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CHEMICAL PROCESSING TECHNOLOGY
QUARTERLY PROGRESS REPORT

April-June, 1962

MASTER

PHILLIPS
PETROLEUM
COMPANY

ATOMIC ENERGY DIVISION

NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION

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QUARTERLY PROGRESS REPORT
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CHEMICAL PROCESSING TECHNOLOGY
QUARTERLY PROGRESS REPORT
APRIL - JUNE, 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 determination of dissolution rates over a wide range of conditions. The addition of oxidants to 4.8M hydrofluoric acid used for the continuous dissolution of 3 percent uranium-Zircaloy-2 fuel decreased the amount of uranium-containing residue in the dissolver at the expense of a decreased dissolution rate. Oxidized fuel was dissolved in 4.8M hydrofluoric acid by use of heat to initiate the reaction; the oxide film remained behind as a dissolver residue. Uranium in the dissolver product was oxidized to the extractable form by one minute treatment at 92°C with aluminum nitrate complexer solution; only 59 percent was extractable after 24-hour treatment at room temperature. Several hundred-hours operation of a continuous bench scale unit indicated that uranium buildup should not be a problem in the dissolver since an apparent equilibrium was soon established. After 650 hours of operation, a Monel dissolver showed some signs of localized corrosion but exhibited generally good resistance.

Preliminary results in a study of aluminum alloy dissolution rates, initiated because of unusually slow dissolution of certain aluminum-based fuel elements, showed that nickel and copper ions in solution significantly retarded the dissolution rate while iron had an accelerating effect. Examination of specimens from the permanent ICPP raffinate storage tanks for aluminum process wastes indicates negligible corrosion to date.

Electrolytic dissolution studies have progressed to a bench scale basket-type dissolver operating at currents up to 500 amperes with Nichrome fuel. Sudden current failures have been essentially eliminated by use of platinum liners and a canted dissolver basket, but sustained operation has not been attained because of a gradual decline in current as dissolution causes recession of the contact points on the dissolving rods. An in-line solution analyzer for nitric acid and Nichrome salt concentrations in the dissolver effluent has operated satisfactorily. Additional supporting studies include measurement of certain dissolver solution physical properties, comparison of cathode potential measurements with laboratory data on corrosion rates, determination of polarization resistance of platinum in nitric acid, and continued investigation of the effect of irradiation on electrolytic dissolver insulator components.

Operation of the Demonstrational Waste Calcining Facility for 1050 hours during this period, under three different experimental conditions, demonstrated that the facility can be continuously operated in a routine manner and that the solids loading in the cyclone and scrubbing sections can be reduced to, and controlled at, satisfactory levels. Preparations are being made for a run with a sodium-24 spike to the feed to evaluate the final off-gas decontamination

equipment prior to operation with high-level wastes. Supplemental pilot plant and laboratory studies include use of sand to control bed particle size, investigation of the role of boric acid and phosphoric acid in control of alumina crystal form, and exploratory studies on the nature of the products of calcination of stainless steel and Nichrome nitrates.

Additional studies on an experimental air pulser showed good agreement between experimental data, analog simulation, and an approximate linear solution which can be studied by hand calculation methods. Further studies on the removal of tributyl phosphate and its decomposition products from dilute aqueous streams indicate that phosphorus species from plant solutions may be absorbed by, and eluted from, hydrous zirconium oxide.

CHEMICAL PROCESSING TECHNOLOGY
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I. ICPP OPERATIONAL SCHEDULE, PERFORMANCE, AND PROBLEMS

1. ICPP PROCESSING SCHEDULE (R. S. P'Pool)

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

By the end of the quarter, J and K cells were ready for entry of maintenance and construction personnel. G cell decontamination was slowed by a lack of available manpower and by the presence of a stainless steel fuel element and stainless steel fuel fragments in the dissolvers. The stainless steel fuel element had been shipped to the ICPP without adequate identification; it was charged to the dissolver as an aluminum fuel element. The stainless steel fragments resulted from processing aluminum MTR-type elements whose stainless steel end pieces had not been completely removed. After the stainless element end pieces were manually removed from the dissolvers, activity level in G cell dropped markedly, and subsequent decontamination operations proceeded routinely. By the end of the period, the background activity level had been reduced to about 350 mr per hour in G cell and about 75 mr per hour in H cell. Entry to G and H cells for equipment maintenance and modification should be permissible by the end of July.

One barium-140 run during this quarter was sufficient to meet the reduced product requirements. The run yielded 22,650 curies (43.8 percent of theoretical) of barium-lanthanum-140.

2. MODIFICATION OF ICPP PROCESS SYSTEMS (R. S. P'Pool)

The design of a new G cell CPM 1-A column feed system was completed; a new column interface control system is currently being studied. These revisions should eliminate the major trouble spots remaining in the first cycle extraction system; increased efficiencies and higher throughputs are anticipated from the revised system.

A completely redesigned process for J cell uranium salvage operations has been approved for construction. Installation will begin as soon as the detailed design is completed.

A new K cell process for cleanup of waste solvent has been turned over to construction. Installation of equipment will start as soon as contract negotiations are complete.

3. PLANT ASSISTANCE PROBLEMS

3.1 Corrosion of Waste Storage Tanks Containing Aluminum Nitrate Raffinates (T. L. Hoffman)

Measurement of corrosion rates for underground stainless steel storage tanks containing high-level radioactive wastes is a continuing program at the ICPP. Specially prepared corrosion test specimens are removed from the tanks periodically and measurements made to estimate the corrosion rates of the tanks. Results of recent measurements are shown in Table I.

TABLE I

CORROSION IN ICPP ALUMINUM PROCESS RAFFINATE STORAGE TANKS

Conditions: Temperature, $25 \pm 5^\circ\text{C}$

Type of Raffinate	Number of Tanks	Number and Type of Specimens(a)	Exposure Time (yr)	Average Corrosion Rate (mil/mo)	Results of Examination
1st cycle TBP	2	Twelve 304L hoops(b)	2.75	0.004	Only slight etching, no pitting or grain boundary attack
1st cycle TBP	2	Twelve 304L hoops(b)	2	0.003	Only slight etching, no pitting or grain boundary attack
1st cycle Hexone	1	One 348 welded pipe, 20 ft length	7	< 0.001	Uniform light etch, no pitting or intergranular attack
2nd and 3rd cycle(c) Hexone	1	Six 304L hoops(b)	2.75	0.004	Heavy etching, pits 5 mils deep

(a) Corrosion specimens and storage tanks are of same stainless steel type.

(b) One-inch-high, welded hoops of schedule 40 pipe.

(c) Corrosive decontaminating agents are blended with the column raffinates in this tank.

In general, the corrosion of the stainless steel tanks (type 304L and 348) used for storage of aluminum fuel processing wastes was considered to be negligible, but measurable. Continued storage of current wastes in existing tanks at the ICPP does not appear to be limited by corrosion.

II. AQUEOUS PROCESS STUDIES

(Section Chiefs: K. L. Rohde, Chemistry; J. I. Stevens, Development Engineering)

1. AQUEOUS ZIRCONIUM FUEL PROCESSING

The existing process at the ICPP for the processing of uranium-zirconium alloy fuel utilizes batch dissolution of the fuel in hydrofluoric acid, batch complexing of the fluoride by aluminum nitrate, and solvent extraction of uranium by tributylphosphate. A modified process of higher capacity, utilizing continuous operation, is under development. In the laboratory, chemical studies are directed to the kinetics of fuel dissolution, continuous dissolution performance, and corrosion behavior of materials of construction. Bench scale studies are being made in a one-half-inch-diameter, continuous dissolver which is being operated in extended continuous runs.

Laboratory dissolutions were made to investigate the limiting conditions under which the process can be operated while the continuous bench scale runs were designed to check out long-term corrosion and solution stability in a flow sheet suitable for use in process design. Batch dissolutions were made for kinetic data to compare with continuous dissolver control calculations.

1.1 Dissolution Rates of Zircaloy-2 in Hydrofluoric Acid-Zirconium Fluoride Solutions (D. W. Rhodes, Problem Leader; B. E. Paige)

In order to get a better understanding of the continuous dissolution operation, coupons of Zircaloy-2 were dissolved in solutions of varying zirconium fluoride-hydrofluoric acid concentration over short periods of time. In this way, the kinetics were obtained over the entire range of the dissolution process. The metal pieces were prepared with approximately uniform surfaces and the surface area was determined by the gross dimensions rather than the microscopic area. Of particular interest is the rate in the composition range of the continuous dissolver effluent.

Experimental. The initial dissolution rates for Zircaloy-2 were measured in solutions containing approximately 1, 2, 5, and 10M total fluoride and various quantities of dissolved Zircaloy-2.

The batch dissolution experiments were conducted in an 800-ml Teflon beaker using 500 ml of solution. A one-liter round-bottom flask coated with polyethylene and cooled with circulating water served as a condenser. Dissolution rates were determined by measuring the weight loss of Zircaloy-2 coupons which were approximately 3.5 x 1.3 x 0.5 cm. Coupons were suspended in the boiling solution ($\approx 95^{\circ}\text{C}$) for 1 to 5 minutes depending on the dissolution rate. The solutions were sampled after each coupon dissolution, and the zirconium and acid concentrations determined analytically. The values for fluoride were then calculated using these two values. During dissolution four moles of HF react with each mole of Zr.

