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CHEMICAL PROCESSING TECHNOLOGY
QUARTERLY PROGRESS REPORT
January - March 1961

PHILLIPS
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COMPANY

ATOMIC ENERGY DIVISION

NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION

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CHEMICAL PROCESSING TECHNOLOGY

QUARTERLY PROGRESS REPORT

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CHEMICAL PROCESSING TECHNOLOGY

QUARTERLY PROGRESS REPORT

January-March 1961

J. R. Bower, Editor

I. SUMMARY

The Idaho Chemical Processing Plant operated on recovery of uranium from ETR fuel until termination of the run was made necessary by development of leaks in the first cycle product evaporator and transfer lines. The operating period had been adequate to demonstrate the successful operation of the newly-installed air pulsing system on the first cycle extraction column, and the decision was made to install the direct air pulsing system on all ICPP pulse columns during the period of plant shutdown required for the repair or replacement of defective equipment. Other changes to be accomplished during the same period include installation of additional air lifts to eliminate remote head diaphragm pumps, replacement of a packed scrubbing column with a mixer-settler unit, installation of neutron poisoning in the disengaging head of a product evaporator, and elimination of gravity cell floor drains.

Barium-140 production was continued on schedule, without incident, averaging approximately 53 per cent recovery of high quality product. First operation of the Demonstrational Waste Calcining Facility as a fully-integrated system led to discovery of further deficiencies which are being corrected.

Continued studies of aqueous zirconium processing, directed at reduction of solution volumes to be processed and stored as waste through separation of bulk zirconium from dissolver solutions, indicate that precipitation of barium fluozirconate is much less efficient at room temperature than at 95° C, requiring larger quantities of reagent, longer reaction periods, and more involved processing techniques. The room temperature studies were conducted since corrosion tests on welded samples of stainless steels showed that corrosion rates were substantially less (0.1 mil/month compared with 10 mils/month) at 35° C than at 95° C.

In a study of precipitation conditions aimed at achieving maximum separation of zirconium, minimum loss of uranium, and maximum stability of filtrates and washes when using sodium formate to precipitate zirconium and fluoride from STR-type dissolver solutions, it was determined that the precipitation should be carried out at 60° C or above, with the addition of 0.4 to 0.8 g/liter of a commercial flocculating agent to the slurry to obtain clear, stable filtrate and wash solutions which could be boiled

without reprecipitating. Use of a flocculating agent results in an approximate 1 per cent loss of uranium to the precipitate; this can be avoided by omission of the flocculating agent and substitution of an additional filtration step, after boildown; to clarify the solution for extraction. Boildown should be in the presence of chromic acid (0.03M), and wash solutions should contain sodium nitrate (0.1M) to minimize uranium loss. Corrosion tests on yttrium for possible use in the hydrofluoric acid-nitric acid system indicated that it was completely unsatisfactory in the presence of nitric acid, although it was extremely resistant to pure hydrofluoric acid.

Either sulfuric acid or hydrofluoric acid was found to effect dissolution of beryllia-uranium dioxide ceramic fuel, but the most feasible system involved dissolution in 12M H_2SO_4 -1M HNO_3 followed by adjustment of the dissolver solution with HNO_3 , leading to a solvent extraction flow-sheet similar to that for stainless steel processing.

In investigation of an alternate to the aqueous stainless steel process used at the ICPP, rate and activation energy expressions were determined for components of stainless steel, under certain specified conditions, undergoing dissolution in dilute aqua regia. Chemical reaction, rather than diffusion, was found to be rate determining for the dissolutions studied.

The behavior of uranyl, zirconium, and aluminum dibutylphosphates, formed as a result of decomposition of TBP in the extractant, is being studied under conditions in which uranium is stripped from the organic phase and tributylphosphate is stripped from the resultant aqueous phase, since these compounds affect extraction performance, and, in quantity, can impair the functions of mechanical equipment. Procedures for synthesis, verification of composition, and determination of thermal stability of these compounds are discussed; solubilities of uranium and aluminum dibutylphosphate in Amsco were found to be quite low (10^{-4} to $10^{-5}M$); distribution of the uranyl dibutylphosphate was found to favor the aqueous phase.

As a result of consideration of the temporary use of boron (boric acid) solution to assure critical safety in a maloperating evaporator, density coefficients and relative stabilities of nitric acid-uranyl nitrate-boric acid solutions were determined and reported.

Pilot plant studies of the fluidized bed calcination process for reduction of radioactive liquid wastes to the more-easily-stored solid form have continued with determination, in the two-foot-square calciner, that the intra-particle porosity of the alumina generated is primarily governed by the concentration of the aluminum nitrate in the feed and the bed temperature; the more desirable low porosity (high density) alumina is produced at lower temperatures ($400^\circ C$ as compared with $500^\circ C$) using a low concentration (1.5M) feed. The formation of alpha alumina was found to be related to calcining temperature and nozzle air-to-liquid volume ratio (NAR) in runs carried out during this period; a low temperature ($400^\circ C$) and a reduced NAR resulted in minimum alpha alumina formation; increasing either factor resulted in increased alpha alumina production which was reversible by again lowering the factor under investigation.

Sand was used successfully as a starter bed, in place of previously calcined alumina, and offered the advantage of being able to assess rapidly (within 24 hours) the characteristics of the newly formed alumina without having to wait for essentially complete bed replacement (50 to 100 hours). Excessive feed nozzle tip erosion rates were experienced with hardened stainless steel and alumina-coated titanium flat-faced nozzle tips.

Laboratory investigation of the conversion of amorphous alumina to alpha alumina, in the presence of sodium nitrate and nitric acid vapors, indicated the optimum temperature to be approximately 500° C. Quantitative assignment of the effect of sodium has not been possible, since it is apparently interrelated with other undefined factors involved in the previous calcination history.

In the first integrated test of the Demonstrational Waste Calcining Facility, control of the calciner bed temperature at 400° C appeared to be adequate with a liquid feed rate of 60 gal/hr and a superficial fluidizing velocity of 1 ft/sec; the NaK pump was operated at 68 per cent of capacity under these conditions. Correction of a number of deficiencies was required before further tests could be undertaken.

