775

The hydrogen form of the resin is significantly more effective than the sodium form. Regeneration with 6M nitric acid solution was accomplished with about 10 column volumes of acid. Approximately 99 percent of the total activity was removed during the regeneration.

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* Work performed under special arrangement with the IDO Health and Safety Division.

The mineral columns have received approximately 220 column volumes of feed to date with cesium and strontium still below one percent breakthrough in the column effluent. Both water-washed material and acid-washed earth material (to remove carbonates) are being tested in the column experiments. No apparent difference in their ability to remove radioisotopes from solution has been detected.

2. DECONTAMINATION OF ALUMINUM NITRATE BY MULTISTAGE MELT-FREEZE TECHNIQUES

(M. E. Weech, D. W. Rhodes, Problem Leaders; B.E. Paige)

Methods of reducing the considerable and continually growing inventory of radioactive aluminum waste volumes have been under study at the ICPP for some time. The fluid-bed calcination is one such approach. An engineering evaluation of a second approach, that of decreasing waste volumes by separating inert aluminum nitrate from the radioactive constituents by a melt-freeze approach, was started in November 1961. The results of this study indicated that large reductions in waste volume would be attained, and further showed that very favorable economics for the operation were possible through the use of a novel multistage, counter-current, continuous melt-freeze apparatus which appears well adapted to the aluminum nitrate-nitric acid-water system. A proposal was presented in February 1962 to the AEC to undertake development work on the proposed apparatus and process [4]. The following paragraphs report work done on phase relationships, physical properties, decontamination factors, and flow sheet variables required to confirm basic assumptions in the flow sheet and to supply design information for the proposed melt-freeze apparatus.

A single-stage laboratory model of the apparatus is shown in Figure 2. This model was used to demonstrate the ability of molten $Al(NO_3)_3 \cdot 9H_2O$ (mp 73°C) to flow through the tray perforations and to refreeze on the cooled surface below. In a plant unit, the trays are stacked one above the other and the tray temperatures alternated from hot (≈80°C) to cold (~10°C) so the aluminum nitrate will melt on alternate trays, flow through the tray perforations, and refreeze on the tray below. At suitable intervals the heating and cooling streams to the trays will be reversed. The cold tray then becomes hot and the crystals remelt and flow downward to the next cold tray below. The aluminum nitrate flows down through the trays counter-current to a continuous 60 percent nitric acid flow. It is essential to the operation of this unit that the aluminum nitrate be introduced and remain throughout the melt-freeze apparatus as $Al(NO_3)_3 \cdot 9H_2O$. The octa-hydrate has a higher melting point. Based upon the findings of the laboratory single-stage unit, a four-stage pilot unit is being constructed.

Figure 3, the operating diagram for the melt-freeze process, uses phase data for the system HNO_3-H_2O-$Al(NO_3)_3$ derived from Milligan and Inamara [5] (up to 60°C) together with data for 80°C which were obtained experimentally. The second phase observed at 80°C was solid, presumably a lower hydrate of aluminum nitrate. The heavy line from 60% HNO_3-40% H_2O to 57% $Al(NO_3)_3$-43% H_2O is the "operating line" for the second through the n^{th} stages of the melt-freeze process since it represents all proportions of dissolved $Al(NO_3)_3 \cdot$

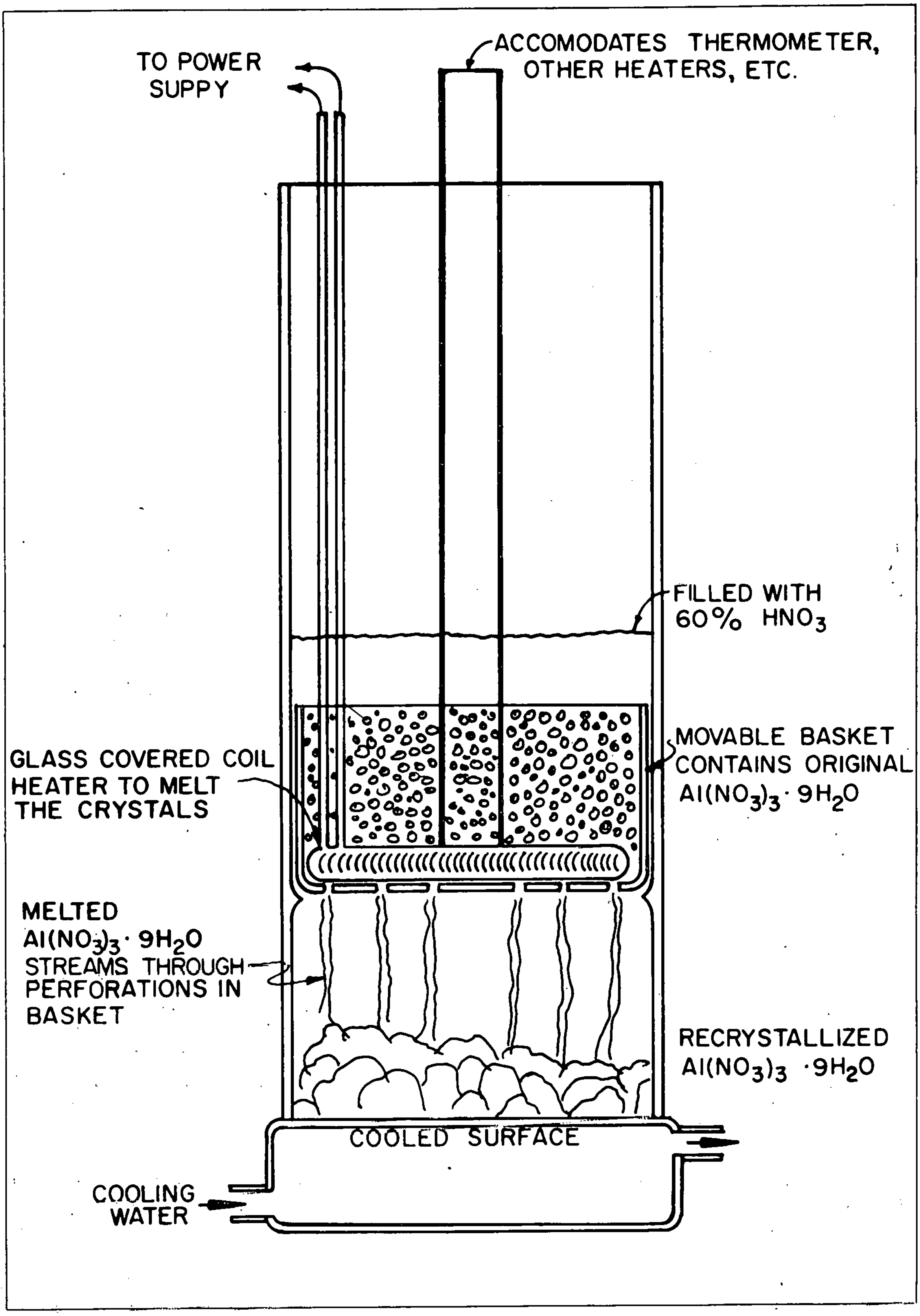

Fig. 2 Single-stage aluminum nitrate melt-freeze decontamination unit.