Results. Figure 1 presents the individual dissolution rates as a function of hydrofluoric acid concentration. The hydrofluoric acid concentrations were determined by measuring the hydrogen ion concentration. Zirconium concentrations can be calculated by using 4/1 HF/Zr stoichiometry and the difference of total F and free HF concentration. In addition, the dissolution rates for

Zircaloy-2 were determined in hydrofluoric acid free from zirconium, and these data are included in Figure 1. The rate constant determined from the slope of this line is $61.2 \text{ mg cm}^{-2} \text{ min}^{-1}$ per mole HF liter⁻¹ and compares favorably with the results of Vander Wall, Whitener, and Bauer [1]. Figure 1 shows that during the first stages of the dissolution, Zircaloy-2 dissolves at a rate corresponding to the amount of residual hydrofluoric acid present. The rate constant does not decrease until considerable zirconium has been dissolved. In the reagent concentrations covered by these studies, approximately two-thirds of the zirconium theoretically dissolvable in a batch dissolution, ie, to the limit imposed by the 4/1 F/Zr ratio necessary for dissolution, was dissolved at the rate constant applicable to dissolution of the metal in zirconium-free hydrofluoric acid. Only after this did the dissolution rate constant begin to fall. This is illustrated in Figure 1 for the solution containing 2.3M total fluoride; this curve leaves the zirconium-free rate curve at a point where 65 percent of the dissolvable zirconium had been dissolved (approximately 0.9M free HF remaining, 1.4M F combined with 0.35M Zr). Extrapolation of the curve for 5.3M fluoride solution indicates approximately 60 percent dissolution of a zirconium batch before the rate constant decreases with increasing zirconium concentration in the solution.

Using the individual curves in Figure 1, rate constants were calculated for dissolution in solutions containing various mole ratios of fluoride to zirconium. These rate constants, shown in Figure 2, can be used to calculate dissolution rates ($\text{mg cm}^{-2} \text{ min}^{-1}$) at total fluoride concentrations other than those given in Figure 1, since the total fluoride concentration and the mole ratio define the moles of hydrofluoric acid per liter in the system. Solutions with fluoride-to-zirconium mole ratios of 6.5 and 7.0 and fluoride concentrations of 2.3M and 5.3M, respectively, dissolved Zircaloy-2 at $61.2 \text{ mg cm}^{-2} \text{ min}^{-1}$ per

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Fig. 1 Dissolution rate of Zircaloy-2 as a function of hydrofluoric acid concentration and as influenced by total fluoride and zirconium content of the solution.

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Fig. 2 Dissolution rate constants of Zircaloy-2 as functions of total fluoride concentration and F/Zr mole ratio.

mole HF liter⁻¹, and therefore the fluoride concentration of this intercept is above the solid line (Figure 2), probably within the area indicated by the shaded region. The F/Zr mole ratio at which the initial change in rate constant occurs is lower for lower total fluoride concentrations, and therefore, the overall rate for a dissolution using a 10M hydrofluoric acid feed will be less than five times the overall rate for a dissolution using a 2M hydrofluoric acid feed.

Figure 2 also shows that the rate constant has reached a limiting value at 4.4 moles of fluoride per mole of zirconium. A white powdery coating formed on all coupons at these low dissolution rates and decreased the rate of dissolution by as much as one-half. This film was not as evident in the higher fluoride solutions, and this no doubt accounts for the slightly higher rate constant at higher fluoride concentrations. The film was readily removed by solutions containing higher mole ratios of fluoride to zirconium.

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

Studies to adapt the hydrofluoric acid dissolution of zirconium-uranium alloy fuel to continuous dissolution are being made in the laboratory in a one-inch-diameter Monel dissolver. Previous work [2] showed that 2 to 3 percent uranium-Zircaloy-2 fuel can be dissolved continuously without the aid of oxidant in 4.8M hydrofluoric acid at a dissolvent-feed-rate-to-fuel-surface-area ratio as low as 0.04 cm/min. The resulting dissolver product was stable. A detailed description of the equipment and operational procedures has been given [2]. Further studies are reported on the use of oxidant in the dissolvent, on the dissolution of oxidized fuel, and on the continuous complexing of dissolver product.

1.21 Effect of Oxidants on Dissolution. The continuous dissolution in 4.8M hydrofluoric acid of Zircaloy-2 fuel containing up to 3 percent by weight uranium dissolves nearly all of the uranium, but leaves some solids containing uranium adhering to the walls of the dissolver, and at the bottom of the dissolver. Current studies were intended to determine whether the addition of oxidant to the hydrofluoric acid feed would increase the percentage of uranium fuel that could be dissolved and the concentration of uranium retained in solution.

Nitric Acid as Oxidant. Upflow dissolutions of 6-1/2-hour duration were made using 4.8M hydrofluoric acid with 0.03, 0.06, 0.15, and 0.5M nitric acid added to dissolve 3 percent uranium-Zircaloy-2 fuel. The dissolvent-feed-to-fuel-surface-area ratio was 0.04 cm/min. The dissolution temperature of all runs was about 90°C. A welded Monel corrosion coupon located at the point of contact between the feed solution and the fuel gave approximate corrosion rates. The results of these runs are shown in Table II. Nitric acid in concentrations up to 0.15M appeared to decrease the uranium loss to the dissolver walls and residue without increasing Monel corrosion, but did not increase the concentration of uranium in the dissolver product solution. Greater than 0.06M nitric acid in the feed increased the amount of tin dissolved, which resulted in a corresponding decrease in the amount of solids remaining in the dissolver at the end of a run. Nitric acid in the dissolver feed decreased the fuel dissolution rate, resulting in a corresponding decrease of zirconium concentration and an increase of fluoride-to-zirconium mole ratio in the dissolver product. Excess nitric acid (0.5M) produced a dissolver product solution less favorable for retention of uranium in solution; in addition, the Monel corrosion rate was

excessively high. There was less uranium in the dissolver product solution and more uranium lost to the dissolver than in runs using less or no nitric acid.

TABLE II

EFFECT OF OXIDANTS ON THE CONTINUOUS DISSOLUTION
OF 3 PERCENT URANIUM-ZIRCALOY-2 FUEL IN 4.8M HYDROFLUORIC ACID

Conditions: Upflow, dissolver, dissolver-feed-to-fuel-surface-area ratio of 0.04 cm/min, and an operating temperature of 90°C for 6-1/2 hours.

Run No.	Oxidant in Dissolver Feed	Dissolution Rate (mg/cm ² /min)	Dissolver Solution					Solid Remaining in Dissolver (g)	Fuel Uranium Content Dissolvable (%U)	% of U Lost to Solids in Bottom of Dissolver	% of U Adhering to Dissolver Walls	Monel Corrosion Rates (mil/mo)
			Zr (M)	F-to-Zr Mole Ratio	U (g/l)	Sn (g/l)	Solid Content (g/l)					
11	None	4.0	1.25	4.4	2.6	0.6	—	—	2.2	4	3	0.7
28	None	3.7	1.26	4.5	2.6	—	—	3.73	2.2	4.6	0.5	< 0.5
26	0.03M HNO ₃	3.7	1.16	4.6	2.7	0.3	—	3.65	2.4	1.1	1.7	< 0.3
21	0.06M HNO ₃	3.5	1.08	4.6	2.6	0.63	0.019	3.64	2.5	1.9	1.2	0.13
25	0.15M HNO ₃	3.5	1.09	4.6	2.6	1.21	0.037	2.66	2.5	1.7	4.0	2.5
23	0.5M HNO ₃	3.2	1.02	4.9	1.5	1.27	0.17	2.45	1.5	6	5	33
19	0.1M H ₂ O ₂	3.5	1.12	4.6	2.7	0.76	0.02	3.51	2.5	2.2	1.3	—
20	0.06M CrO ₃	3.5	1.10	4.7	2.6	0.94	0.008	2.34	2.5	1.6	0.6	6.7
22	0.03M Al(NO ₃) ₃	3.5	1.06	4.7	2.5	0.59	0.015	4.24	2.5	2.1	1.8	1.1

One dissolution was carried out (under the conditions of Table II) using 4.8M hydrofluoric acid-0.06M nitric acid to dissolve an alloy which was 5 percent uranium, 1 percent tin, and 94 percent zirconium. The dissolution rate, fluoride-to-zirconium mole ratio, tin concentration, and zirconium concentration of the dissolver product were about identical to those observed in dissolving 3 percent uranium-Zircaloy-2 fuel under the same conditions. A dissolver product solution containing 3.3 g of uranium per liter was produced and probably represents the maximum uranium concentration possible when 4.8M hydrofluoric acid is used as the dissolver. As was expected, uranium lost to the dissolver (12.6 percent), dissolver product solution solid content (0.45 g/l), and solids remaining in the dissolver (4.43 g) were greater than for dissolution of 3 percent uranium fuel.

Other Oxidants. Dissolutions under the same conditions as those utilizing nitric acid were made, using as feed 4.8M hydrofluoric acid with 0.1M hydrogen peroxide, 0.06M chromic acid, or 0.03M aluminum nitrate. As shown in Table II, these oxidants acted similarly to nitric acid in that their presence depressed the dissolution rate with a corresponding decrease in the zirconium concentration and an increase in the fluoride-to-zirconium mole ratio in the dissolver product. The amount of uranium lost to the dissolver decreased, and there was essentially no effect on the percentage of uranium in the fuel that could be dissolved. Neither hydrogen peroxide nor aluminum nitrate appeared to offer any advantages over nitric acid. The aluminum nitrate resulted in a greater quantity of solids remaining in the dissolver, probably due to depletion of free fluoride. Chromic acid appeared to be more effective than the other oxidants in decreasing uranium lost to the dissolver and increasing the amount of tin dissolved, but the high corrosion rate on Monel prohibits its use.

1.22 Dissolution of Oxidized Fuel. Since much of the fuel processed at the Idaho Chemical Processing Plant is oxidized in the reactor environment, the effect of the oxide film on dissolution of the fuel was studied. Three percent uranium-Zircaloy-2 fuel was oxidized in a muffle furnace for 45 minutes at 1500°F. The batch dissolution characteristics of this oxidized fuel were compared to those for fuel oxidized in an autoclave (oxidation in an autoclave is closely related to reactor oxidation). Both fuels immersed in boiling 4.8M hydrofluoric acid required an induction period to initiate the dissolution. This induction period was three times longer with the air-oxidized fuel than with the autoclave-oxidized fuel, or six vs two minutes. Since air-oxidized fuel was easier to obtain, and proved to be even more resistant to reaction initiation than the autoclaved fuel, air-oxidized fuel was used in the subsequent studies directed at determining the effect of this refractory film.