Additional studies on removal of long-lived radioisotopes from waste solutions (a program directed at simplifying long-term storage and disposal problems) indicated greater efficiency in removal of cesium from solution by adsorption on ammonium phosphomolybdate by operation at faster liquid flow rates over smaller size APM particles; e.g., a flow rate of 70 gal/(ft)²(hr) over 1 mm diameter particles was more effective than a flow rate of 5 gal/(ft)²(hr) over 4 mm particles. This higher capacity was attributed to the fact that more cesium was loaded on the column with less dissolution of the APM by the waste solution. Additional studies on the adsorption of strontium from acidic waste solution, by ion exchange with Amberlite 200 resin, indicated a distribution coefficient (in salt-free 0.1N nitric acid solution) that was essentially constant at 1×10^4 from tracer levels up to the concentration in ICPP waste (0.02 g/l). Increasing nitric acid concentrations above 0.003N and increasing concentrations of sodium, calcium, or aluminum nitrates from 0.001M to 1M decreased the K_d value for strontium.

In continued study on the separation of iron, nickel, and chromium from stainless steel waste solutions by mercury cathode electrolysis (a method for achieving a lower volume, less costly waste storage package), the apparent inhibiting effect of 1N sulfuric acid on the room temperature electrolysis was traced to the ionic state of chromic sulfate; increasing the temperature to 35° C apparently changes the form, allowing the electrolysis to proceed at an accelerated rate.

Since electrolytic dissolution has shown promise of wide applicability, and the operational behavior of an electrolytic dissolver is dependent both on the reactions which occur in the dissolver and the current density distribution, as affected by cell and electrode geometry, a study of these fundamentals has been underway. Potential-current density curves for a chromium electrode in various concentrations of nitric acid are presented, showing a Tafel relationship with a slope of 0.047 volt

over a wide range, some concentration polarization in the case of high acid concentrations (12M), but no secondary passivation as observed for stainless steel. From a study of potential-current density relationships for type 304 stainless steel over a wide range of conditions, it was concluded that the secondary passivation reported last period was a function of hydrogen ion concentration and disappeared above 4M acid. Demonstration and evaluation of the effects of stray currents in the vicinity of electrodes, with particular concern for corrosive situations in electrolytic process equipment, was pursued, both with direct measurements by means of Luggin probes in an operating test cell and by determination of lines of equal potential on conductive sheet analogs. An extensive pictorial presentation of results is included with the discussion of the findings. As a result of a search for means of determining and controlling the conditions existing in an operating electrolytic dissolver, the comparison of electrical conductivity measurements of original and diluted dissolver solution gives promise of simultaneous determination of acid and stainless steel concentrations by instrumental analysis.

Investigation of electrolytic disintegration of Zircaloy-2 in nitric acid, a process in which Zircaloy undergoes oxidation and disintegration to form a sludge, has been continued in an effort to define the most favorable conditions for the zirconium reaction. The incomplete dissolution of uranium from the alloy fuels remains the paramount problem. Efficient stirring was necessary to maintain the highly exothermic reaction at the optimum temperature of 70° C; at the boiling point, the rate was only 65 per cent of the maximum at the lower temperature. The optimum acid concentration for the reaction (8M HNO₃) gave an oxidation rate of 6.9 mg/(cm²)(min) and also resulted in the lowest cathode corrosion rate; severe cathode corrosion occurred in 4M HNO₃.

Corrosion evaluation of materials of construction for use in electrolytic dissolver systems indicated titanium to be completely resistant to boiling dissolver solution (1M HNO₃, 75 g/l dissolved stainless steel), while corrosion rates for stainless steels 304L, 316, 347, and Carpenter-20 rose steadily to 4-5 mils/month for the first 60 days of the test, after which they increased rapidly to 5-7 mils/month by 78 days, when the test was terminated; Inconel was found to be unsuitable after the second day of the test. Among plastic materials, fluorocarbons, polyethylene, and polyvinyl chloride were found to be resistant to the boiling dissolver solution, while phenol-, urea-, and melamine-formaldehyde resins and furan resin disintegrated. Exposure of stainless steel and Carpenter-20 coupons in an operating electrolytic dissolver resulted in severe corrosion in locations adjacent to, and unshielded from, the active cathode, indicating the existence of current paths far outside the direct path between the anode and cathode and emphasizing the limitations to be placed on the use of stainless steel near the active regions of the dissolver.

Studies involving the ARCO Process as applied to stainless steel (dissolution in molten PbCl₂ through which Cl₂ is passed) indicate that volatilization of the ferric chloride from the melt increases as the chromium and nickel content of the melt increases; in preliminary experiments with type 347 stainless steel, the percentage of dissolved iron which was volatilized in normal 550° C melts was increased steadily to

45 per cent as the chromium and nickel content was raised by continuing the dissolution for progressively longer times (chromium and nickel are much less volatile). In a single experiment raised to "red heat", 78.9 per cent of the iron, 15 per cent of the nickel, and 5 per cent of the chromium were volatilized, giving promise to the possibility of effecting nearly complete separation of the iron from the melt. Volatilization of niobium chloride was found to be essentially complete.

Successful performance of the ICPP first cycle direct air pulsed extraction column has led to replacement of all of the ICPP mechanical-hydraulic pulsers with air pulsers. The theoretical advantages cited earlier for these units⁽¹⁾ were reinforced by several generalizations obtained from results of the test run: (1) A much wider range of pulse energy input was available; (2) setting and maintenance of desired operating conditions were simpler and faster; (3) extraction efficiency was at least as good as with the mechanical pulser; and (4) initial installed costs for air pulser equipment were about 12 per cent of those for the mechanical pulsers.

In continued study of large vessel criticality control, directed at safe containment of enriched uranium in large-diameter vessels, neutron multiplication tests have been run using an ICPP-designed boron stainless steel cartridge in a 3-foot-diameter vessel; results of the tests are not yet available.

II. ICPP OPERATIONAL SCHEDULE, PERFORMANCE, AND PROBLEMS

A. ICPP Processing Schedule, J. R. Bower

Idaho Chemical Processing Plant Run No. 17, involving the dissolution and recovery of uranium from ETR elements, as well as the recovery of uranium from RaLa solutions and various recycle operations which had been in storage for some time, was undertaken during this period. Equipment failure forced termination of the run prior to completion of the planned program, but not before newly-installed air lifts in the head end section and the direct air pulser on the first cycle extraction column⁽¹⁾ had been proved to operate satisfactorily. An orderly shutdown was possible, with complete emptying and rinsing of all dissolution, storage, and extraction equipment, so that a complete decontamination and renovation could be undertaken.

Five barium-140 product runs were completed satisfactorily, with recovery as listed in Table 1.

TABLE 1

BARIUM-140 PRODUCTION AT ICPP, JANUARY-MARCH 1961

<u>Run No.</u>	<u>Curies</u>	<u>Per Cent Recovery</u>
050 RP	31,346	50.4
051	27,012	55.1
052	27,500	52.2
053	25,000	48.2
054	32,350	56.8

A strontium recovery run was made, following Run 053 RP. Approximately 48 curies of strontium-90 (64 per cent) were recovered; 23 per cent was accounted for in measured losses, and 13 per cent remained unaccounted for.