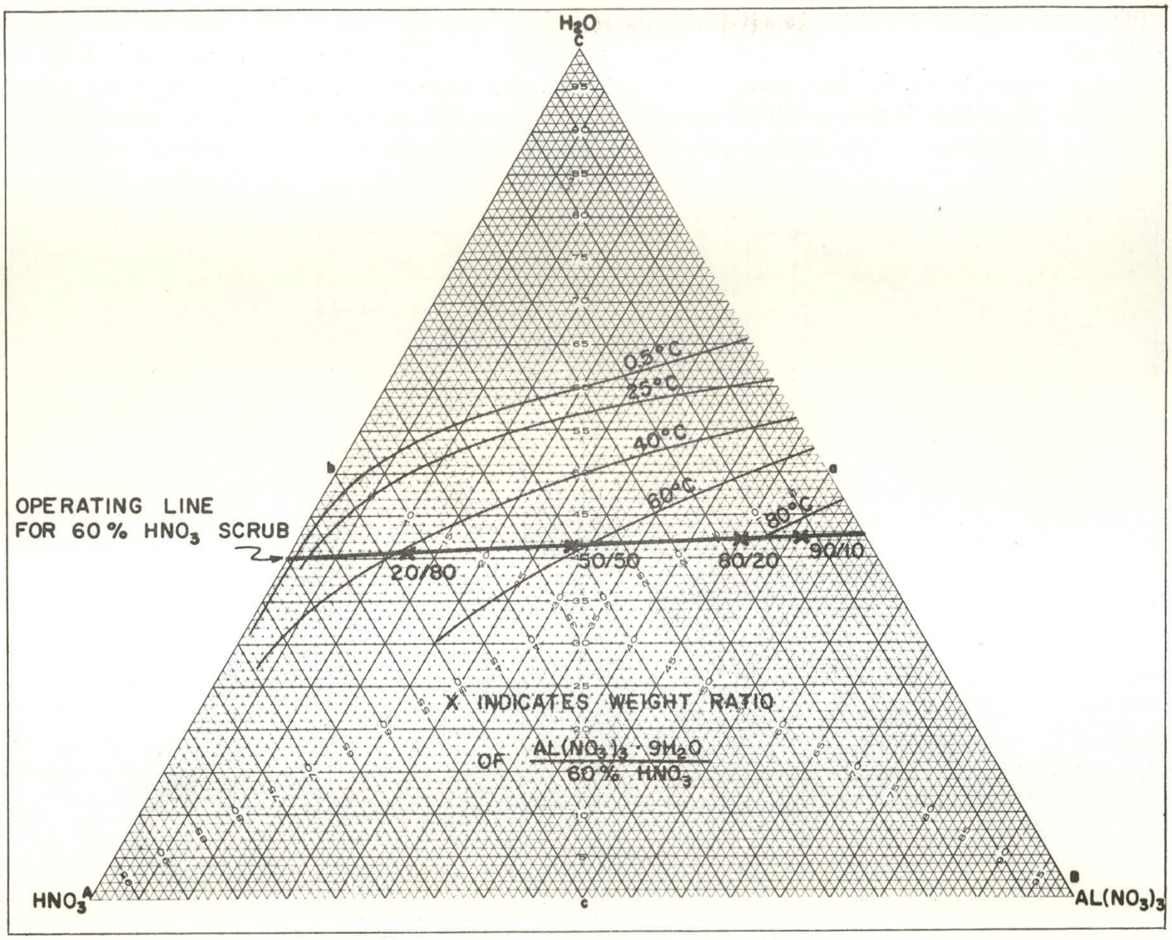

Fig. 3 Operating diagram for aluminum nitrate melt-freeze process giving ANN solubility data.

$9H_2O$ in 60 percent nitric acid. A few of the compositions [weight ratio $Al(NO_3)_3 \cdot 9H_2O/60\%\ HNO_3$] are indicated by points along the line. Similarly, "operating lines" can be drawn for other concentrations of nitric acid scrub. Calculations indicate that, in using a 10-to-1 weight ratio of feed to scrub, the $Al(NO_3)_3 \cdot 9H_2O$ carried in the scrub will be 0.4 percent of that fed with a 60 percent nitric acid scrub at 25°C.

The diagram indicates that in actual operation, if the stage-phase ratio for the process [weight ratio $Al(NO_3)_3 \cdot 9H_2O/60\%\ HNO_3$ in a stage] were about 50/50, the midpoint of the operating line, the system would be workable for plant application. Crystallization in the first stage probably will not follow this operating line since a pure molten aluminum nitrate feed will not be a homogeneous solution.

Calculations of material balances were made to establish the parameters for the feed and scrub which will produce a maximum yield of $Al(NO_3)_3 \cdot 9H_2O$ with a minimum quantity of aqueous waste in the operation of the continuous unit. Parameters varied were the concentration of aluminum nitrate and nitric acid in the feed, and the concentration and flow rate of the nitric acid scrub. The concentration of aluminum nitrate and nitric acid in the feed have a greater effect on the aluminum nitrate yield and aqueous waste volume than either the nitric acid concentration of the scrub or the ratio of the feed to scrub.

The feed must therefore be evaporated to as high a concentration of aluminum nitrate as possible. Phase data for 80°C in Figure 3 show that the highest feed concentrations which will be completely homogeneous solutions lie above and to the left of the 80°C isotherm. Within the narrow limits of interest for a feed material, increasing the nitric acid concentration in the feed improves the yield of $Al(NO_3)_3 \cdot 9H_2O$, but lowering the aluminum nitrate creates a greater volume of aqueous waste. Higher temperatures will not increase the solubility significantly but will increase the decomposition of nitrate. Density measurements at 80°C showed that existing formulas [6] for HNO_3-$Al(NO_3)_3 \cdot 9H_2O$ mixtures can be applied to the highly concentrated feed solutions.