To initiate the dissolution of air-oxidized fuel in 4.8 M hydrofluoric acid, external heat was necessary; but once the dissolution was started the heat of reaction maintained the temperature at 87°C. The hydrofluoric acid dissolved the oxide film very slowly, if at all, but seemed to penetrate beneath the film and flake it off. As a result, the quantity of residue remaining in the dissolver was about three times as great as that remaining in most of the runs with unoxidized fuel summarized in Table II.

Table III compares the dissolution of oxidized and unoxidized fuel under the same conditions. The presence of the oxide film depressed the dissolution rate which resulted in a corresponding decrease in the zirconium and uranium concentration and an increase of the fluoride-to-zirconium mole ratio in the dissolver product solution. This effect may not be quite so pronounced in the dissolution of fuels oxidized in reactor environments.

TABLE III

EFFECT OF FUEL OXIDE FILMS ON THE CONTINUOUS DISSOLUTION OF 3 PERCENT URANIUM-ZIRCALOY-2 FUEL IN 4.8M HYDROFLUORIC ACID

Conditions: Upflow dissolver, feed-to-fuel-surface-area ratio of 0.04 cm/min, and an operating temperature of 90°C.

Run No.	Oxidized Fuel Used	Dissolution Rate (mg/cm ² /min)	Dissolver Product Analysis			Fuel Uranium Content Dissolvable (%U)
			Zr (M)	F-to-Zr Mole Ratio	U (g/l)	
11	No	4.0	1.25	4.4	2.6	2.2
27	Yes	3.2	1.02	4.9	1.8	1.9

1.23 In-line Adjustment of Dissolver Product. Prior to extracting with tributyl phosphate, the dissolver product solution is adjusted to make it less corrosive to stainless steel extraction columns, to add salting strength, and to oxidize the uranium. The current studies indicate the desirability of elevated

temperatures during adjustment to obtain complete oxidation of the uranium. The dissolver effluent produced in run 26 of Table II was fed continuously into an adjustment vessel where it was mechanically stirred for one minute at 46°C with adjustment solution before overflowing from the adjustment vessel. This solution was cooled and immediately extracted with an equal volume of 10 percent tributyl phosphate in Amsco. Only 45 percent of the uranium present was oxidized to the extractable form. Allowing the adjusted dissolver solution to stand at room temperature for 24 hours prior to extraction increased the extractable uranium to 59 percent.

Effluent from run 27 of Table III was adjusted continuously at 92°C for one minute contact time. This converted essentially all of the uranium to the extractable form, indicating the necessity for using elevated temperatures for the in-line feed adjustment step.

Table IV presents the dissolver and adjustment solution compositions, together with the adjusted extraction process feed compositions.

TABLE IV

ZIRCONIUM PROCESS DISSOLVER AND ADJUSTMENT SOLUTION COMPOSITIONS

Run	<u>Dissolver Solution</u>			<u>Adjustment Solution</u>				<u>Adjusted Dissolver Solution</u>						
	Zr (M)	F/Zr Mole Ratio	U (g/l)	HF (M)	HNO ₃ (M)	Al(NO ₃) ₃ (M)	H ₂ CrO ₄ (M)	F ⁻ (M)	H ⁺ (M)	NO ₃ ⁻ (M)	Al (M)	Zr (M)	U (g/l)	H ₂ CrO ₄ (M)
26	1.16	4.6	2.7	1.86	0.82	1.53	0.04	3.83	1.31	2.03	0.58	0.68	1.6	0.015
27	1.02	4.9	1.8	1.95	0.62	1.27	0.033	3.6	1.7	2.1	0.6	0.5	0.9	0.016

1.3 Continuous Zirconium Fuel Dissolution in the Pilot Plant (D. K. MacQueen, Problem Leader; H. V. Chamberlain, A. P. Roeh)

Previous tests of continuous zirconium dissolution resulted in the selection of a dilute flow sheet (4.8M HF dissolvent) in a Monel system for the new ICPP continuous zirconium headend [3]. Variations of the 4.8M HF flow sheet were tested in one-half-inch-diameter miniature dissolvers to study the formation of solids during dissolution and measure the corrosion of the vessel. The results of these tests were reported previously [2].

Two additional miniature dissolver tests, using a 4.8M HF - 0.03M HNO₃ dissolvent, have been completed. The first test was made with a mixture of Zircaloy fuel pieces containing 5.25 percent uranium and sufficient additional uranium-free Zircaloy pieces to produce an average uranium content of two percent. This test, of 190-hour duration, was made to determine any effects that might result from processing a typical fuel charge with the uranium content in the "meat" section substantially higher than the overall average uranium content of the elements. The second test was made with Zircaloy fuel pieces containing a nominal 2.3 percent uranium. This test was continued for a total of 300 hours, with periodic inspection of the dissolver, to determine whether

solids deposition in the dissolver would reach a state of equilibrium at a tolerable level of dissolver fouling.

The results from the first test showed no significant differences from the results of comparable tests with uniform uranium distribution in the fuel charge; the amount of solids produced, the solids composition, and the concentrations of uranium, zirconium, and tin in the dissolver product solution were closely comparable. It appears that a fuel element with a uranium content of five percent in the "meat" section and an overall uranium content of two percent can be processed with no more difficulty than if it contained two percent uranium evenly dispersed through the element.

During the second test, visual observations of the inside of the dissolver were made at 50-hour intervals. A rapid initial buildup of uranium precipitate on the dissolver wall occurred during the first 100 hours, but subsequent inspections revealed no significant change in the quantity of dissolver deposits. It appears that, after an initial period of operation, precipitate buildup on the dissolver wall either reached an equilibrium state or the additional buildup occurred at such a slow rate that it could not be detected. After 300 hours, the quantity of solids deposited did not affect the operability of the dissolver.

At the conclusion of the 300-hour test, a simulated heel cleanout was made. Uranium-free zirconium pieces were fed for 10 hours, keeping the original dissolvent fuel rate and composition constant. The dissolver was then flushed with water and inspected. A noticeable reduction in dissolver deposition resulted, but a substantial amount of precipitate remained. A repeat of the same cleanout procedure for an additional 14-hour period was not visibly effective. Mechanical removal of the deposition on the dissolver wall following the completion of the two heel cleanouts showed that a substantial quantity of $\text{UF}_4 \cdot 3/4 \text{H}_2\text{O}$ precipitate was still adhering to the dissolver wall. A satisfactory cleanout procedure remains to be developed.

1.4 Corrosion Studies in Nitric-Hydrofluoric Acid Solutions (D. W. Rhodes, Problem Leader; T. L. Hoffman)

1.41 Corrosion of Monel. A one-half-inch-diameter welded Monel continuous dissolver from the pilot plant was inspected after 650 hours in uranium-Zircaloy-2 dissolution service using 4.8M hydrofluoric acid and 4.8M hydrofluoric acid - 0.03M nitric acid as dissolvents for 270 and 380 hours, respectively. The alloy used to make the dissolver was wrought Monel (65.5% nickel, 31.7% copper, and 1.5% iron).

The dissolver was cut in half lengthwise and a careful inspection made of the walls of both halves. This examination indicated that localized attack and pitting occurred at various places on the inside walls of the dissolver. Pits up to 20 mils deep were present midway up the dissolution section, presumably the location where the most vigorous fuel dissolution occurred. Pits less than 5 mils deep were present in the vapor space where the fuel enters the dissolver. Except for these localized sites, pitting and general corrosion were absent.

1.42 Corrosion of Corronel-230 in Nitric-Hydrofluoric Acid. Corrosion studies were made using Corronel-230 alloy. Corronel-230 is basically a binary 60/35 nickel-chromium alloy which was developed by United Kingdom

metallurgists to resist corrosion by hot nitric acid. In addition, it has appreciable resistance to specific nitric-hydrofluoric acid mixtures.

The current laboratory studies were intended to determine the corrosion rate for Corronel-230 in nitric-hydrofluoric acid mixtures which were known to be highly corrosive to conventional materials of construction. Solutions containing 6.0M nitric - 1.0M hydrofluoric acid and 0.25M nitric - 6.0M hydrofluoric acid were used. Pairs of Corronel-230 coupons (1 x 1-1/4 x 0.035 inch) in the "as received" annealed condition were immersed in 325 ml (65 ml/inch² of coupon surface) of the boiling acid mixture. The procedure consisted of two 48-hour periods at boiling temperature with a fresh test solution used for each 48-hour period. The results are shown in Table V.

TABLE V

CORROSION OF CORRONEL-230 IN BOILING NITRIC-HYDROFLUORIC ACID MIXTURES

Acid Mixture	Corrosion Rate (Inch Penetration/Month)			Average
	First 20 hr	First 48 hr	Second 48 hr	
0.25M HNO ₃ -6.0M HF	0.5582			0.5473
	0.5364			
6.0M HNO ₃ -1.0M HF		0.0578	0.0318	0.0467
		0.0568	0.0321	

These experimental data indicate that Corronel-230 is not suitable for use with boiling nitric-hydrofluoric acid mixtures high in hydrofluoric acid concentration. Specific applications may exist, however, for boiling mixtures high in nitric acid but low in hydrofluoric acid. Both acid mixtures resulted in severe grain boundary attack.

2. AQUEOUS ALUMINUM FUEL PROCESSING

2.1 Aluminum Dissolution Rate Studies (R. D. Fletcher, Problem Leader; M. E. Jacobson)

The slow dissolution rate of some aluminum alloy fuels (such as the Chalk River and ETR fuels recently dissolved in the continuous dissolvers at ICPP) leads to excessive cost charges for processing as well as scheduling difficulties. In order to achieve a better understanding of the abnormal dissolution rates of these fuels, a four-phase program has been initiated to study the following effects:

- (1) Catalytic or retarding effects of the ions in solution derived from constituents of the alloy
- (2) Effects of alloy composition in the metal as well as in solution

(3) Effects of metallurgy or working

(4) Effect of irradiation

Phase one of the program, which is essentially complete, consisted of batch dissolution rate measurements with standard coupons of 99.999% aluminum in 6.6M nitric acid - 0.005M mercuric nitrate at 90°C. Nitrate solutions of the typical aluminum-alloying elements were added to the initial solutions to give a solution composition equivalent to that for a 1 or 2 percent alloy at the end of the dissolution. The resulting batch dissolution times are compared to those for the pure aluminum in Figure 3. Iron, nickel, and copper gave results significantly different from those for pure aluminum at the 98 percent confidence level, iron having an accelerating effect, and nickel and copper a retarding effect, on the dissolution rate. Other metallic ions showed little effect. For application to continuous dissolution conditions the instantaneous dissolution rates can be calculated at any aluminum concentration up to 35 grams per liter from the detailed data.