Functional testing of the process components in the Demonstrational Waste Calcining Facility was completed, and an integrated process test operation was conducted with the calciner charged with alumina which had been produced in the pilot plant and operating at 400° C while feeding water at a rate of 60 gal/hr. Correction of deficiencies discovered as a result of this operation (Section IV of this report) consumed the remainder of the period.

B. ICPP Renovation and Modification, J. R. Bower

Termination of uranium recovery operations was prompted by discovery

of leakage of product from the first cycle product evaporator to the cell floor, and leakage from a product line to the floor of N cell (feed and first cycle product storage) which, in turn, was draining to the waste system through a floor drain valve which would not hold. Decision was made to decontaminate the whole system and enter into an extensive renovation program, rather than to make only those repairs and replacements necessitated by actual equipment failures.

The first cycle product evaporator is presumed to have failed due to corrosion (leakage is at the upper tube sheet), although this can be verified only after the unit is removed and disassembled. This evaporator, in combination with the associated feed steam stripper and overflow tanks, has been the source of many operating difficulties and is being completely redesigned with elimination of the steam stripper and incorporation of boron stainless steel neutron poisoning in the disengaging head to reduce the possibility of incurring a critical incident. The remote-head diaphragm product pumps, moving product from this evaporator to the second cycle, have been a continual source of trouble and have seriously limited the capacity of the system. Air lifts will be installed in parallel with these pumps, in hope of eventual elimination of the pumps.

The second cycle product evaporator will be modified at the same time, with a reduction in the size of the disengaging head to minimize the possible criticality hazard.

The first cycle Amsco scrub column, which treats the aqueous uranium strip stream to remove traces of TBP prior to evaporation, will be replaced by a five-stage mixer-settler in an attempt to secure better scrubbing. Carryover of TBP to the evaporator has contributed to past operating difficulties through formation of complexes of the decomposition products with uranium and/or zirconium.

Reflecting the successful operation of the air pulser on the first cycle extraction column⁽¹⁾, air pulsers are to be installed on the scrub and strip columns, also, and on all three columns in the zirconium-stainless steel head end process.

Incidents of leaking through closed cell floor drains have led to the decision to cap, permanently, all floor drains in processing cells. An additional steam jet will be installed in each cell floor sump so that material can be transferred to the waste system or to the recovery system, as desired, but cannot leave the cell floor by gravity drain.

In addition to these major changes, numerous smaller repairs, pipe reroutings, elimination of temporary tie-ins, etc., will be accomplished.

III. AQUEOUS PROCESSING STUDIES

Section Chiefs: H. T. Hahn, Chemical Research
K. L. Rohde, Process Chemistry

The process in use at the ICPP for recovering uranium from uranium-zirconium alloy fuels utilizes hydrofluoric acid as a dissolvent and aluminum nitrate to complex the fluoride ion prior to solvent extraction. Since the alloy fuels under consideration are 95 to 99 per cent zirconium, the extraction process capacity is limited by the requirement for handling this large volume of zirconium (a diluent of the uranium), and the extraction raffinates generated involve an expensive storage problem because of the large volume and corrosive nature.

Precipitation reactions with the dissolver solution have been under study as a means of removing the bulk zirconium and excess fluoride in order to achieve reduced waste volumes, less corrosive process streams, and increased process equipment capacity in terms of uranium throughput. Current studies on the barium fluozirconate process, in which zirconium and fluoride are precipitated concurrently through the use of barium nitrate-barium hydroxide, report the results of carrying out the reaction at room temperature in an effort to minimize corrosion anticipated at higher temperatures; results of corrosion tests in simulated barium fluozirconate process solutions at 35° C and 95° C are reported. Further studies on an attractive alternate method for simultaneous removal of zirconium and fluoride, through precipitation with sodium formate, deal with the effect of flocculating agents on solution stability and uranium loss and means of minimizing uranium loss. A brief corrosion study indicates the stability of yttrium metal in hydrofluoric acid as contrasted to its failure in a mixed acid system containing nitric acid.

Work has continued in a series of scoping studies directed at processing of beryllia-uranium dioxide ceramic fuels, with results being reported on the feasibility of a process for dissolution in a 12M sulfuric acid-1M nitric acid mixture, followed by adjustment with nitric acid to lead to a solvent extraction flowsheet similar to that for stainless steel fuel reprocessing.

In investigation of an alternate to the sulfuric acid process for dissolution of stainless steel, results of studies on individual components of stainless steel undergoing dissolution in aqua regia are reported.

A study of uranyl, zirconium, and aluminum dibutylphosphates, under conditions in which uranium is stripped from the organic phase and tributylphosphate is stripped from the resultant aqueous phase in the ICPP extraction process, is underway, since these compounds affect extraction performance and, in quantity, can impair the functions of mechanical equipment. Solubilities in diluent Amsco and distribution coefficients between Amsco-TBP and uranium-nitric acid solutions are reported, as well as methods for preparation and characterization of the pure compounds.

A report is made on the density and stability to precipitation of aqueous solutions containing boric acid, nitric acid, and uranyl nitrate

as a result of the proposed use of boric acid to assure critical safety under certain emergency conditions.

A. Aqueous Zirconium Fuel Processing

1. Barium Fluozirconate Precipitation Process J. W. Coddington, Problem Leader; B. E. Paige

The precipitation of barium fluozirconate at room temperature (22° C) has been studied as a means of avoiding corrosion problems associated with higher temperatures in the mixed nitric acid-hydrofluoric acid solutions present in the process. Tests on welded samples of stainless steels in simulated barium fluozirconate process solutions showed that corrosion rates of the order of 0.1 mil/month with no pitting were observed at 35° C (Section A-2), while rates of the order of 10 mils/month with extensive weld pitting were observed at 95° C⁽²⁾. The fluoride in evaporator feeds can be complexed with aluminum to eliminate corrosion, but the addition of aluminum during the precipitation step greatly decreases the zirconium removal. The purpose of the present work has been to develop a method for the precipitation of barium fluozirconate at room temperature, at rates acceptable for process applications, without increasing the volumes in the process or the quantity of barium added.

Efforts to date have been only partially successful, in that large excesses of barium reagent and hydrofluoric acid were required to achieve greater than 90 per cent precipitation of zirconium at room temperatures. Solid reagents proved to be unacceptable for low temperature precipitation, due to slow and incomplete reaction.