3. IMPREGNATION OF CALCINED ALUMINA WITH SULFUR

(C. M. Slansky, D. W. Rhodes)

It is recognized that the calcined product from a fluidized bed calciner does not have a sufficiently low leachability or high integrity for ultimate permanent storage. Therefore, various post-calcination treatments of calcined alumina have been under consideration at the ICPP. One such treatment is the impregnation of inter-particle voids of the alumina by fused salts or molten metals like aluminum, thereby reducing leaching rate, increasing the thermal conductivity, and making the material free of dusting and readily accountable [7]. A similar process using sulfur has been investigated recently at the ICPP.

In preliminary experiments on the impregnation of calcined alumina from the DWCF with molten sulfur, the casting was essentially free of voids. Visual observation of a sectioned piece and the measured density both indicated that nearly all of the alumina particles had been completely penetrated by the molten sulfur. The deep penetration of the particles by sulfur, and the absence of sulfate compounds, indicate that the material is at least as resistant to leaching as the material prepared by calcination in molten sulfur by a process recently developed by duPont [8]. Also, because the molten sulfur is aspirated into a container filled with the calcined material, the final bulk volume is not increased by the sulfur and the alumina distribution in the casting should remain unchanged even if the centerline temperature exceeds the sulfur melting point. Sulfates and sulfides are not formed in the simple S-Al_2O_3 system, nor is stirring necessary to get the desired penetration of the alumina particles by molten sulfur.

V. WASTE CALCINATION DEVELOPMENT AND DEMONSTRATION

(Section Chiefs: J. A. Buckham, Development Engineering; K. L. Rohde, Chemistry)

1. OPERATION OF THE DEMONSTRATIONAL WASTE CALCINING FACILITY

(L. T. Lakey, Problem Leader; G. E. Lohse, P. N. Kelly)

The results of DWCF run 9, started last period [1] and completed this period, led to the selection of: (a) amorphous alumina as the preferred bed material, and (b) transfer of cyclone fines to storage with the bed as the preferred method of cyclone fines disposition. The production of amorphous alumina, which is less friable than the alpha crystalline phase, is effected by the inclusion of boric acid in the aluminum nitrate-nitric acid feed solution. Alpha alumina can be produced by omitting the boric acid and providing 0.06 - 0.08M sodium nitrate in the feed. Amorphous alumina has an additional advantage in that particles of the material which escapes from the primary cyclone are soluble in the nitric acid quench and scrub solution, resulting in a low concentration of undissolved solids in the recirculating scrub solution. This minimizes erosion and prolongs quench pump life. When compared with the return of cyclone fines to the calciner, the transfer of these fines to storage minimizes fines carry-over to the scrub system.

In run 9, 885 hours of operation were accumulated. Amorphous alumina was produced in the absence of boric acid until the feed sodium concentration was increased to change the alumina crystalline form from amorphous to alpha. When amorphous alumina was being produced, the cyclone fines were transferred to storage. When alpha alumina was being produced, the cyclone fines were either transferred to storage or returned to the calciner. Return of fines to the calciner resulted in rates of solids carry-over from the primary cyclone which were up to twice those obtained when cyclone fines were transferred directly to storage. Maximum fines carry-over to the scrub system was 33 percent of the nominal product rate with an alpha bed and fines return to the calciner. Minimum fines carry-over was 15 percent with an amorphous bed and fines transfer to storage.

Recycle of scrubbing solution to the feed was conducted satisfactorily for the first time during the final 10 days of the run. The high undissolved-solids content of the scrubbing solution associated with the high alpha bed did not interfere with the operation.

Preparations are in progress for run 10, during part of which sodium-24 will be added intermittently to the calciner feed to test the efficiency of the off-gas cleanup system.

1.1 Solids Carry-over

Solids carry-over from the calciner primary cyclone to the off-gas quench and scrub system during previous test runs has consistently exceeded the design loading. In spite of these high solids loadings, however, off-gas cleanup has been adequate. The highly efficient liquid scrub system collects the overwhelming majority of the particulate matter which passes overhead from the primary cyclone. For ultimate cleanup, this system is backed up by fixed silica gel beds and absolute filters. High-solids loading in the liquid quench and scrub system has contributed to plugging, erosion, and decontamination difficulties. The major DWCF engineering effort to date has involved the resolution of this problem. A number of approaches have been investigated to minimize the fines problem, including:

(1) Installing a baffle in the calciner vapor space to deflect solids away from the cyclone entrance

(2) Increasing the cyclone pressure drop, and thus its efficiency, by blanking several of the elements in the multiclone unit

(3) Minimizing calciner bed attrition by installing deflector discs (modified bubble caps) over the holes in the air distributor plate

(4) Minimizing quench pump difficulties by installing vertical, suspended, centrifugal pumps having non-wetted bearings and packing

(5) Minimizing the solids elutriation rate by reducing the fluidizing air rate

(6) Transferring cyclone fines to product storage instead of returning them to the calciner bed

(7) Determining that amorphous is the desirable form of alumina to minimize attrition.

(8) Using three feed nozzles instead of two, to provide better distribution of feed within the fluidized bed.

(9) Using an external cyclone dipleg to eliminate gas backflow which was characteristic of an internal open dipleg

Other planned changes include:

(1) Replacing the multiclone unit with a single-element cyclone of conventional design

(2) Replacing the 2-1/2-inch-diameter deflector discs over the distributor plate air holes with 3-inch-diameter discs

As a result of all these changes, scrubbing solution loadings of total solids will be reduced nearly to design values, and insoluble solids loadings will be reduced to considerably below the design value.

As mentioned in the previous quarterly report [1], an external cyclone fines collection system was installed prior to run 8. This external system eliminated the use of the internal dipleg and provided more flexibility in operation by permitting fines to be returned to the calciner or transferred to storage.

During run 8, excessive elutriation of the amorphous bed was experienced. However, the cyclone knocked out most of the elutriated solids and allowed only 12 pounds per hour of solids (20 percent of theoretical product rate) to reach the quench and scrub system. Most of these solids dissolved, leaving an undissolved solids content of only 0.2 weight percent in the recirculating scrubbing solution. This solution was handled adequately, but certainty of maintaining an amorphous bed while feeding actual waste has not been proven. Run 9 was undertaken to investigate the cyclone solids carry-over with an alpha bed while disposing of fines to storage. For this run a louvered baffle was installed in the calciner vapor space to reduce elutriation. During part I (Table IX) of the run, when amorphous alumina was produced and fines were

TABLE IX

OPERATING CONDITIONS, PRODUCT PROPERTIES, AND SOLIDS CARRY-OVER FROM THE DWCF, RUN 9

Conditions: Feed rate, 80 gph; nominal product rate, 60 lb/hr; superficial fluidizing velocity, 0.7 ft/sec; bed temperature, 400°C.