Fig. 3 Relative batch dissolution times for pure aluminum in nitric acid dissolver solutions containing dissolved alloying elements.

III. ELECTROLYTIC DISSOLUTION SYSTEMS

(Section Chief: K. L. Rohde)

1. FUEL-ELECTRODE DIRECT CONTACT PRINCIPLE

A bench scale basket-type continuous electrolytic dissolver, capable of operating at 500 amperes, has been placed in operation. Experiments this quarter were designed to attain sustained operation of the unit at the 500-ampere level. Various modifications to the originally vertical 1-1/2- x 12-inch niobium anode basket have been made in order to improve the contact with the dissolving pieces.

Concurrent with these dissolver experiments two in-line analytical instruments have been installed and operated in the circulating system. A solution composition analyzer is based upon electrical conductance measurements which yield the nitric acid and metal nitrate compositions. Luggin probes have also been installed to measure cathode potential. Specific conductance and specific gravity data also were obtained for Nichrome solutions.

1.1 Bench Scale Dissolver Operation (H. T. Hahn, Problem Leader; M. R. Bomar; J. R. Aylward, A. P. Roeh)

The test dissolver consists of a 1-1/2-inch-diameter x 12-inch-high niobium anode basket set concentrically in a 2-1/2-inch-diameter niobium outer shell which functions as the cathode. A variable speed pump permits continuous circulation of dissolver solution through the dissolver vessel and heat exchangers are provided to control the temperature of the dissolution medium. A suitable power supply is used to give the desired voltage and current levels.

In all tests, 3/8-inch Nichrome rods cut in 11- or 12-inch lengths were dissolved in 8N HNO₃. The circulation rate of dissolver contents has been approximately two liters per minute. The perforated height of the dissolver basket was 12 inches. When the dissolver was operated in the vertical position, frequent current failure resulted. In order to improve the fuel-anode contact, various modifications were made to the equipment.

The modifications included:

- (1) Screwing an 0.008 x 1-1/2-inch-diameter platinum disc to the basket bottom.
- (2) Adding a weighted Teflon piston to press down on the rods.
- (3) Canting the dissolver 45 degrees to increase the area of contact.
- (4) Screwing a 2- x 12-inch platinum sheet to the inside of the basket, thereby forming an unperforated trough on the lower side of the canted dissolver.

The results of operation with these modifications are given in Table VI.

At least four problem areas have become apparent. The first is a loss of electrical contact with the dissolving pieces. The current may be restored

TABLE VI

ELECTROLYTIC DISSOLVER PERFORMANCE
WITH VARIOUS ANODE BASKET MODIFICATIONS

Modification	Volts	Duration of Test (hr)	Current (amp)		Current Failure Frequency (hr ⁻¹)	2/3 Decay ^(a) Time (hr)	Mechanical Shock or Vibration
			Maximum	Final			
Unmodified vertical niobium basket	6.4-8.0	2.1	500	0	5	0.2	Both
Pt disc in bottom	5.1-9.1	5.3	500	180	1.3	0.2	Both
Pt disc + Teflon piston	5.0-9.4	5.8	510	200	4.3	0.7	Both
No disc + 45° cant	5.6-5.7	3.2	485	200	1.3	1.2	Mechanical shock
Pt disc + 45° cant	5.4-5.9	4.5	500	140	1.1	1.6	Both
Pt disc + Pt trough	5.8	3.1	190	130	0	3.1	One blow
Pt disc + 45° cant	6.2-9.4	5.0	330	220	0	3.9	Mechanical shock

(a) The time for current to decline to 2/3 maximum current, with mechanical shock applied if necessary.

generally by mechanical shock or rotation of the piston. The frequency of current failure was appreciably reduced by adding platinum sheet and by canting the dissolver.

The second problem is one of gradual current decline during operation. This probably is due to recession of contact points and decrease of contact area as the rods dissolve. It is not due to changes in solution composition or conductance, or to insufficient fuel. To some extent it was alleviated by assuring that the rods were completely in the perforated region of the basket, in order to reduce nonuniformity of the current field. It was alleviated also by the platinum trough, in which most of the dissolution occurred on the upper side of the rods. The current decline has not been eliminated, however. No modification tested to date has permitted sustained operation of the unit with charges of 80-20 Nichrome rod.

The remaining problem areas involve slime deposition and corrosion. The deposition of a silicon- and niobium-bearing slime (principally on the cathode) may influence operation and will be investigated further. Corrosion due to stray currents has also been encountered in the stainless steel tubing immediately above and below the dissolver.

1.2 Corrosion in Electrolytic Dissolver Solutions (H. T. Hahn, Problem Leader; J. R. Aylward)

Studies of the corrosion rate of Type 304 stainless steel in electrolytic dissolver solutions, as reported last quarter [2] continued. At that time it

was assumed that the heat of activation was constant between 25 and 85°C. The validity of this assumption has been established by the latest experiments.

The cathode potential of the bench scale electrolytic dissolver was measured by back-side Luggin probes. Values ranging from -0.4 to -0.6 volts vs a saturated calomel electrode at a current density of approximately 600 ma/cm² were in agreement with laboratory data, but an attempt to correlate cathode potentials with off-gas volume and composition is not possible at present due to other operational difficulties.

Potential measurements of the stainless steel tubing in the immediate vicinity of the dissolver indicated stray current corrosion. In the absence of stray current, potential measurements and visual inspection verify that the magnitude of the corrosion rates are as measured in laboratory experiments. However, the short runs did not allow a quantitative comparison.

1.3 Electrolytic Dissolver Product Analyzer (H. T. Hahn, Problem Leader; D. P. Pearson)

The electrolytic conductance dual analyzer described in the previous quarterly report [2] has been installed in the bench scale electrolytic dissolver circuit. Concentrations of Nichrome salts and nitric acid may be monitored at will.

The analyzer was calibrated with synthetic mixtures of nitric acid and Nichrome salts. During operation of the dissolver, samples were taken and submitted for chemical analysis and the results compared with those from the analyzer. For 29 samples the standard deviation between the analyzer and chemical analysis was 0.20 equivalents Nichrome per liter and 0.24 equivalents acid per liter. A positive bias of about 0.1 equivalent per liter exists in the conductance results for both quantities.

Analyses for oxidizable nitrogen and chromium (VI) were made on several samples. No correlation between these quantities and other solution properties is apparent. No sample has contained both NO₂⁻ and chromium (VI).

During about five weeks use of the analyzer, the cell constants of the two conductance cells have decreased, four percent for the solution cell and eight percent for the mixture cell. The metal particles in the slime which deposits on the apparatus may be partially short-circuiting the cells.

At times, trouble has been experienced with particles clogging the capillary tubes, but these are easily dislodged. A more serious difficulty, which has occurred only twice, is the production of gas bubbles near the water capillary tube. These are not easily detected. Both flow impediments destroy the invariance of flow ratio required for operation of the instrument. These deficiencies in operation of the analyzer have just come to light, and no remedial measures have been instituted as yet.

In connection with the calibration of the electrolytic dissolver product analyzer, the electrical conductances and specific gravities of a series of mixtures of nitric acid and "Nichrome nitrate" were measured. The Nichrome composition is 80-20 wt% Ni-Cr. The results are listed in Table VII.

TABLE VII

SPECIFIC CONDUCTANCES AND SPECIFIC GRAVITIES OF
NITRIC ACID-NICHROME NITRATE MIXTURES IN WATER AT 25°C

HNO_3 (Eq/l)	NiCr (Eq/l)								
	0	1	2	3	4	5	6	7	8
0	0	0.067 ^(a)	0.103		0.131		0.113		0.074
	1.000	1.072 ^(b)	1.143		1.275				1.540
1	0.329	0.312	0.286	0.257	0.225	0.188	0.149	0.116	
	1.034	1.105	1.174	1.242	1.308	1.373	1.439	1.501	
2	0.562	0.489	0.422	0.347	0.286	0.225	0.175		
	1.067	1.136	1.205	1.273	1.339	1.404	1.463		
3	0.714	0.601	0.498	0.407	0.320	0.245			
	1.099	1.168	1.235	1.299	1.367	1.432			
4	0.805	0.662	0.540	0.426	0.333				
	1.132	1.200	1.266	1.333	1.394				
5	0.849	0.689	0.552						
	1.163	1.231	1.295						
6	0.856	0.691	0.538						
	1.192	1.258	1.325						
7	0.844	0.668							
	1.224	1.278							
8	0.816								
	1.249								

(a) Specific conductance.

(b) Specific gravity.

Figure 4 shows a plot of specific conductances vs specific gravity. From the plot, it appears that the simultaneous measurement of these solution properties would also provide an analysis of Nichrome and nitric acid over most of the composition range.

2. FUEL-SOLUTION-ELECTRODE INDIRECT CONTACT PRINCIPLE (H. T. Hahn, Problem Leader; J. R. Aylward)

The necessity for metal-metal contact between fuel and anode may be avoided by designing the dissolver so that the fuel is oriented between the electrodes and contacts only the solution [4]. The possible use of platinum anodes in a dissolver of this type has led to a measurement of the polarization resistance of platinum in nitric acid.