Precipitation at 22° C with Solid Barium Precipitant

Solid alkaline barium precipitants reacted rapidly and completely with acid solutions at 90° C, and were, therefore, good candidates for room temperature precipitation. The relative amounts of heat generated by the addition of the precipitant to the STR dissolver solution were measured for three alkaline barium precipitants: barium hydroxide, barium oxide, and barium peroxide. The addition of barium peroxide did not increase the solution temperature, the addition of barium hydroxide increased the solution temperature only a few degrees, but the addition of barium oxide increased the solution temperature more than 50° C in 30 seconds. This eliminated barium oxide as a precipitant for low temperature precipitations. Solid barium peroxide as a precipitant gave only 20 per cent zirconium removal in 5 hours at 22° C. X-ray analysis showed that most of the barium peroxide remained in the precipitate. Barium hydroxide was the best of the solid alkaline precipitants for room temperature precipitations.

Barium hydroxide precipitations were made using 1 mole of barium per mole of zirconium originally present in the STR dissolver solution. The solid precipitant and solution were stirred vigorously with a mechanical stirrer in a plastic beaker at 22° C. Data obtained from dissolver solutions containing fluoride-to-zirconium mole ratios of both 5 to 1 and 6 to 1 are shown in Figure 1. Only 70 per cent of the zirconium was

Fig. 1. Barium Fluozirconate Precipitation with Solid $\text{Ba}(\text{OH})_2$

removed in 2 hours, and in both cases the rate of removal decreased greatly with time. The fluoride-to-zirconium ratio in solution also decreased during the precipitation. X-ray analysis showed that considerable barium fluoride had been precipitated. In both cases, unreacted barium hydroxide precipitant was found in the precipitate, even though the hydrofluoric acid had not been entirely neutralized. This indicated that inadequate mixing or surface coating had prevented thorough contact of the solution with the precipitant. Since the rate of zirconium removal was nearly the same for both ratios of fluoride to zirconium, a solution having a fluoride-to-zirconium mole ratio of 5 to 1 was used in other experiments to decrease the total acidity.

Previous studies at 90°C had shown that the addition of barium nitrate was necessary to obtain good zirconium removal when using barium hydroxide as the pre-

cipitant. Therefore, mixtures of solid barium hydroxide and barium nitrate were used in an effort to increase the rate and degree of zirconium removal at room temperature. A mixture of 20 mole per cent barium nitrate and 80 mole per cent of barium hydroxide, the proportions used in previous precipitations at 90°C, precipitated only 35 per cent of the zirconium in 2 hours. A mixture of 33 mole per cent barium hydroxide and 67 mole per cent barium nitrate removed less than 15 per cent of the zirconium. X-ray analysis showed that these precipitations produced barium fluoride and that a considerable portion of both of the reagents remained unreacted.

Since room temperature precipitation rates with barium hydroxide were not satisfactory for process use, the effect of increased temperature upon rates of precipitation was measured for barium nitrate. Data obtained at 20°C and 40°C are shown in Figure 2, together with data obtained previously for 90°C. Although the 40°C reaction was progressing at a rate which was reasonable for process use, the formation of extremely thick slurries eliminated this precipitation method from process consideration. The decrease in zirconium concentration in the supernate is proportional to the increase in temperature at one-hour reaction time. It was therefore concluded that in order to speed reaction rates with solid precipitants, the temperature would need to be increased to the region of high corrosion rates.

Precipitation at 22° C with Solutions of Barium as Precipitant

A solution of barium produces rapid precipitation of barium fluozirconate at 90° C; however, the increase in volume of supernate is a disadvantage. A saturated solution of barium nitrate contains 0.426M barium at 25° C. A saturated solution of barium hydroxide contains only 0.264M barium at 25° C. A phase diagram prepared from solubility data for mixed solutions of barium nitrate and barium hydroxide⁽³⁾ shows that the concentrations in solution at 25° C can be as high as 0.836M in barium and 0.66M in hydroxyl ion in mixed solutions. This solution of mixed salts is sufficiently concentrated to be considered as a precipitant for a barium fluozirconate process. The concentration selected for actual experiments was 0.7M in barium and 0.56M in hydroxyl ion.

Precipitations using the 0.7M barium solution were made at 25° C by adding a mole of barium per mole of zirconium originally present. This solution was pumped into the STR dissolver solution, while stirring, at the rate of 1 to 2 per cent of the reagent per minute. The zirconium concentration in a solution having a 6-to-1 fluoride-to-zirconium mole ratio was reduced to 0.22M in zirconium, representing a 65 per cent zirconium removal; in an STR dissolver solution containing a fluoride-to-zirconium mole ratio of 5 to 1, it was decreased to 0.16M in zirconium, a 70 per cent zirconium removal. No further reaction was produced by

stirring for 1 hour after the addition of the precipitant. When sufficient additional barium solution was added to increase the barium-zirconium mole ratio to 1.4, the zirconium concentration was reduced to 0.032M, but due to the increase in supernate volume, the zirconium removal was still only 92 per cent. The "efficiency" of the precipitant, or the moles of zirconium precipitated per mole of barium added, is only 67 per cent for this case. The supernate was heated at 40° C and 90° C, but no further precipitation occurred. The fluoride-to-zirconium mole ratio in the supernate had decreased to 3, and the addition of hydrofluoric acid to increase the fluoride concentration to about 0.6M resulted in a decrease in zirconium concentration to less than 0.001M, or essentially complete removal of the zirconium. This supernate was about 0.6M in in hydrogen ion.

Fig. 2. Barium Fluozirconate Precipitation with Solid Ba(NO₃)₂

The addition of excess barium solution increases the volume of supernate to be evaporated as well

as the bulk of barium to be stored as waste, whereas the addition of hydrofluoric acid increases the residual hydrogen ion concentration. Following a precipitation with the 0.7M barium solution using 1 mole of barium per mole of zirconium originally present, two series of precipitations were made using stepwise additions of hydrofluoric acid and barium solution in an attempt to find conditions of minimum reagent addition. In one series, the additions were made directly to the slurry. In the other series, they were made to the supernate following centrifugation of the slurry resulting from the preceding precipitation step. Data are presented in Table 2.