Part No.	Nozzle Air-to-Liquid Volume Ratio(a) (NAR)	Alpha Alumina Content (wt%)	Mass Median Particle Diameter of Product (mm)	Solids Collected From Cyclone Dipleg (lb/hr)	Solids Rate in Off-Gas from Cyclone (lb/hr)
1	300 to 500	0	0.25 to 0.65	16	9
2	300 to 400	65	0.65 to 0.45	24	11
3	400	70	0.45 to 0.53	120(b)	20
4(c)	400	75	0.53 to 0.59	—	10
5(d,e)	400	75	0.59 to 0.55	27	8

(a) Air volume measured at the metered temperature and calciner vacuum.

(b) Cyclone fines were returned to bed in part 3; in all other cases, fines were removed to storage.

(c) Feed proportioned between three nozzles in part 4; two nozzles used in all other cases.

(d) Scrubbing solution was recycled to the feed for part 5. Raw feed rate was then 60 gph, recycle rate was 20 gph; the combined rate to the calciner was 80 gph.

(e) Superficial fluidizing velocity increased to 1.1 ft/sec in part 5 only. This is the linear velocity that would be attained by the fluidizing air in the empty vessel at the operating temperature.

transferred to storage, the baffle did reduce the bed elutriation rate to 25 to 35 pounds per hour, compared to 150 to 200 pounds per hour without the baffle. The reduction in solids elutriation was effected by retaining particles larger than 0.1 millimeter in the bed. Theoretically, such relatively large particles should not be elutriated by the fluidizing velocities (approximately 1 ft/sec) employed, even if no baffle was used. The presence of such large particles in the cyclone inlet can only be accounted for by the kinetic energy imparted to them by bursting bubbles at the surface of the fluidized bed. Indeed, such a phenomenon was observed through a plexiglass flange when the calciner was being fluidized at room temperature between runs 8 and 9. The baffle, then, merely serves as a deflector for most of the large particles. If this is correct, smaller particles should pass through the baffle to the cyclone, resulting in a smaller particles size in the fines passing the cyclone. A general trend in this direction is observed in Table IX.

In part 2 of the run, after the bed was converted to 65 percent alpha, the solids elutriation rate increased slightly and the mean diameter of elutriated particles decreased. The latter may be due in part to higher particle densities associated with alpha alumina. In spite of higher cyclone inlet loadings, the effluent loading was relatively unchanged at 15 to 18 percent of theoretical product rate.

In part 3, the cyclone fines were returned to the calciner instead of being transferred to storage. Obviously, this increased the inventory of fines in the calciner. As a result the bed elutriation rate increased four-fold as shown in Table IX. However, cyclone effluent loading was held to a two-fold increase, bringing solids carry-over to 33 percent of theoretical product rate. The undissolved solids content of the scrubbing solution in part 3 became excessive.

In parts 4 and 5, the transfer of cyclone fines was diverted from the calciner to product storage. Bed elutriation and cyclone effluent loading both dropped to levels comparable to those obtained in part 2. The results of run 9 demonstrated that the problem of bed depletion did not exist with either an amorphous or an alpha bed when a baffle was used in the calciner vapor space to minimize bed elutriation. When cyclone fines are routed to storage, solids loading in the cyclone effluent is essentially the same (approximately 10 lb/hr) whether amorphous or alpha alumina is being produced. No difficulties were experienced in handling the scrubbing solution when operating with either type of bed when fines were sent to storage. When operating with an alpha bed, the higher undissolved-solids concentration would result in greater equipment wear.

1.2 Process Control

For the sake of flexibility, it is desirable to be able to operate with either alpha or amorphous material, and with fines transfer either to the calciner or to product storage. From the standpoint of calciner control alone, run 9 demonstrated the desired flexibility. However, as mentioned in the preceding section, operability with an alpha bed is limited to the process in which fines are transferred directly to storage.

Feed simulating the contents of ICPP waste tank WM-185 (1.74$\underline{M}$ aluminum nitrate, 0.59$\underline{M}$ nitric acid, and 0.04$\underline{M}$ sodium nitrate) was calcined in run 9 at an equivalent product rate of 60 lb/hr. A sand starting bed was used, and boric acid was omitted from the feed in order not to inhibit alpha alumina formation. After nine days of operation (90 percent bed replacement), the alpha alumina concentration was only 2.2 percent, and the mass median particle diameter (MMPD) was increasing. This result was similar to that obtained in run 7 [1]. At this point, the nozzle air-to-liquid ratio (NAR) was increased to 500 to arrest continued particle growth. The undissolved-solids content of the scrubbing solution was only 0.2 weight percent, and the dissolved aluminum was 2.0 percent. These conditions were stable by the end of part 1 of the run (Table IX). For part 2, the sodium concentration in the feed was increased from 0.04 to 0.06$\underline{M}$ (in run 7 it had been increased from 0.04 to 0.08$\underline{M}$), and the NAR was reduced to 300 to prevent excessive attrition of the expected friable alpha alumina. Two days later, the alpha alumina had increased as desired to 65 percent, but the MMPD unexpectedly continued to increase. Five days after the increase in sodium concentration, the NAR was raised to 400, constituting part 3 of the run. Thereafter, the average MMPD stabilized near 0.5 mm. During part 3, the cyclone fines were returned to the bed. After the particulate loading in the cyclone off-gas increased to 20 lb/hr, the cyclone fines were again routed to product storage; this portion of the run constituted part 4. By this time the alpha alumina concentration had stabilized at 75 percent. The undissolved-solids content in the scrubbing solution increased to 3.0 weight percent, and the dissolved aluminum stabilized near 0.9 percent. In part 4, calciner feed was introduced through three nozzles. Two nozzles were used in all other parts of the run. Effects of three nozzles, if any, are not discernible from effects of two nozzles.

During the final 10 days of run 9 (part 5), scrubbing solution was successfully recycled to the raw feed even though the slurry concentration was significantly higher than the design flow sheet value. For ease of operation in previous parts of the run, the scrubbing solution had been discarded at the equivalent recycle rate (20 gal/hr). For operation with radioactive feed, of course, there is no alternative but to recycle scrubbing solution to the raw feed in order to control solids concentration in the recirculating scrubbing solution. Successful handling of the concentrated (4 percent) slurry leads to the conclusion that no problems should be encountered in handling the less-concentrated (0.1 to 0.2 percent) slurry resulting from production of the soluble amorphous alumina. In part 5, it was necessary to increase the superficial fluidizing velocity to 1.1 ft/sec to maintain thorough mixing and bed temperature uniformity. In other parts of the run, it was 0.7 ft/sec.

The run was terminated voluntarily as scheduled.