Experiments have been conducted with both platinum and platinized platinum anodes in 5M nitric acid at 25°C. At the high current densities of interest (>100 amps/ft²) there is no significant difference due to platinization. The anodic polarization resistance ($R_{a.p.}$) over the range 100 to 30,000 amp/ft² is given by

$$R_{a.p.} = \frac{1}{A} \left(\frac{1.2}{I} + 2.4 \times 10^{-4} \right)$$

where I is in amp/ft² and A is the electrode area in ft². The kilowatts of power at the platinum anode are then given by

$$Kw = IA (10^{-3})(1.2 + 2.4 \times 10^{-4}I).$$

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Fig. 4 Specific conductances of nitric acid-Nichrome nitrate mixtures as a function of specific gravity at 25°C.

3. INSULATOR MATERIALS FOR ELECTROLYTIC DISSOLVERS (R. D. Fletcher, Problem Leader; L. A. Decker)

In the study of electrical insulating materials for the electrolytic program, samples of Marlex*, G-7 glass fabric silicone resin laminate, and alumina ceramic were exposed to 10^{10} R total gamma dose in boiling dissolver product solution (about 1M nitric acid and 75 g/l stainless steel components).

The Marlex* samples started to decrease in size between 2×10^9 R and 6×10^9 R. A 1/2-inch-wide strip lost 1/8-inch width near the lower level, increasing to a 1/4-inch loss at the higher level. The samples were still straight and intact after 10^{10} R.

* Registered trademark of Phillips Petroleum Company for its family of polyolefin resins.

The G-7 laminate was intact, straight, rigid and showed only slight evidence of delamination after 10^{10} R.

The ceramic alumina showed no visible changes after 10^{10} R.

Kynar* was completely destroyed sometime before 4×10^9 R. At 1×10^9 R Kynar was intact, straight, and rigid.

Samples of each of the above are being tested for changes in physical properties.

* Pennsalt Chemicals' name for its polyvinylidene fluoride resin.

IV. NEW WASTE TREATMENT METHODS

(Section Chief: K. L. Rohde, Chemistry)

1. DISPOSAL OF LOW-LEVEL RADIOACTIVE WASTES

(D. W. Rhodes, Problem Leader; M. W. Wilding)

Laboratory investigations were continued on the possible use of locally available natural earth materials as ion exchangers for the removal of cesium and strontium radioisotopes from low-level radioactive waste at the NRTS. Four earth materials were selected for further testing from among 26 different materials studied previously [2]. Both column capacity determinations and batch equilibrium experiments were performed with these materials.

Column Capacity Determinations

Experiments were started using columns 15 cm long x 0.62 cm diameter containing 5 grams of earth material with a particle size 1.0 to 2.0 mm diameter. The flow rate of the feed solution through the columns was approximately 700 gal/(ft²)(day) but varied briefly by as much as ± 60 percent during adjustment of equipment. The feed solution contained 1.0 mg per liter cesium or strontium with cesium-137 or strontium-85 tracers. Feed solution was adjusted to a pH of 3.5, typical of the MTR-ETR disposal pond water.

The earth material containing clinoptilolite had the highest column capacity for cesium. In a test which was still continuing at the end of the quarter, the throughput has exceeded 5000 column volumes without any detectable breakthrough. The capacity for cesium of the other three materials ranged from 350 to 580 column volumes at 50 percent breakthrough.

Column capacity determinations for strontium were still in progress for all four materials, and by the end of the quarter had reached the 2000 column volume mark without detectable breakthrough.

Batch Equilibrium Experiments

Batch equilibrium experiments were performed on the same four materials, and the material containing clinoptilolite had the highest distribution coefficient for both strontium and cesium. . ICPP fuel storage basin water with a total hardness of 200 ppm as CaCO₃ was used at a pH of approximately 7.0 for these tests; the hardness apparently had no serious inhibiting effect on the removal of cesium or strontium. Distribution coefficients determined by supernatant solution analyses after 24-hour tests at 23°C ranged from 200 to 1300 for strontium and from 270 to 4200 for cesium.

Comparison of Core-Drilled and Ground Material

The exchange capacity of a core-drilled basalt sample was found to be 0.003 milliequivalents per gram, half that of the same material ground to under 2-mm-diameter particles, at a vacuum-induced flow rate of 0.5 gal/(ft²)(day). Apparently, the porous basalt core did not permit liquid transfer through all pores sufficient to provide an exchange surface equivalent to the ground sample.

V. WASTE CALCINATION DEVELOPMENT AND DEMONSTRATION

(Section Chiefs: J. I. Stevens. Development Engineering: K. L. Rohde, Chemistry)

Laboratory and pilot plant studies of the fluidized bed calcination process for reduction of high-level aqueous wastes to granular, free-flowing solids have been underway at the ICPP for several years. Early studies were conducted in 3- and 6-inch-diameter units; currently, a 12-inch-diameter, electrically heated unit and a 24-inch-square, NaK-heated unit are used for pilot plant studies with nonradioactive material. The 48-inch-diameter Demonstrational Waste Calcining Facility (DWCF) will demonstrate this process with full-level wastes; cold testing of the DWCF is well advanced, and preparations are being made for a run in that unit with radioactive tracer material.

Exploratory studies have demonstrated the feasibility of this process for stainless steel and zirconium fuel wastes, but the overwhelming majority of the work has been with aluminum fuel wastes. A typical waste of this type contains 1.74-molar aluminum nitrate, 0.6-molar nitric acid, 0.01-molar mercuric nitrate, 0.04-molar sodium nitrate, fission products, and other minor components.

Feed rates from 5 to 150 liters per hour per air-atomizing nozzle have been used, with capacity of all units being limited by the rate of heat introduction through internal surfaces. Measured heat transfer coefficients range from 40 to 100 Btu/(hr)(°F)(ft²), depending upon bed particle size and fluidized bed density.

Particle size has been controlled by varying the atomizing air rate, the major factor governing particle attrition. Quantitatively this effect is very dependent on the crystalline form of alumina produced. Various operating factors make significant differences in the rate of conversion of amorphous alumina calcine to the alpha (or, in isolated cases, gamma or iota) crystalline form. Particle attrition increases with alpha alumina content; hence, average bed particle size decreases and particle elutriation rate increases with increasing alpha content. High alpha-content beds have a higher absolute material density and contain less nitrate, both desirable features. Sodium is a necessary feed ingredient for alpha alumina formation; its effect can be overcome by addition of boric acid to the feed. Addition of one of these components to the feed has been employed to obtain the desired product form.

Intra-particle porosity varies from 5 to 60 percent and is a direct function of bed temperature (from 250 to 550°C) and feed concentration (from 0.8 to 2.0M aluminum), but not a significant function of any other variable. Superficial fluidizing velocities from 0.5 to 2.5 feet per second have been used; best results are obtained with velocities under 1.0 foot per second.

Studies have been made with and without condensing the off-gas stream and with near-total recycle of non-condensable off-gas for fluidization. The latter method of operation shows promise for minimizing atmosphere contamination.

Operation of the DWCF this period showed good mechanical operability and close control over the process. Solids carry-over past the primary cyclone has been reduced to acceptable levels for several modes of operation. Additional

pilot plant studies were conducted on the solids carry-over problem, while laboratory studies were continued on the role of boric acid in alpha alumina formation.

1. OPERATION OF THE DEMONSTRATIONAL WASTE CALCINING FACILITY (DWCF)

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

Further changes were made in DWCF equipment to correct deficiencies, to improve operability, and to reduce a high solids elutriation rate from the calciner vessel. During this period, more than 1050 hours of operation were accumulated on the DWCF in three runs, the last of which is still in progress. The results from these runs have demonstrated that the solids loadings of the scrubbing solution can be reduced to, and controlled at, a satisfactory level, and that the DWCF can be continuously operated in a routine manner. Results to date indicate that the system is operable with a bed of either predominantly alpha or predominantly amorphous alumina, but that the acid solubility of the amorphous form makes it preferable from the standpoint of trouble-free handling of the scrubber solution and ease of decontamination.

The first run this period, run 7, showed that the cyclone dipleg height was insufficient to provide for return of fines to the bottom of the bed under all conditions, and the run was terminated because of a plugged dipleg. The last two runs, 8 and 9, were made with an external, temporary cyclone fines collection system with provisions for returning these fines either to the bed or to solids storage by pneumatic transport. On these runs, operability was demonstrated with both methods of cyclone fines disposition and with both amorphous and alpha beds. When run 9 is completed, sufficient data should be on hand to permit selection of the desirable form of bed, alpha or amorphous, and the desirable method of cyclone fines disposition, return to the bed or to storage, for future operations.

Although some deficiencies remain and some additional operating procedures must be established, it is believed that the information acquired from the runs to date has identified all significant problems and that solution of these problems is imminent. Preparations are being made for a run with a sodium-24 spike to the feed for the purpose of evaluating the final off-gas decontamination equipment prior to operation with high-level wastes.

1.1 Solids Carry-over

Run 7 was made with a reduced superficial fluidizing velocity of 0.5 ft/sec, but this resulted in no significant reduction in the rate of solids carry-over from the primary cyclone. This rate averaged 18 lb/hr in the first portion of the run while the bed was amorphous. The bed was then converted to alpha alumina, and the rate rose rapidly to over 30 lb/hr; the calciner was then shut down because the cyclone dipleg and dust hopper were filled with fine solids. This run indicated that the dipleg height was insufficient for satisfactory return of the low-density cyclone fines to the bed.

In preparation for run 8, an external cyclone fines collection system was installed in a temporary manner. The fine solids removed from the off-gas by the primary cyclone were collected in one hopper and intermittently transferred

to another hopper from which they could be pneumatically conveyed either back to the calciner vessel or directly to cold storage. This system permitted sampling of the fines in the return loop and estimating the rate of fines return to the bed. An amorphous bed was maintained throughout run 8 by boric acid addition to the feed. Bed elutriation rates up to 300 pounds per hour of solids slightly smaller than bed material were measured in this run; the rate averaged about 175 pounds per hour. Scrubbing solution analyses showed that only approximately 12 pounds per hour of solids passed through the primary cyclone, however. Size distribution data on solids collected from the off-gas downstream from the cyclone indicated that over 70 percent of these solids were finer than 325 Tyler-mesh (44 micron).