TABLE 2

EFFECT OF POST-ADDITION OF REAGENTS UPON ZIRCONIUM REMOVAL
BY BARIUM FLUOZIRCONATE PRECIPITATION AT 22°C

Slurry: STR dissolver solution precipitated
at 22° C with a solution of 0.7M
barium using 1 mole of barium per
mole of zirconium

Experiment No. (Order of Addition)	Reagent Added	Quantity Added	Zirconium Remaining in Solution, M	
			Reagent Added to the Supernate	Reagent Added to the Slurry
Slurry	--	---	0.16	0.16
1	HF	1 mole F/mole Zr	0.093	0.13
2	HF	1 mole F/mole Zr	0.064	0.11
3	HF	1 mole F/mole Zr	0.063	0.11
2A	0.7M Ba Soln.	0.4 mole Ba/mole Zr	0.042	0.090
2B	HF	4 moles F/mole Zr	< 0.001	0.086

In every case, additions to the supernate were more effective than the additions to the slurry. In experiments 1, 2, and 3, the fluoride-to-zirconium mole ratio in solution was increased from 3 to 4, from 4 to 5, and finally from 5 to 6 by the addition of hydrofluoric acid. Zirconium concentrations were decreased by the first two additions of hydrofluoric acid, but not by the third addition, indicating a deficiency of barium at this point. The addition of 20 per cent more barium solution at this point, as in experiment 2A, further decreased the zirconium concentration. The 0.042M zirconium concentration obtained by this treatment of the supernate was considerably better than the 0.092M zirconium concentration obtained by the addition of 20 per cent more barium when no increase in fluoride concentration had been made. Once again, essentially-complete removal of zirconium was achieved by a

final addition of excess hydrofluoric acid to the supernate containing excess barium, but the addition of hydrofluoric acid had little effect when the barium fluozirconate precipitate was present. A 0.7M hydrogen ion concentration and a 0.4M fluoride concentration remained. An experiment, similar to number 2 where the fluoride-to-zirconium mole ratio was increased from 3 to 5, was performed using a single centrifugation following the addition of 1 mole of barium per mole of zirconium and a single addition of hydrofluoric acid. This method removed 85 per cent of the zirconium originally present.

Summary of Observations

Using standard mixing techniques with solid reagents, the precipitation of zirconium as the barium fluozirconate at 22° C is too slow for process consideration. The rapid precipitation rate obtained with barium solution shows that the slow rates obtained with solid precipitants are due to poor contact of the solid precipitant with the zirconium solution. Residual alkaline precipitant in the precipitate also indicated inadequate contact of the precipitant with the acidic solution. A more efficient mixing or blending of the slurry could possibly increase the precipitation rates.

Precipitation with a mixed solution of barium nitrate and barium hydroxide, using 1 mole of barium per mole of zirconium, removes 70 per cent of the zirconium and reduces the fluoride-to-zirconium mole ratio to 3 in solution. This can be increased to 85 per cent removal of the zirconium by increasing the fluoride-to-zirconium ratio to 5 by the addition of hydrofluoric acid. Such a step is most effective when the hydrofluoric acid is added to the supernate after the precipitate has been removed by centrifugation.

The initial addition of 1.4 moles of barium per mole of zirconium removes 92 per cent of the zirconium, and a final addition of excess hydrofluoric acid further precipitates the zirconium, removing better than 99 per cent. Although good removal of zirconium at 22° C can be accomplished in this way, such a precipitation technique increases the quantity of barium in waste storage, the volume of evaporator feed, and the hydrogen ion and fluoride concentration in the supernate.

Maximum removal of zirconium is obtained when the fluoride-to-zirconium mole ratio is 5 or greater. This ratio has been observed to decrease to 3 during precipitation with 1 mole of barium per mole of zirconium. A better precipitation system can be developed by correlation of the decrease in fluoride-to-zirconium ratio during precipitation with the "efficiency" of the barium precipitant used. Further studies will be designed to decrease the quantity of barium reagent and the concentration of residual acid while maintaining a zirconium removal of better than 90 per cent.

2. Barium Fluozirconate Process Corrosion Studies N. D. Stolica, Problem Leader; M. R. Bomar

Information was desired on the corrosion rates to be expected

in the barium fluozirconate process if precipitation were carried out at 35° C, to verify the premise that the excessive corrosion characteristic of operation at 90° C⁽²⁾ could be avoided. Average corrosion rates for duplicate coupons of welded and unwelded Carpenter-20 Cb, stainless steel 347 Cb, and stainless steel 304L have been observed. Rates for exposure in two solution compositions at 35° C were found to be acceptable except in the case of welded Carpenter-20 Cb.

Experimental

Corrosion coupons of the materials to be tested were finished with 100-grit sandpaper, passivated in 35 per cent HNO₃ and weighed.

The solutions to which the coupons were exposed were 4M and 1M HNO₃ saturated with BaZrF₆. The solutions were prepared by dissolving BaZrF₆ in the desired concentrations of HNO₃ at 80° C. The solubility of BaZrF₆ in 4M HNO₃ was 43 g/l, and in 1M HNO₃, 17 g/l — both at 35° C. The solutions, when prepared, contained approximately these quantities of BaZrF₆, but during the course of the 15-day exposure, considerable quantities of BaZrF₆ precipitated. The solutions were maintained at 35° C and gently stirred during the test.

The corrosion coupons were suspended at the vapor-liquid interface with approximately 50 per cent of the surface immersed. After a 15-day exposure, the coupons were cleaned and weighed. The results are given in Table 3.

TABLE 3

CORROSION IN BARIUM FLUOZIRCONATE PRECIPITATION PROCESS

<u>Alloy</u>	<u>Corrosion Rates (mils per month) at 35° C</u>	
	<u>4 molar HNO₃ saturated with BaZrF₆</u>	<u>1 molar HNO₃ saturated with BaZrF₆</u>
C-20 Cb	0.098	0.004
C-20 Cb welded	0.18 *	0.044
SS 347 Cb	0.22	0.042
SS 347 Cb welded	0.24	0.070
SS 304L	0.19	0.32
SS 304L welded	0.29	0.35

* Carpenter-20 Cb suffered selective weld attack.

Note: The above values are average rates observed on two coupons.

Conclusions

Since the corrosion rates are considerably less than 2 mils per month, these alloys can be considered satisfactory for process equipment, with the exception of Carpenter-20 Cb, which suffered selective weld attack and is not recommended.

3. Zirconium Precipitation with Sodium Formate J. W. Coddington, Problem Leader; B. J. Newby

Precipitation with sodium formate has been demonstrated to be an attractive means of simultaneously removing zirconium and fluorine from hydrofluoric acid-zirconium fluoride dissolver solutions.⁽¹⁾ A rapid removal of greater than 97 per cent of the zirconium and fluorine over a wide range of precipitation temperatures is realized when two moles of sodium formate are added per mole of zirconium in solution. Uranium loss is of the order of 0.1 per cent, provided the uranium has been oxidized to the hexavalent state prior to precipitation. Work has continued during this quarter in an attempt to find precipitating conditions which would result in a solution easily adjusted to a suitable feed for a TBP extraction system.