1.3 Equipment Performance

During the run, one of three electromagnetic (EM) flowmeters in the feed system failed. Feed control was switched to the original differential pressure (DP) type of control. As determined previously, DP control is not satisfactory because it is erratic and does not provide positive rate control. The effect of this substitution on the run is difficult to assess. Generally, the imposition of erratic feed rate on an already complex system is undesirable. Poor atomization resulting from an excessive feed rate may lead to bed caking; fluctuating feed rate results in bed temperature control difficulties. Inspection after the run revealed longitudinal cracks in the vitreous enamel liners of all three EM meters. The most likely cause of cracking is adjudged to be mechanical strain attendant in the connected piping. The meters were returned to the manufacturer for repairs.

A tandem thrust bearing on an off-gas blower failed during the run. Cause of the failure is believed to be excessive torque imposed by improper alignment, inadequate bearing support, or strain caused by piping stresses. The spare blower performed satisfactorily during the remainder of the run.

A post-run inspection of the three feed nozzles revealed slight caking on one of them. It is unlikely that this caking disturbed nozzle performance significantly. Nozzle leakage after shutdown indicated that the feed control valves were not holding.

All three feed control valves and one quench solution control valve were removed for inspection. All four valves contained Stellite plugs and seats which were severely corroded. The ICPP had previously experienced severe corrosion with Stellite valves in thermally hot concentrated nitric acid. Calciner service also includes undissolved solids which may contribute some erosion in addition to corrosion of Stellite. The valves involved are being rebuilt with various stainless steels (17-4 PH, 440-C, and 347) to determine the most resistant material in actual service tests. All Stellite valves in corrosion service will be replaced with the most resistant material available.

2. PILOT PLANT DEVELOPMENT STUDIES

(L. T. Lakey, B. M. Legler, Problem Leaders;
B. P. Brown, W. B. Kerr, J. E. Arnold)

2.1 Control of Solids Carry-over with Wet Spray Return

The concept of mixing recycled cyclone fines with calciner feed provides a possibility of minimizing fines carry-over from the primary cyclone. As reported previously [1], returning dry cyclone fines to the calciner results in high rates of solids carry-over in the cyclone off-gas. Operation of the two-foot-square calciner was continued to test the concept of deliberately combining recycled fines and raw aqueous feed. For this test, a new combination cyclone fines return jet and feed nozzle, as shown in Figure 4, was constructed and installed in the vapor space of the calciner. The cyclone itself was of conventional design and contained a hardened, stainless steel, cylindrical tip which was welded to the bottom cone outlet of the cyclone. Two concentric lines were routed down the axis of the cyclone to provide for feed and jet air introduction. The central feed line, which also was made of hardened stainless steel, terminated at the lower end of the hardened cyclone tip mentioned above. The annular air line terminated in an annular orifice within the bottom cone of the cyclone and formed the primary air nozzle for the jet. This primary air plus that aspirated from the cyclone by the jet action served to atomize the raw feed. Test stand data showed that this jet was capable of inducing a secondary air mass flow of 50 percent of the primary air mass flow while working against the usual 10-inch water head. The test data also indicated that the jet could continue to operate satisfactorily at working heads of up to 20 inches of water, so that it had the apparent capability of continuing to function during bed level surges. The intent was that the resulting spray pattern would cause the recycled fines to be coated along with feed solution onto larger particles or to serve as nuclei for normal particle growth particles. Initial results were disappointing; severe erosion occurred in the new device during the first few days of testing and precluded a satisfactory analysis of its capability to perform as intended. The hardened cyclone tip and the exposed feed line which protruded from the annular air jet orifice to the cyclone tip were eroded severely.

Although it was recognized that the jet efficiency would be reduced thereby, both eroded pieces were cut off in order to permit operation to continue. The modified nozzle is shown in Figure 4 together with the original design. Upon resumption of operation a 5 percent alpha bed was used and stable operation was attained. The MMPD responded to adjustments in the NAR in a manner similar to that observed with the regular feed nozzle used in previous runs.