Prior to run 9, a Venetian-blind-type baffle was installed in the calciner vapor space to deflect surges of calcine material away from the cyclone entrance. During the first portion of this run, the cyclone fines were admitted to the solids transport line and transferred to solids storage. The baffle reduced the solids elutriation rate from the bed to less than 35 lb/hr of material, as compared to 150 to 200 lb/hr under the same conditions without the baffle. Most of the reduction in solids elutriation rate effected by the baffle was in the larger-sized particles; with the baffle in position, 50 percent of the solids collected in the primary cyclone passed through a 325 Tyler-mesh screen. Use of the baffle together with transfer of dry fines to storage resulted in a low solids carry-over rate from the cyclone of approximately 8 to 10 lb/hr. This run is being continued to obtain data for an alpha alumina bed with fines return to the bed.

1.2 Process Control

Feed of the approximate composition noted earlier (simulating the contents of WM-185 waste tank) was calcined in the DWCF during runs 7, 8, and 9. Run 7 was started with product made during the preceding run, in which boric acid had been added to the feed to inhibit formation of the alpha crystalline form of alumina. No boric acid was added to the feed during run 7, however, in order not to inhibit alpha alumina formation. During the first eight days, the mass median particle diameter (MMPD) of the product increased from 0.40 to 0.65 mm; the alpha content of the bed during this period remained low (10 to 15 percent), possibly because of the residual boron in the bed material. On the sixth day, the sodium nitrate content of the feed was increased from 0.04 to 0.08M. On the ninth day, the alpha content of the alumina in the bed started to increase, and it reached a final value of 75 percent at shutdown on the 13th day when the cyclone dipleg plugged; the MMPD of the product during this four-day period decreased to 0.40 mm. Some product agglomeration on a temporary tube support in the calciner was observed after the run.

A sand starting bed and a 0.01M boric acid concentration in the feed were used in run 8 with the modified cyclone fines disposal system. As expected, an essentially amorphous alumina bed was maintained throughout the run. The alpha alumina content of the bed was only 0.5 weight percent after 14 days of operation (98 percent bed replacement) as determined by a newly instituted technique of X-ray diffraction of the nitric-acid-insoluble portion of the material. The MMPD of the product increased from 0.26 to 0.71 mm until particle growth was arrested on the tenth day by an increase in the nozzle air-to-liquid volume ratio (NAR) from 300 to 580. The MMPD of the product then declined to 0.50 mm within 36 hours and remained near this value until the run was terminated to permit installation of the baffle. The essentially amorphous solids removed in

the recirculated scrubbing solution dissolved almost completely, leaving a very low undissolved solids content (0.2 weight percent). Some feed nozzle plugging occurred during the latter part of the run, and slight caking around the nozzles was observed after the run.

A sand starting bed was used also in run 9, but boric acid was not added to the feed in order not to inhibit alpha aluminum formation. After nine days of operation (90 percent bed replacement) the alpha alumina content of the bed was only 2.2 percent, as determined by X-ray diffraction of the acid-insoluble portion. At NAR values of 250, 300, and 400, the average particle diameter in the largely amorphous bed increased steadily; at an NAR of 500, the particle size began to decrease. The undissolved solids content of the scrubbing solution remained at a low level (0.2 weight percent) over this period as it had in run 8, when an essentially amorphous material was also produced. The sodium concentration in the feed was increased from 0.04 to 0.06M on the ninth day of the run; simultaneously the NAR was reduced to 300 in anticipation of the formation of the friable alpha alumina. By the 11th day, the alpha alumina had risen to and stabilized near 65 percent; the particle size, however, increased until the NAR was raised to 400, at which value the MMPD stabilized near 0.5 mm. An increase in the undissolved solids content of the scrubbing solution to 3 weight percent accompanied the transition to alpha alumina. This run was still in progress at the end of the quarter.

For convenience, scrubbing solution was not recycled to the feed on any of these runs, but no problem would be expected from so doing on the last two runs, inasmuch as the undissolved solids content was generally at acceptably low levels.

1.3 Product Transport System Modification

Operation of the product transport system, modified between runs 6 and 7 to eliminate the use of troublesome blowers, proved to be very satisfactory on runs 7, 8, and 9. In the modified system, the motivation force for pneumatically transporting product to solids storage is supplied by the negative pressure in the calciner vessel. Product drawn from the bottom of the vessel is pneumatically conveyed to the solids storage vault where the product is separated from the air by a cyclone. The transport air is then returned to the vapor space of the calciner. An air jet provides additional transport air motivation when unloading the solids from the bed; using this jet, the bed was unloaded in only 1-1/2 hours after run 8.

2. PILOT PLANT DEVELOPMENT STUDIES

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

2.1 Solids Carry-over

Factors affecting the elutriation rate of solids from a fluidized bed were further defined and studied during operation of the two-foot-square pilot plant calciner. These studies were a continuation of those reported previously [2] and were made to obtain data relevant to reducing the excessive solids loading in the off-gas leaving the DWCF calciner cyclone. Three runs, 29, 30, and 31, were made in the two-foot-square calciner to study the effects of nozzle air rate and

finer return to the bed on the solids elutriation rate. The crystalline structure of the product was controlled, as on previous runs, either by adding boric acid to or by increasing the sodium nitrate content of the feed. Alpha alumina was produced in runs 29 to 30 with a sodium nitrate concentration of 0.2M. No alpha alumina was detected in the bed material in run 31 when boric acid at a concentration of 0.01 M was used. Pertinent data on solids carry-over obtained in these runs are given in Table VIII along with similar data from an earlier run, 27.

TABLE VIII
SOLIDS CARRY-OVER IN THE TWO-FOOT-SQUARE CALCINER

Conditions: Feed rate, 150 liters/hr; nominal solids make rate, 12.4 kg/hr; bed temperature, 400°C.

Run No.	Nozzle Air-to-Liquid Volume Ratio ^(a) (NAR)	Superficial Fluidizing Velocity ^(b) (ft/sec)	Approximate Alpha Content of Product (wt%)	Fines Return to Bed ^(c)	Mass Median Particle Diameter of Product (mm)	Approximate Carry-over from bed to Cyclone ^(d) (kg/hr)	Approximate Carry-over from Cyclone (kg/hr)
27	300	0.5	35-45	no	0.30-0.36	4.0-6.0	0.2-0.3
29	300	0.5	30-40	no	0.46-0.70	4.0-5.0	0.2-0.4
29	200	0.5	35-50	no	0.42-0.48	2.5-3.5	0.2-0.3
29	150	0.5	25-30	no	0.48-0.58	2.0-2.5	0.1-0.3
30	200	0.5	20-25	no	0.52-0.60	1.5-2.2	0.2
30	250	0.75	15-25	no	0.40-0.60	3.0-6.0	0.25-0.5
30	250	0.75	25-40	yes	0.40-0.56	10-24	1-3
31	250	0.75	< 5	no	0.59-0.66	1.5-2.0	0.3 -0.4
31	250	0.75	< 5	yes	0.50-0.66	5.0-9.0	0.5 -1.0

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

(b) The superficial fluidizing velocity is the linear velocity that would be attained by the fluidizing gas in the empty vessel at the operating temperature and vapor space pressure. The fluidizing gas includes only that admitted through the distributor plate; it does not include the nozzle air, the water vapor, or the decomposition products of the feed.

(c) Returned those fines collected in the cyclone to the bottom of the bed by means of an auger conveyor.

(d) Total solids removed by the primary cyclone and venturi scrubber.

Major observations made during these runs are:

(1) While introducing feed at a rate of 150 l/hr to a bed containing 25 to 50 percent alpha alumina, a decrease in the nozzle air rate lowered both the calciner solids elutriation rate and the solids carry-over from the primary cyclone. This confirms results obtained on run 26 [2]. The decreased nozzle air rate also resulted in a lowering of the alpha alumina content of the solids elutriated

from the calciner; at an NAR value of 150, only a trace of alpha alumina was found in the elutriated solids, whereas these solids generally contain about half the alpha content of the bed. Apparently, at a reduced NAR, the elutriated fines are composed of chips containing much less of the high-alpha content cores of bed particles and much more of the largely amorphous outer layers.

(2) The elutriation rate of solids from the calciner increased markedly when the solids were returned to the bed. The solids elutriated from the calciner vessel and separated from the off-gas by the primary cyclone were collected and returned to the bottom of the bed with an auger conveyer on runs 30 and 31. In run 30 with an alpha alumina bed, the return of fines to the bed increased the elutriation rate from the calciner to a maximum of 24 kg/hr---about six times the elutriation rate obtained without fines return. In run 31, in which an amorphous bed was used, the return of fines to the bed increased the elutriation rate from the calciner to about 7 kg/hr---about four times the elutriation rate obtained without fines return.

(3) The return of fines to the bed also resulted, as would be expected, in higher concentrations of solids in the off-gas downstream of the calciner cyclone with both high- and low-alpha alumina beds. High-alpha beds showed the highest carry-over rates.

(4) The smaller effect of alpha content on fines carry-over from the cyclone than on that from the bed, when fines are not returned to the bed, indicates that the alumina structure of the bed influences the size as well as the quantity of fines generated in a fluidized bed.

In all runs to date, many fine particles were produced which are apparently too small to function as seed particles in the bed. Thus, means are needed for more effective incorporation of these fines into the crusts of growing particles. To this end, means of introducing the fines with or near the feed spray are under study. In flow tests of two configurations of a combined fines-return jet and feed nozzle, more than half the fines introduced to the jet were trapped in the spray on a single pass. A device of this type is being installed in the two-foot-square pilot plant calciner for testing.