Effect of Precipitation Temperature and Flocculating Agents

Studies were performed to select the smallest quantity of flocculating agent combined with the lowest precipitation temperatures which would yield filtrate and wash solutions free from residue. Flocculating agents studied were potato starch, General Mills' Galactasol CAM, Dow's Separan NP10, Stein Hall's Jaguar, and Cyanamid's Aerofloc 550 Reagent. Precipitations carried out below 60° C required very rapid addition of precipitant to prevent the formation of thick immobile slurries. Instability of filtrates and wash solutions was not prevented even with concentrations of flocculating agents greatly in excess of the manufacturers' recommendations.

In precipitations carried out at 60° C or higher, the physical appearance of the slurry was independent of rate of precipitant addition (26 weight per cent of sodium formate solution added to an equal volume of dissolver solution). With the exception of potato starch, use of 0.4 g of flocculating agent per liter of slurry resulted in filtrates and wash solutions free of residue; potato starch was ineffective.

The slurries formed with sodium formate filter quite rapidly. Treatment with flocculating agents does not increase the filtration rates, but does make uranium removal from residues more difficult. Table 4 shows the uranium removal obtained when precipitates formed as described were washed four times with 13 ml of 0.1M sodium nitrate. The use of flocculating agents invariably resulted in a greater percentage of uranium being lost to the precipitate.

The concentration, by boiling, of filtrates and wash solutions from precipitations carried out at 60° C requires the addition of 80 mg/liter of one of the commercial flocculating agents studied (plus a

TABLE 4

LOSS OF URANIUM TO SODIUM FORMATE PRECIPITATES AS A
FUNCTION OF FLOCCULATING AGENT CONCENTRATION

Conditions: 8.5 g of sodium formate precipitate
was washed 4 times with 0.1M NaNO_3 ;
the precipitate was formed at 60°C
in the presence of H_2O_2 , using 2.5
moles of sodium formate per mole of
zirconium present.

Flocculating Agent Used	Flocculating Agent Concentration (mg/liter of slurry)	Per Cent of Uranium Lost to Precipitate
None		0.2
None		0.2
Separan NP10	40	1.4
Jaguar	60	0.9
Jaguar	40	0.8
Galactasol CAM	40	0.9
Potato starch	400	0.7
Aerofloc 550 Reagent	20	0.3
Aerofloc 550 Reagent	40	1.1

fluoride complexing agent such as aluminum nitrate) if an additional filtration step is to be avoided. The same effect might be accomplished by using filtrates and wash solutions produced during precipitations performed at boiling temperatures.⁽¹⁾ If an additional filtration step after the wash solutions and filtrates are concentrated is not objectionable, the use of flocculating agents should be avoided.

Effect of Wash Solutions

Water and 0.1M solutions of seven different reagents were examined for their ability to remove uranium from precipitates formed at 60°C between 25 ml of STR process dissolver solution made 0.03M in chromic acid and 25 ml of solution containing 6.7 g of sodium formate. Wash solutions tested were nitric acid, hydrofluoric acid, formic acid, sodium formate, sodium nitrate, sodium fluoride, and aluminum nitrate. Approximately 8.5 g of residue were washed four times with 13 ml of wash solution. Table 5 summarizes the uranium removal and precipitate dissolution information pertinent to each system. The water and acid washes dissolve more of the precipitate than do the sodium-containing washes while being no more effective for uranium removal. Water, the aluminum nitrate wash, and the acid washes contained residue immediately after use, while the sodium-containing washes were stable for at least a day; only a trace of residue was found in the sodium washes after a week.

TABLE 5

EFFECT OF VARIOUS WASH SOLUTIONS ON URANIUM REMOVAL
AND PRECIPITATE DISSOLUTION

Conditions: 8.5 g of precipitate washed 4 times
with 13 ml of wash solution; precipi-
tate formed at 60° C in the presence
of 0.015-0.03M chromic acid.

Wash Solution	Per Cent of Total Uranium Remaining in Washed Precipitate	Zirconium Concentration in the Used Wash Solutions (M)
Water	0.17	0.036
0.1M sodium formate	0.24	0.021
0.1M sodium nitrate	0.16	0.023
0.1M sodium fluoride	0.25	0.029
0.1M formic acid	0.19	0.048
0.1M nitric acid	0.16	0.045
0.1M hydrofluoric acid	0.18	0.058
0.1M aluminum nitrate	0.12	0.030

Thus, sodium wash solutions should be used if there is the possibility that stable combined washes and filtrates can be complexed with aluminum nitrate and boiled down to a small volume without appearance of solids.

Preliminary Boildown Studies

A few scoping boildown experiments were performed on filtrates combined with 0.1M sodium nitrate wash solutions resulting from precipitations with sodium formate. These studies were performed to determine how the boildown was affected by precipitation temperatures, flocculating agents, oxidants, and boildown techniques. Twenty-five ml of standard sodium formate solution were added at 60° C, or at boiling temperature, to 25 ml of STR dissolver solution which was either 0.03 or 0.06M in chromic acid or had been treated with hydrogen peroxide; the precipitations carried out at boiling in the presence of a flocculating agent contained 40 mg of Jaguar per liter of slurry; those carried out at 60° C with a flocculating agent contained 60 mg per liter. The precipitates were filtered, washed four times with 13 ml of 0.1M sodium nitrate, and the wash solution and filtrate were combined. The resulting solution was boiled down to either 4 or 10 ml, and the resulting slurry filtered and washed again. The 1.5 ml of solution used to wash the solid from the 4 ml of slurry was combined with the filtrate for analysis; that used to wash the solid from the 10 ml of slurry was kept separate from its filtrate and the two analyzed separately. In experiments involving hydrogen peroxide, the oxidant was added continually during boildown and also was used in the 0.1M sodium nitrate wash solutions.

A summary of the uranium removed from precipitates, the fluoride and zirconium removed from filtrates, the solids produced during boil-down, as well as other information obtained during these boil-down experiments is shown in Table 6. Chromic acid was much more efficient than hydrogen peroxide in keeping uranium in the hexavalent state; no difference could be discerned between the efficiency of the two chromic acid concentrations used. None of the other variables studied had any appreciable effect on the boil-down.

TABLE 6

BOILDOWN CHARACTERISTICS OF FILTRATES AND 0.1M SODIUM NITRATE WASH
SOLUTIONS PRODUCED DURING SODIUM FORMATE PRECIPITATION

Conditions: Precipitate was formed by adding 25 ml of sodium formate solution containing 6.7 g of sodium formate to 25 ml of dissolver solution; 8.5 g of sodium formate precipitate was washed four times with 13 ml of 0.1M sodium nitrate.