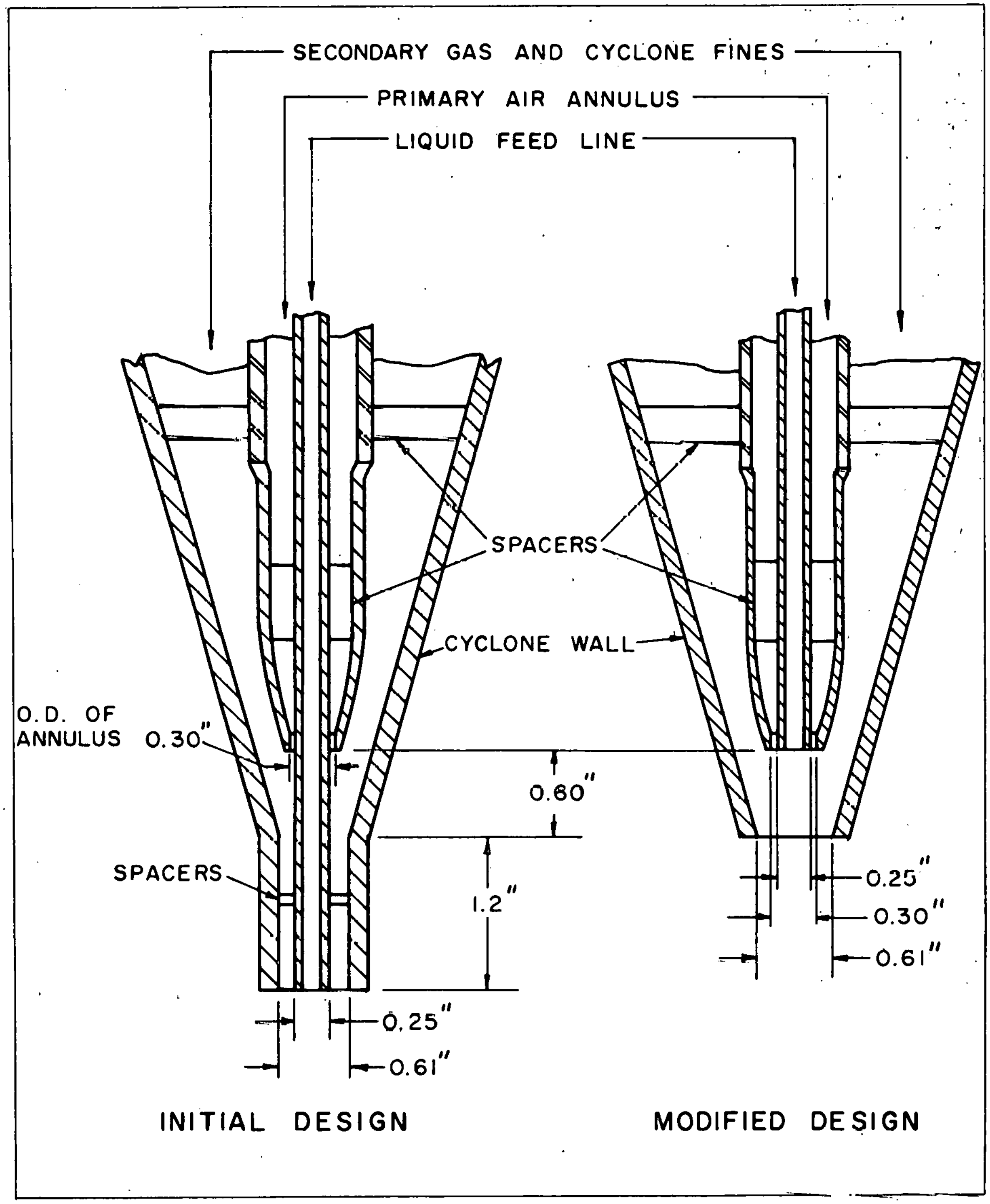

Fig. 4 Combined fines return and feed nozzle jet.

At primary jet air velocities below 225 ft/sec, backflow occurred in the jet as evidenced by bed size material appearing in the cyclone off-gas. At primary jet air velocities above 400 ft/sec, high scrub loadings of particles considerably smaller than bed size were obtained. From the data obtained during this limited operating period, positive conclusions cannot be drawn about the effectiveness of combining feed and fines. With the modified cyclone fines return jet and feed nozzle in use, fines carry-over in the cyclone off-gas varied from 7 to 52 percent of theoretical product rate. In one part of the run, a regular feed nozzle was used while cyclone fines were returned to the calciner by the fines jet in the cyclone cone section. At that condition, solids carry-over was more than 100 percent of theoretical product rate; obviously, the bed was being depleted. Continued study of combining feed and fines return is being suspended for the time being in favor of investigations involving immediate DWCF support.

2.2 Control of Particle Size by Addition of "Seed" Material

Control of MMPD by varying the NAR is sometimes undesirable because high NAR values can result in excessive fines generation due to attrition. Theoretically, the MMPD can be controlled instead by the addition of "seed" particles which grow to the desired size.

Particle size control by the addition of sand nuclei was demonstrated in the two-foot-square calciner [1]. Because of the large sand MMPD (0.26 mm), excessive quantities were required (about one-third of the product rate) to furnish sufficient "seed" area for product deposition. In current work in the 12-inch calciner, sand in the 80- to 115-mesh range appears to be satisfactory. For a feed rate of 10 l/hr and an NAR of 200, the product MMPD was 0.6 to 0.7 mm when 41 g/hr (6 percent of product rate) of sand seeds were added. Without sand seed addition, an NAR of 650 was necessary to stabilize the MMPD. Sand seeds in the 100- to 200-mesh range were not satisfactory because of excessive elutriation of the seeds. Additional studies on the control of particle size by sand seeding are planned in the two-foot-square calciner.

3. BASIC LABORATORY CALCINATION STUDIES

3.1 Stainless Steel and Nichrome Nitrate Calcination (H. T. Hahn, Problem Leader; E. M. Vander Wall)

The thermal decomposition study of the stainless steel nitrates [2] was completed and the results compiled in IDO-14597 [9]. The conclusions were as follows:

(1) Thermal decomposition of chromium nonahydrate results in the formation of a mixed chromium oxide. This material is stable to 390°C; then it begins to decompose to chromic oxide.

(2) Thermal decomposition of nickel nitrate hexahydrate results in the formation of an intermediate material which has the empirical formula $Ni(NO_3)(OH) \cdot 1/2\ H_2O$. On further heating the latter decomposes to nickel oxide.

(3) Thermal decomposition of ferric nitrate nonahydrate produces a crystalline intermediate, either a basic nitrate or lower hydrate of ferric nitrate, which further decomposes to alpha ferric oxide.

(4) The presence of chromium prevents the formation of crystalline products during the decomposition of stainless steel nitrates at temperatures up to 450°C in air.

(5) Calcination of Nichrome and stainless steel nitrates to the oxides appears to be feasible in the 400 to 500°C temperature range.

VI. THE ARCO PROCESS
DISSOLUTION OF FUEL ALLOYS IN MOLTEN-CHLORIDES
(Section Chief: K. L. Rohde, Chemistry)

The ARCO process [10] employs molten lead chloride as a solvent for reactor fuel alloys. Zirconium and aluminum alloys dissolve readily in the molten salt, and the respective chlorides are volatilized; uranium and thorium also dissolve readily, but exhibit no volatility. Dissolution of stainless steel requires the addition of chlorine to the melt in order to effect dissolution. The lead chloride-chlorine system also dissolves chromium and niobium at feasible rates.

To investigate the possibility of a totally pyrochemical process, a study of uranium volatilization from uranium chloride-lead chloride melts with excess chlorine has been undertaken. Volatilizations up to 90 percent of the total uranium have been achieved at 550°C. Proportionately less chlorine is required as the uranium composition of the melt increases.

1. URANIUM CHLORIDE VOLATILIZATION
(H. T. Hahn, Problem Leader; E. M. Vander Wall, D. L. Bauer)

A nitric acid leach has been used to recover the uranium from the salt matrix produced by the ARCO process [10]. As an alternative to this procedure, a study has been initiated to determine the feasibility of volatilizing uranium from the salt matrix in a stream of chlorine. A series of experiments was conducted at 550°C in which various amounts of uranium were dissolved in lead chloride (20 g) to obtain the desired uranium concentration. The principal products from the reaction of uranium metal and molten lead chloride are uranium trichloride and lead. Since the uranium trichloride-lead chloride system solidifies with approximately 30 mole percent uranium present at 550°C, it was necessary to pass chlorine into the reaction mixture as the uranium metal dissolved in order to achieve initial melts of higher uranium content. This procedure converted the lead back to lead chloride and also converted the uranium trichloride to the tetrachloride which remains a completely molten system to at least 80 mole percent uranium in lead chloride at 550°C. No uranium volatilized during the metal dissolution step. In fact, no volatilization occurred until two moles of chlorine per mole of uranium had reacted with the melt, indicating that the uranium was in the form of the tetrachloride. Volatilization was achieved by passing excess chlorine through this resultant melt. The data are presented in Table X.