2.2 Particle Size Control by Use of Sand Nuclei

Seeding a bed with inert material for effective control of particle growth rate is a desirable goal because the use of high nozzle air rates for seed production also generates excessive fines which increases the solids loading of the calciner off-gas. Sand "seeds" introduced to an amorphous bed on run 31, while operating at a feed rate of 150 l/hr, successfully controlled the particle growth rate of the bed at a lower NAR value than was found necessary in the DWCF with the same nozzle at the same conditions. On previous runs with amorphous beds, feed rates as high as 150 liters per hour could not be maintained in the two-foot-square calciner because of excessive particle growth rates; the usual method of controlling particle size by adjusting the NAR could not be employed because the available quantity of high pressure atomizing air at the pilot plant is limited. The actual quantity of sand used on run 31, one-

third of the product rate, was much higher than necessary because oversized material was employed; 4 to 5 kg/hr of unscreened sand (MMPD = 0.25 mm) were required to maintain the MMPD of the bed at about 0.5 mm. However, calculations show that a sand addition rate of only two percent of the product rate would have achieved the same result if the sand had been screened and only the portion under 0.1 mm in diameter added to the bed.

3. LABORATORY INVESTIGATIONS OF THE ROLE OF BORIC ACID (D. W. Rhodes, Problem Leader)

While boric acid has proven to be an effective inhibitor of the formation of alpha alumina, the mechanism for this inhibition is not clearly understood. Also, the possibility that boric acid addition to the feed would promote undesirable fluxing and caking in the fluidized bed required laboratory investigation.

3.1 Thermal Decomposition (E. M. Vander Wall)

The thermal decomposition of sodium nitrate, boric acid, and their mixtures was briefly investigated using the thermobalance. An average heating rate of 2.6°C per minute was used and the samples were heated to about 900°C, at which temperature the final products appeared to be glasses. When heated alone, the boric acid began decomposing around 100°C and the decomposition was 90 percent complete at 270°C; sodium nitrate did not decompose appreciably under these conditions until the temperature reached 600°C. However, mixtures of these two compounds, with mole ratios of sodium nitrate to boric acid of 1.7, 2.0, and 7.5, exhibited a third accelerated decomposition region between 420 and 470°C in addition to the rapid decomposition regions due to the individual components themselves. This result indicates that a third compound may exist in these mixtures between 300 and 420°C. Further work is necessary to establish the identity of this compound.

3.2 Cementing Tendency

Boric acid was added to calcined alumina and to aluminum nitrate crystals in an attempt to "cement" the alumina particles together. Intimate mixing of an amount of boric acid equal to 10 percent by weight of the alumina followed by firing to 600°C in a muffle furnace did not affect the free-flowing characteristics of the alumina.

3.3 Calcine Boron Leaching (C. M. Slansky, Project Liaison)

Additional studies on the role of boric acid were made under subcontract to Phillips by the Stanford Research Institute. Since the role of boron in retarding formation of the alpha alumina may be related to the bonding of boron with aluminum, or to its tying up the sodium in some manner, leaching studies were made to permit differentiation between various possibilities. Water extraction removed about half the boron from the calcined alumina, and ethanol extraction removed only one to six percent of the boron and very little sodium.

The water solubility indicates either that much of the boron exists as free boric acid, that it is tied up with sodium in a water soluble compound, or that it exists in such a combination with aluminum that it is subject to hydrolysis. The inextractability in alcohol eliminates the possibility that the boron is

present as free boric acid or in certain alcohol-soluble sodium compounds. However, additional studies are required to define more explicitly the mechanism by which boric acid inhibits alpha alumina formation.

4. BASIC LABORATORY CALCINATION STUDIES (C. M. Slansky, Project Liaison)

Additional basic calcination studies were made under subcontract to Phillips by the Stanford Research Institute. These studies included a brief study of the effect of phosphoric acid on aluminum nitrate calcination, and an initial investigation into stainless steel and nichrome nitrate calcination.

4.1 Effect of Phosphoric Acid on Aluminum Nitrate Calcination

In a series of 16 laboratory calcination tests in which either boric acid or phosphoric acid were added to the liquid feed, at concentrations ranging from 0.01 to 0.17 molar, alpha alumina was detected in the calcine to the extent of four percent on those samples employing only 0.01M boric acid or 0.01M phosphoric acid; but was not detected in any of the other samples employing higher additive concentrations. A control sample without additives produced 36 percent alpha alumina. These results indicate that boric acid and phosphoric acid are equally effective in retarding the formation of alpha alumina.

4.2 Stainless Steel and Nichrome Nitrate Calcination

Initial laboratory studies of the calcination of stainless steel and nichrome nitrates were made, using methods developed during studies of aluminum nitrate calcination. As would be expected for the complex systems involved, a wide variety of crystalline and amorphous compounds can be formed in these systems. The iron in these compounds always formed some alpha-Fe₂O₃, although the relative amounts varied; some gamma-Fe₂O₃ was detected also. Results indicated that boric acid and phosphoric acid might not be effective in hindering crystallization of alpha-Fe₂O₃. Nickel oxide (NiO) was formed in all of the samples containing a large amount of nickel. Other nickel compounds identified include NiFe₂O₄ and gamma-NiOOH; most of these samples also contained unidentified X-ray diffraction lines. Alpha-Cr₂O₃ was identified in calcine, apparently as a solid solution with alpha-Fe₂O₃.

5. POT CALCINATION (B. R. Wheeler, Problem Leader)

The AEC's Division of Reactor Development during April, 1962, transferred the responsibility for the operations phase of the radioactive pot calcining demonstration to the Hanford Atomic Products Operation. At that time, the engineering process flow sheet had been fully developed, and the detailed design of essentially all major equipment had been completed. A report is being prepared summarizing the design of this facility.

VI. BASIC PROCESS STUDIES AND EQUIPMENT DEVELOPMENT (Section Chiefs: J. I. Stevens, Development Engineering; K. L. Rohde, Chemistry)

1. EXPERIMENTAL AIR PULSER (E. E. Erickson, Problem Leader; S. J. Horn)

Experimental Studies

The single-phase (water) studies on the experimental air pulser have been completed. The equipment used in these studies was described elsewhere [3, 5], as was the method used for simulation on the analog computer [6, 7]. The results of the analog simulation were verified by the experimental studies.

The effects of air pressure and pulse frequency on the pulse amplitude were studied in the experimental equipment. The pulse amplitude was determined by direct visual measurement in the glass pulse leg and by electronically integrating the flow signal from a Ramapo flow transducer [3]. During the experimental studies it was determined that the calibration of the flow transducer was in error by approximately 20 percent. This calibration change probably was caused by an accidental freezing of the equipment during the winter.

The flow transducer and position-computing equipment were recalibrated by applying a step pressure input to the pulse leg. The depression of the water level in the pulse leg was measured directly and the output voltage of the integrator was recorded. The system was calibrated for reverse flow by releasing the pressure. These distance and voltage measurements were used to calculate an overall calibration factor. The average calibration factor from a series of such step input tests was within one percent of a similar factor calculated from pulse amplitude data.

The results of the experimental studies are shown in Figures 5 and 6. In Figure 5, the pulse amplitudes, as measured visually in the pulser leg, are compared with the results of the analog simulation. Figure 6 shows a similar comparison for pulse amplitudes computed by the integration of flowmeter signals. These computations use the calibration factor obtained from the step input recalibration tests. A comparison of Figures 5 and 6 shows that the pulse amplitude data obtained by direct visual measurement have a greater spread. This is a consequence, especially at higher pulse frequencies, of the difficulty in visually determining the extreme positions of the water level.

Linearization of the Equation

The equation describing the performance of the air pulser and used in the analog simulation [6, 7] is nonlinear in that it involves the square of the velocity and the product of the dependent variable and its derivatives. As a consequence, the equation can be handled conveniently only on a computer. However, if the equation can be approximated by a linear differential equation, it can be solved for a suitable pressure forcing function and studied using hand calculation methods. A general form of the nonlinear equation is:

$$(ay + b) \ddot{y} + [(c_1 y + c_2) \dot{y} + d] |\dot{y}| \dot{y} + ey - h = -P \quad (1)$$

Fig. 5 Comparison of pulse amplitudes obtained by analog simulation with results of visual measurement in glass pulser leg.

Fig. 6 Comparison of pulse amplitudes obtained by analog simulation with results of computation from integrated flowmeter signals.

where:

$\dot{y}$, $\ddot{y}$ = first and second derivatives of y , with respect to time, respectively

y = water level in pulser leg, referred to a suitable datum level

P = pressure (a function of time)

f = Fanning friction factor (a variable)

a, b, c , etc = numerical constants, determined by the physical properties of water and the geometrical configuration of the equipment.

For the linearization, it was assumed that Equation (1) could be written in the form:

$$M\ddot{y} + R\dot{y} + Ey - H = -P \quad (2)$$

where:

$$M = (a\bar{y} + b)$$

$$R = [(c_1\bar{y} + c_2)\bar{f} + d]\bar{y}$$

$\bar{y}$ = average position

$|\bar{y}|$ = average or "effective" velocity

$\bar{f}$ = average Fanning friction factor

Equation (2) was solved for a Morse Dot pressure function, which is essentially a half-wave rectified rectangular wave. While the pressure function in an actual air pulser is not a pure Morse Dot function but contains "ringing" transients, and the leading and trailing edges of the pressure pulse have finite slopes, the analog studies showed that these refinements of the pressure function had a negligible effect on the pulse amplitude.

The solution was obtained using Laplace transform methods. Since the Morse Dot function is a periodic function, the solution consists of two portions: a transient portion which dies out in time, and a steady-state portion.