Boildown Techniques	Oxidant Conc. in Dissolver Solution	Precipitation Temperature	Analysis of Process Streams before Boildown				Analysis of Process Streams after Boildown										Per Cent Zr Removed
			Per Cent of Total U Lost to ppt	Filtrate		Wash Soln. Zr (M)	Solids		Filtrate			Wash Soln. Zr (M)	Filtrate and Wash Solution				
				Zr (M)	H+ (M)		Wt in g	Per Cent of Total U Lost to Solid	Zr (M)	F (M)	H+ (M)		Zr (M)	Zr (M)	F (M)	H+ (M)	
A, D	H ₂ O ₂ used ^(C)	60° C	0.9	0.010	0.94	0.027	0.45	> 2	0.002	< 0.16	0.03	~ 0.008				99.8	
A, F	H ₂ O ₂ used ^(C)	60° C	1.8	0.015	1.04	0.020	0.45	> 2	0.004	< 0.16	0.5	< 0.01				> 99.7	
B, D	H ₂ O ₂ used ^(C)	Boiling	0.6	0.025	0.97	0.025	0.34	1.3					0.004	< 0.08	0.11	99.9	
B, E	H ₂ O ₂ used ^(C)	Boiling	0.3	0.023	1.13	0.014	0.33	0.97					< 0.004	< 0.16	0.08n ^b	> 99.9	
A, D	0.06M CrO ₃	Boiling	0.4	0.023	1.0	0.026	0.23	0.07	0.005	< 0.11	1.6	0.007				99.8	
A, E	0.06M CrO ₃	Boiling	0.4	0.018	0.95	0.020	0.24	0.2	0.006	< 0.11	1.5	< 0.01				> 99.7	
A, F	0.03M CrO ₃	60° C	0.2	0.012	1.15	0.021	0.19	0.008	0.004	< 0.11	0.6	0.015				99.7	
B, D	0.06M CrO ₃	60° C	0.3	0.014	1.04	0.021	0.35	0.05					0.007	< 0.08	0.74	99.8	
B, E	0.03M CrO ₃	Boiling	0.3	0.022	0.98	0.021	0.23	0.03					0.11	< 0.11	1.3	99.7	

- A) 52 ml of 0.1M NaNO₃ and 25 ml of filtrate were boiled down to 10 ml, the resulting residue was filtered and washed 4 times with 1.5 ml of 0.1M NaNO₃; the latter wash solution and filtrate were kept separate.
- B) 52 ml of 0.1M NaNO₃ and 25 ml of filtrate were boiled down to 4 ml, the resulting residue was filtered and washed 4 times with 1.5 ml of 0.1M NaNO₃; the latter wash solution and filtrate were combined.
- C) 25 ml of dissolver solution were boiled 10 minutes with 1 1/2 ml of 30 per cent H₂O₂ prior to sodium formate precipitation; 2 ml of 30 per cent H₂O₂ were added a little at a time during the boildown; 0.1M NaNO₃ wash solutions were made 2.8M in H₂O₂ before using.
- D) No flocculating agent present.
- E) Precipitation carried out in the presence of 40 mg of Jaguar per liter of slurry.
- F) Precipitation carried out in the presence of 60 mg of Jaguar per liter of slurry.

4. Corrosion of Yttrium in Hydrofluoric and Nitric Acids
N. D. Stolica, Problem Leader; T. L. Hoffman

Yttrium is quite resistant to atmospheric attack and corrosion⁽⁴⁾ and was therefore considered for possible use in the highly corrosive hydrofluoric acid-nitric acid system. A scoping study was conducted in boiling 14.2M hydrofluoric acid; in 13M nitric - 2M hydrofluoric acid mixture at 30 - 70° C; and in 65 per cent nitric acid at 20° C.

The yttrium metal used in these experiments was obtained from Iowa State College, Ames, Iowa. Its purity was 99.9 per cent. Coupons having an area of 1.375 square inches were studied in 60 ml of the different acid environments. Table 7 lists the results of this work.

TABLE 7
CORROSION OF YTTRIUM IN MIXED ACIDS

Type Acid	Temp. (°C)	Exposure Time (Hr)	Corrosion Rate (IPM)	Remarks
2M HF-13M HNO ₃	30-70	1	33.84	Milky ppt. in solution
65% HNO ₃	20	0.5	73.86	Specimen dissolved
14.2M HF	Boiling	24	0.0000	White deposit film

The yttrium failed completely in pure nitric acid and the mixed acid system. It was extremely resistant to pure hydrofluoric acid, due, probably, to the formation of an insoluble fluoride film.⁽⁵⁾

B. Aqueous Ceramic Fuel Processing

1. Chemical Reprocessing of BeO-UO₂
J. W. Coddling, Problem Leader; L. A. Decker

Work has continued in the study of various methods of preparing beryllia-uranium dioxide ceramic fuel for chemical reprocessing. Scoping studies have been done during the quarter on aqueous dissolution methods using sulfuric or hydrofluoric acids, either of which will effect dissolution or disintegration of the ceramic fuel. The most feasible process appears to be complete dissolution in 12M sulfuric acid-1M nitric acid.

Sulfuric Acid System

Dissolutions with sulfuric acid were carried out in 250 ml Erlenmeyer flasks fitted with reflux condensers. In each experiment approximately 2.5 grams of fuel in four pieces were placed in about 50 ml of dissolver reagent. All dissolutions were carried out at the boiling

point; no stirring was used other than that resulting from boiling action.

Use of 12.0M sulfuric acid alone resulted in dissolution of four fuel pieces, having a total initial surface area of about 20 cm², in less than 18 hours, leaving a greenish-white residue. Addition of nitric acid converted that residue to a white crystalline precipitate of BeSO₄·4H₂O which dissolved completely in water. The final stable filtered sulfuric and nitric acid dissolver solution contained 29 per cent of the beryllium and 90 per cent of the uranium of the fuel. The water solution of the precipitate was 1.0M in beryllium and contained the balance of the beryllium and uranium. These solutions could be blended to form a solvent extraction feed.

Addition of nitric acid to the sulfuric acid dissolver solution prior to fuel addition resulted in practically no attack with high (5.0M) nitric acid and complete dissolution with low (1.0M) nitric acid; 12M sulfuric acid was used in every case.

With 12M H₂SO₄ - 5M HNO₃, the fuel pieces appeared only slightly affected after 22 hours. The 0.7 g weight loss which occurred during that time was mostly uranium dissolution. Only 150 mg of beryllium appeared in solution.