Increasingly favorable conditions for volatilization of uranium chloride from the melt occur as the initial uranium concentration is increased. The mole ratio of excess chlorine used to uranium volatilized decreases rapidly as this concentration is increased. At 550°C and with higher uranium concentrations, it does not appear possible to obtain a final melt which contains less than 20 mole percent uranium. Practical operating conditions would therefore require a relatively low volume of dissolvent (to minimize uranium inventory) containing a relatively high concentration of uranium (to maximize volatilization).

TABLE X

VOLATILIZATION OF URANIUM CHLORIDE IN A CHLORINE STREAM FROM THE URANIUM CHLORIDE-LEAD CHLORIDE SYSTEM AT 550°C

Initial Melt Composition (mol% U)	Chlorine Usage (moles excess Cl/mole U volatilized)	Total U Volatilized (%)	Final Composition (mol% U)	
			Sublimate	Melt
21.0	82.2	17.6	72.6	17.7
20.7	65.3	32.7(a)	59.8	15.8
37.0	21.9	30.5	92.8	29.2
36.5	36.9	21.6	95.4	31.5
36.4	34.0	34.5	88.0	27.2
36.8	33.1	48.7	87.9	26.0
36.4	35.8	43.3	90.5	25.7
54.0	11.3	57.8	94.2	33.3
54.6	17.9	82.3	93.5	20.0
53.8	19.1	74.8	96.8	23.8
52.1	28.8	77.9	90.3	19.8
55.6	24.0	80.8	94.8	21.7
75.5	12.4	87.6	96.2	28.3
77.2	6.4	90.0	94.9	23.1

(a) The temperature used for this experiment was 600°C.

The results of another experiment demonstrated the necessity of using chlorine in the volatilization procedure. Approximately 150 moles of argon were passed through a melt (54.7 mole percent uranium in 20 g of lead chloride) which had been completely chlorinated to form uranium tetrachloride. Only 2 percent of the uranium volatilized. This was followed by the passage of 1.7 moles of chlorine through the melt which caused 57 percent of the uranium to be volatilized. This indicates that perhaps a higher uranium chloride is involved in the volatilization mechanism. However, the only crystalline material in the sublimate is uranium tetrachloride while the only crystalline material in the melt after cooling is lead chloride. These results were obtained by X-ray diffraction analysis. It has not been possible to obtain a consistent value for the chloride-to-uranium ratio in the sublimate.

VII. BASIC PROCESS STUDIES AND EQUIPMENT DEVELOPMENT

(Section Chiefs: M. E. Weech, Plant Processes; K. L. Rohde, Chemistry)

1. EXPERIMENTAL AIR PULSER

(E. E. Erickson, Problem Leader; S. J. Horn)

The study of methods of determining the amplitude and mean operating position of the pulse in an air pulser is continuing. The electronic integration of a suitably conditioned flowmeter signal has proven to be successful for a Ramapo flow transducer [1]. Recent improvements in a filtering circuit for the demodulated flow signal from a Foxboro magnetic flowmeter may allow this flowmeter to be used in the same manner. However, at the present state of development, the system with the Ramapo flow transducer is superior to the Foxboro magnetic flowmeter in that the former has a more reliable drift characteristic.

A possible alternate method that is being investigated involves the use of a capacitance type of level detection instrument. Such an instrument requires that a capacitance probe be installed in the air pulser leg, and determines the liquid level either as a change in effective electrode area or as a change in the dielectric constant of the fluids between the electrodes.

If the liquid in the pulser leg is highly conducting, as is the case with water, and the center electrode of the capacitance probe is covered with an insulating sheath, the liquid itself functions as an external concentric electrode. The capacitance change thus results from the change in electrode area as the liquid level changes. If the liquid is not conducting, as in the case of an organic extractant, the wall of the pulser leg functions as the external electrode, and capacitance change is the result of change in the dielectric constant as the relative amount of air and liquid between the electrodes varies. The change in probe capacitance is measured by making the probe part of one arm of a capacitance bridge. The output of the instrument is a nonlinear function of the total capacitance of that arm of the bridge, but can be made to be approximately linear for small changes in effective probe capacitance.

Preliminary tests of a 15-foot Teflon sheathed capacitance probe, with water as the external concentric electrode, have yielded anomalous values of probe capacitance. The exact cause of the anomalies has not been determined. However, since this mode of operation is not the usual form, it is believed that the use of an organic extractant will result in better operation.

2. PULSE COLUMN DYNAMICS

(E. E. Erickson, Problem Leader; L. A. Jobe)

A novel method has been used in securing flooding data to define disturbance regions for the dynamic tests in pulse column control studies. This involved the use of column weight control of the organic feed rate. The pulse frequency and amplitude and the aqueous rate were fixed; the column weight-controller set point was decreased stepwise and the column allowed to stabilize at the new column weight. This automatically regulated the amount of organic feed coming to the column. When the column finally reached flooding conditions, the column weight controller automatically reduced the organic feed rate instead of allowing it to increase, thus signifying flooding.

A series of tests varying the aqueous feed rate, with pulse frequency and amplitude as parameters, gave data leading to the curves shown in Figure 5. The slopes for the various conditions of pulse frequency and amplitude are similar and show that a much greater increase of aqueous flow than of organic flow is necessary to cause flooding. The relative importance of pulse amplitude and frequency also can be seen. From these curves and initial flow and pulser conditions, the size of a flow disturbance can be chosen to either cause or prevent flooding during transient pulse column control tests.

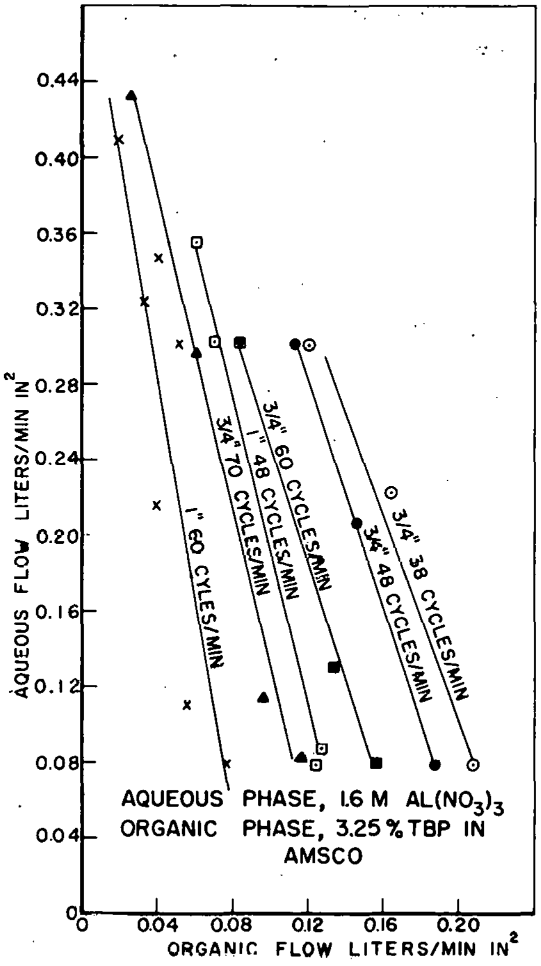

Fig. 5 Flooding flow rates for laboratory pulse column.