Transient Portion

$$y(t) = \left\{ Y(0) - \frac{H}{E} + \frac{P}{E} \left[\frac{e^{rb} (\cos wb + B \sin wb) + 1}{(e^{rb} + \cos wb)^2 + \sin^2 wb} \right] \right\} e^{-rt} \cos wt$$

$$- \left\{ B \left[Y(0) + \frac{H}{E} \right] - \frac{RY(0)}{Mw} + \frac{P}{E} \left[\frac{e^{rb} (\sin wb - B \cos wb) - B}{(e^{rb} + \cos wb)^2 + \sin^2 wb} \right] \right\} e^{-rt} \sin wt \quad (3a)$$

Steady-state Portion

$$y(T) = \frac{H}{E} - \frac{P}{E} \left[\frac{(-1)^n + 1}{2} \right] + \frac{P}{E} \left[\frac{e^{rb} (\cos wb + B \sin wb) + 1}{(e^{rb} + \cos wb)^2 + \sin^2 wb} \right]$$

$$\left[(-1)^n e^{rT} \cos wT \right] - \frac{P}{E} \left[\frac{e^{rb} (\sin wb - B \cos wb) - B}{(e^{rb} + \cos wb)^2 + \sin^2 wb} \right] \left[(-1)^n e^{rT} \sin wT \right] \quad (3b)$$

where:

M, R, E, and H are defined in Equation (2), et seq.

$Y(0)$ = y at $t = 0$

$$r = \frac{R}{2M}$$

$$w = \left[\frac{E}{M} \left(\frac{R}{2M} \right)^2 \right]^{1/2}$$

$$B = \frac{r}{w}$$

$b = 1/2$ period

$n =$ any positive integer

$t =$ time

$T = t - (n + 1)b$

$P =$ maximum pressure

In any general interval of time $[nb < t < (n + 1)b]$, $[-b < T < 0]$.

Only the steady-state portion of the solution is used to calculate pulse amplitudes. It can be differentiated with respect to T to yield steady-state velocity and acceleration functions.

The results of calculations using Equation (3b) are shown in Figure 7. In these calculations, the following assumptions were made.

$$\bar{y} = Y_{(o)} - \frac{P/k}{\rho} \quad (1)$$

where

$\rho =$ density of the liquid in pulser leg

$k = 2$

This assumption was verified by both the analog and experimental data, where k varied with frequency approximately from 1.8 to 2.3.

$$|\bar{y}| = \frac{2}{3} |\bar{y}|_{\max} \quad (2)$$

It was assumed that the integral of pressure loss due to friction, ΔP_f , with respect to velocity, V , is a measure of the loss in kinetic energy due to friction.

therefore:

$$(\Delta P_f)_1 = \alpha V^2$$

$$(\Delta P_f)_2 = \alpha V(V_{\text{eff}})$$

Fig. 7 Comparison of pulse amplitudes obtained by analog simulation with results of calculations from linear Equation 3b.

$$\int_0^{V_{\max}} V^2 dV = V_{\text{eff}} \int_0^{V_{\max}} V dV$$

$$V_{\text{eff}} = \frac{2}{3} V_{\max} = |\bar{y}|$$

$$\bar{F} = 0.01 \quad (3)$$

This is a reasonable and convenient average for the range of Reynold's numbers involved.

The most-time-consuming step in calculating pulse amplitudes using Equation (3b) is a trial and error solution for $|\bar{y}|$ involving the first and second derivatives of Equation (3b) with respect to T and an initial assumed value of $|\bar{y}|$.

The agreement between the experimental data, analog simulation, and the linear solution is very good within the range of conditions studied. The assumptions made in deriving Equations (1) or (3b) do not specifically restrict application to conditions near those of the study. However, the limit of application could be more accurately established by further investigation. This is especially true in the case of two-phase operation.

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

Modification of the calculational technique [2] developed for the uniform plate spacing in the Rocky Flats experiments has been undertaken to optimize spacing of vertical neutron-poison plates in large-diameter ICPP storage tanks. An investigation was made for a poison-vessel system containing non-uniformly spaced plates based on the cosine distribution--spaced to yield equal areas under the cosine curve. The calculated k_{eff} for this system of nonuniformly spaced plates was not less than the k_{eff} for a similar system with uniformly spaced plates, as had been expected, but was essentially the same. Both systems contained the same number of poison plates. A comparison of the fast and thermal neutron flux plots for the two systems showed that the flux for the nonuniform plates was suppressed considerably in the center of the vessel where the plates were close together, and that the flux peaked toward the edge of the vessel where the plates were further apart. This work is continuing with other bases for plate distributions, and for the cosine distribution with an added condition that the terminal plates remain in the same position as in the uniform plate system.

3. REMOVAL OF TRIBUTYL PHOSPHATE FROM DILUTE AQUEOUS STREAMS (H. T. Hahn, Problem Leader)

The removal of tributyl phosphate (TBP) and its decomposition products from first-cycle aqueous streams will prevent further degradation and complex

formation during product concentration. It was shown previously that the removal of TBP by means of an Amsco wash can be successful [6]. 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, therefore, to remove the impurity from aqueous phases corresponding to C column and mixer-settler product. It has been established that dibutyl phosphoric acid will absorb on hydrous zirconium oxide ionexchange crystals. Trace phosphorus was removed from simulated mixer-settler products. In preliminary tests of plant solutions it appears that phosphorus species may be absorbed by, and eluted from, these crystals.

3.1 Capacity of Hydrous Zirconium Oxide for Absorption of Phosphate Compounds (E. M. Vander Wall, D. L. Bauer)

The absorption of dibutyl phosphoric acid (HDBP) on hydrous zirconium oxide ion exchange crystals (Bio Rad HZO-1, 100-120 mesh) was investigated. The solutions used were 0.03M nitric acid with various concentrations of HDBP, TBP, and uranium. Experiments were conducted in packed columns of high length-to-diameter ratio and were continued to crystal saturation, ie, until effluent phosphorus concentration equaled the feed concentrations. Pertinent capacity data are given in Table IX.

Absorption of TBP on the crystals is negligible. The total anion capacity of the crystals is about 1.3 milliequivalents per gram of hydrous zirconium oxide. In the presence of 0.03M nitric acid, the capacity for HDBP is between one-third and one-half of the total anion capacity. The presence of 0.02M uranium in the solutions reduces the capacity for HDBP approximately tenfold.

TABLE IX
CAPACITY OF HYDROUS ZIRCONIUM OXIDE FOR HDBP AND TBP
UNDER VARIED CONDITIONS

Feed Solution	Flow Rate (ml cm ⁻² min ⁻¹)	Capacity (millimole PO ₄ ⁼ per gram)
0.03M HNO ₃ + 5 x 10 ⁻⁴ M HDBP	1.3	0.60
0.03M HNO ₃ + 5 x 10 ⁻⁵ M HDBP	3.6	0.43
0.03M HNO ₃ + 5 x 10 ⁻⁵ M HDBP	3.6	0.36
0.03M HNO ₃ + 5 x 10 ⁻⁵ M HDBP + 2 x 10 ⁻² M U	3.6	0.054
0.03M HNO ₃ + 5 x 10 ⁻⁵ M HDBP + 2 x 10 ⁻² M U	2.1	0.048
0.03M HNO ₃ + 4.3 x 10 ⁻⁴ M TBP	7.1	< 0.001
0.03M HNO ₃ + 4 x 10 ⁻⁵ M TBP + 5 x 10 ⁻⁵ M HDBP	3.6	0.54

3.2 Phosphorus-32 Absorption (E. M. Vander Wall, D. L. Bauer)

Radioactive-phosphorus-traced aqueous-favoring phosphorus species [6] in mixer-settler product has been absorbed on zirconium oxide crystals. In a typical experiment the aqueous product of four successive contactings with Amsco was found to contain 2.7×10^{-4} g/l phosphate. After four equilibrations of approximately 100 ml of the product with one gram of HZO-1, the level was reduced to 1.5×10^{-5} g/l phosphate.

3.3 Plant Solution Tests (H. T. Hahn, D. L. Bauer, L. L. Allaman)

Since the plant extraction columns have not been operating recently, the acquisition of typical first-cycle solutions was difficult. However, three samples of evaporator product were available and these were used for the column absorption tests shown in Table X. The solutions contained 0.3N nitric acid and from 93 to 163 g/l uranium, in addition to the phosphate indicated in the table.

TABLE X

ABSORPTION OF PLANT PHOSPHORUS SPECIES ON HYDROUS ZIRCONIUM OXIDE

<u>Phosphate Concentration (mg/l)</u>		<u>Linear Flow Rate</u> (cm/min)	<u>Decontamination</u> <u>Factor</u>
<u>Column Feed</u>	<u>Effluent</u>		
34	0.4	0.31	85
34	2.5	0.31	14
34	1.8	0.31	19
189	30	0.35	6.3
189	129	0.35	1.5
189	160	0.35	1.2
189	120	0.22	1.6
189	145	0.24	1.3
267	55	0.056	4.9
267	37	0.022	7.2

The solutions were fed successively through the same packed column (276 mg of zirconium oxide crystals) without changing absorbent between feed materials, and the column effluent was sampled at approximately one-hour intervals. Decontamination results at the successive sampling periods are shown. When the linear flow rate was decreased near the end of the experiment, to give increased retention time, the decontamination factor was considerably improved.

All but the first sample are known to originate from plant cleanout operations and to contain relatively large amounts of zirconium. If the absorption is anionic in nature it may not be effective when zirconium is also present in solution. Absorption occurred in all cases, even in the presence of relatively large concentrations of uranium and nitric acid. The capacity of the column was greater than 0.045 millimoles phosphate per gram of exchanger. No uranium absorption has been noted.

Regeneration is possible, if desired, by elution with sodium hydroxide solutions. For example, 68 percent of the phosphorus absorbed in the above tests was eluted by 12 milliliters of 0.2N sodium hydroxide. Here again, residence time was significant.

Both the flow rate and the chemical composition of the solution will have a bearing upon the decontamination obtained. Although data are insufficient to predict, at this time, the decontamination factors obtainable in plant streams, some decontamination has been demonstrated in the available plant solutions tested in the laboratory. Therefore, contacting of evaporator feed with hydrous zirconium oxide crystals prior to concentration should decrease decomposition and complex formation in the evaporator by reduction in quantity of the offending phosphorus species.

VII. REPORTS AND PUBLICATIONS ISSUED DURING THE QUARTER

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IDO-14585, Ceramic Fuel Reprocessing - Preliminary Dissolution and Leaching Studies, L. A. Decker

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VIII. REFERENCES

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