3. EVAPORATOR CONTROL
(E. E. Erickson, Problem Leader; L. A. Jobe)

Recommendations of instrumentation to provide good control for the new uranium salvage cell evaporator at a reasonable cost were made and adopted. The system includes: a computing relay for calculating true level by dividing column weight by density, a level controller to be used on start-up, a density controller which is automatically switched in when the minimum control range value of density is reached, and a selector manifold with master transfer switch. The low-level limit of the evaporator before steam is supplied to the heat exchanger will be achieved by setting the liquid-level control range at 70 to 90 percent of the overflow height. A disturbance may occur during the switch from level to density control; controller settings to minimize this will be calculated but may require modification in plant start-up procedures.

4. CALCULATIONAL TECHNIQUES FOR NUCLEAR POISONS
(E. E. Erickson, Problem Leader; W. G. Morrison)

The calculational technique [1, 2] developed for uniform plate spacing in the Rocky Flats experiments was used to show the relationship between U-235 concentration and plate spacing for safe storage of enriched uranium solution in large-diameter vessels. A solution height of 60 inches was used for a bare

36-inch-diameter vessel containing 0.138-inch-thick boron-stainless-steel plates. Boron content of the plates was 1.28 weight percent. Plate spacing for this system for a k_{eff} of 1.0 is shown in Table XI.

This work is continuing with other plate distributions and modifications of the calculational technique to give better agreement with the Rocky Flats results for the lower concentration solutions or wider plate spacings.

TABLE XI

PLATE SPACING VS U-235 CONCENTRATION

U-235 Concentration (g/l)	Edge-to-Edge Plate Spacing (in.)
475	0.72
237	1.11
127	1.63

5. REMOVAL OF TRIBUTYL PHOSPHATE FROM DILUTE AQUEOUS STREAMS

(H. T. Hahn, Problem Leader)

The removal of tributyl phosphate and its decomposition products from first-cycle aqueous streams will prevent further degradation and complex formation during product concentration. It has been shown previously that the removal of tributyl phosphate by means of an Amsco wash in a mixer-settler can be successful[1]. However, an aqueous-favoring phosphorus species, present in concentrations of about 0.01 millimoles phosphate per liter, and believed to be dibutyl phosphoric acid, cannot be extracted quantitatively into the organic phase. Means have been sought to remove the impurity from aqueous phases corresponding to back-extraction column and mixer-settler product. It has been established that dibutyl phosphoric acid and plant phosphorus species will absorb on hydrous zirconium oxide ion exchange crystals[1]. Tracer phosphorus also was removed from simulated mixer-settler products. Elution of the plant phosphorus species from the exchange crystals was accomplished on a small scale with dilute sodium hydroxide.

During this quarter synthetic tributyl phosphate degradation products were subjected to multiple extractions with Amsco, and absorption on zirconia in laboratory scale experiments, preliminary to pilot plant tests.

5.1 TBP Degradation and Absorption on Zirconium Oxide (D. L. Bauer, M. R. Bomar)

In support of the zirconium oxide crystal development program three additional experiments have been completed on a larger scale. In all cases a TBP-saturated, 0.02M uranyl nitrate-0.04M nitric acid solution was chemically degraded, equilibrated four successive times with Amsco (1/10 volume ratio), and the aqueous phase passed through a zirconium oxide bed (HZO-1). In the first two experiments the mesh size was -50+60; in the third it was -20+40. These are larger crystals than those used previously[1].

The degradations proceeded at close to the predicted rate (1% per hour at 70°C). In the first experiment the solution was heated at 76°C for 27 hours. Following four successive extractions with Amsco, the "unstrippable" phosphate analyzed 12.8 mg/1. This corresponds to 1.32 percent degradation per hour if all the "unstrippable" phosphate is HDBP. In the second experiment the solution was heated at 74°C for 66 hours. Here the "unstrippable" phosphate analyzed 23.3 mg/1. This corresponds to a degradation rate of 0.98 percent per hour.

Data for the absorptions on hydrous zirconium oxide are given in Table XII.

TABLE XII

ABSORPTION OF DEGRADED PHOSPHATE ON HYDROUS ZIRCONIUM OXIDE (HZO-1)

	Experiment 1	Experiment 2	Experiment 3
Crystal weight (g)	3.89	3.96	4.0
Mesh size	-50+60	-50+60	-20+40
Flow rate (ml/hr)	27	12	4
Flow rate (l/hr/lb)	3.15	1.38	0.45
Influent $PO_4^{\equiv}$ (mg/l)	12.8	23.3	23.3
Sample size (ml)	23	18	10
Effluent $PO_4^{\equiv}$ (mg/l)			
Sample 1-2	2.76	1.81	< 0.5
Sample 3-4	3.40	2.04	< 0.5
Sample 6	—	—	< 0.5
Sample 9	3.32	1.80	—
Sample 15	3.56	1.80	—
Sample 20	3.52	1.76	—
Sample 25	3.43	1.69	—
Sample 30	3.36	—	—
Sample 35	3.41	—	—
Average decontamination factor	3.7	13.2	> 46

Effluent samples in each experiment are of equal volume and are numbered in sequence. Their analyses indicate that the absorptive capacity was not reached. However, the absorption step did not produce the decontamination at 3.15 l/hr/lb anticipated from earlier work with 100- to 120-mesh particles. This probably reflects less favorable absorption kinetics within the larger crystal particles. Diffusion into the particle apparently controls the absorption. The flow rate was reduced with much more satisfactory results in experiment 2. In experiment 3 still larger particles were used and the flow rate reduced again. In the latter case the decontamination was excellent, perhaps more than is needed. For the larger particles a rate of 0.5-1.0 l/hr/lb probably would provide adequate decontamination.

VIII. REPORTS AND PUBLICATIONS ISSUED DURING THE QUARTER

IDO-14587, Development of a Fluidized Bed Calcination Process for Aluminum Nitrate Wastes in a Two-Foot-Square Pilot Plant Calciner. Part II. Factors Affecting the Intra-Particle Porosity of Alumina, B. R. Wheeler, E. S. Grimmett, J. A. Buckham (July 25, 1962).

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