Complete dissolution with no residue was obtained in about 8 hours using 12M H₂SO₄ - 1M HNO₃ as dissolving reagent. Upon cooling, white crystals of BeSO₄·4H₂O appeared; these dissolved upon further heating and subsequent dilution. The final stable solution was 1M HNO₃ and 6M SO₄⁼, containing about 8 g/l of beryllium and all of the uranium. The overall rate of dissolution for this condition was about 0.3 mg/(cm²)(min). While this is not a particularly rapid rate of attack, the rates of dissolution were even lower in the other media tried.

Hydrofluoric Acid System

A dissolution using hydrofluoric acid was carried out in a Teflon flask fitted with a Teflon reflux condenser. Fuel weights and solution volumes were approximately the same as those described above. A black precipitate remained after contacting the fuel pieces with 14M HF for 24 hours at the boiling point. Addition of CrO₃ to make the solution 0.02M Cr(VI) converted the black precipitate to a greenish-white residue which contained about 19 per cent of the total uranium.

An attempt was made to precipitate the beryllium from solution as calcium fluoberyllate by the addition of calcium nitrate. Results were not of process interest, since the precipitate formed was not crystalline and failed to separate satisfactorily upon filtration or centrifugation.

Conclusions

Previous reports in this series have discussed scoping studies of two other systems for handling ceramic fuels, i.e., using molten ammonium bifluoride as dissolvent, and a grind-leach procedure using nitric acid. This report completes the presentation of experimental data

in the preliminary study of the four chemical processing methods originally proposed. A topical report will be issued summarizing the results of this investigation, and will present processing flowsheets for the four methods studied.

On the basis of studies so far reported, the most feasible processing scheme for handling ceramic fuels containing beryllia and uranium oxide involves complete dissolution of the fuel in 12M sulfuric acid - 1M nitric acid, followed by adjustment of the dissolver product with additional nitric acid. This method leads to a solvent extraction flowsheet similar to that for stainless steel fuel reprocessing.

C. Aqueous Stainless Steel Fuel Processing

1. Dissolution Rates of Nickel and Iron in Dilute Aqua Regia N. D. Stolica, Problem Leader; R. D. Cannon

The use of dilute aqua regia for dissolution of stainless steel-containing fuels has been considered for some time as an alternate to the sulfuric acid process used at ICPP. An effort was made to determine empirical rate expressions for the dissolution of pure iron and pure nickel in dilute aqua regia.

The relative effects of the system variables on the dissolution rate were determined by series runs in which one component (i.e., HCl concentration) was varied while the others (i.e., temperature, stirring speed, HNO_3 concentration) were held constant. Apparent activation energies were determined by series runs in which the temperature was varied while the other variables were held constant.

The complexity of the dissolution reaction made it impossible to determine a general empirical rate expression for the dissolution of these metals, but the effect of certain individual components can be described by:

$$R_I = 1.34 \times 10^{-4} [\text{HCl}]^{-0.62} \quad \text{in } 2\text{M } \text{HNO}_3 \text{ at } 50^\circ \text{C} \quad (1)$$

$$R_N = 4.67 \times 10^{-5} [\text{HCl}]^{1.38} \quad \text{in } 7\text{M } \text{HNO}_3 \text{ at } 80^\circ \text{C} \quad (2)$$

$$R_N = 1.76 \times 10^{-8} [\text{HNO}_3]^{4.18} \quad \text{in } 1.5\text{M } \text{HCl} \text{ at } 80^\circ \text{C} \quad (3)$$

where:

R_I = Iron dissolution rate (eq./ $(\text{cm}^2)(\text{min})$)

R_N = Nickel dissolution rate (eq./ $(\text{cm}^2)(\text{min})$)

$[\text{HNO}_3]$ = Nitric acid concentration (moles/liter)

$[\text{HCl}]$ = Hydrochloric acid concentration (moles/liter)

These expressions are valid in the presence of both acids and vigorous stirring.

The apparent activation energies were determined by solving for E_a in the expression:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left(\frac{T_2 - T_1}{T_2 T_1} \right) \quad (4)$$

where:

E_a = activation energy R = gas constant
 k_1 = rate constant at T_1 T_1 = temperature 1
 k_2 = rate constant at T_2 T_2 = temperature 2

The activation energy for iron dissolution in 2M HNO_3 - 1M HCl , calculated using data taken at 50, 60, and 70° C, varied from 10.5 to 19.3 kcal per mole. The activation energy for nickel in 7M HNO_3 - 1.5M HCl at 60, 70, and 80° C varied from 9.9 to 17.2 kcal per mole.

It is apparent from the rate expressions derived from the data that the mechanism of dissolution is complex. Expressions describing the dissolution rate data can, therefore, only be written to cover a limited range of conditions. The magnitude of the activation energies found indicates a chemical reaction rather than diffusion as the rate determining process for the dissolutions studied.

D. General Aqueous Studies

1. Dibutylphosphate Chemistry

Section Chief: H. T. Hahn, Chemical Research

The primary decomposition product of tributylphosphate (TBP) is dibutylphosphoric acid (HDBP). The disposition of HDBP between various aqueous and organic plant streams has considerable significance, since it is known to affect extraction performance and may form precipitates which impair the function of moving parts of equipment. Of immediate interest is the behavior of uranyl, zirconium, and aluminum dibutylphosphates under conditions in which uranium is stripped from the organic phase and tributylphosphate is stripped from the resultant aqueous phase.

The metal-dibutylphosphates were characterized to a limited extent. Their solubility was determined in the hydrocarbon diluent Amsco-125-90W. Partition coefficients for U-233 were determined for the aqueous-TBP-Amsco and the aqueous-Amsco systems as a function of HDBP concentration.

The solubility of uranium and aluminum dibutylphosphates in Amsco is quite low (10^{-4} to 10^{-5} M), while preliminary results indicate a somewhat higher solubility for the zirconium compound. The distribution of uranyl dibutylphosphate considerably favors the aqueous phase in both of the extraction systems studied at HDBP concentrations up to 10^{-2} M.

a. Preparation and Thermal Stability of Dibutylphosphate Compounds, E. M. Vander Wall, Problem Leader

The HDBP used in these studies was 99.6 per cent pure, as determined by titration with base. The titration curves were typical for a monobasic acid. Chemical analysis of this compound showed it to contain 14.9 per cent P compared to the theoretical value of 14.74 per cent P.

Uranium Dibutylphosphate, $\text{UO}_2 [(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_2$

Uranium dibutylphosphate was prepared by adding 200 ml of 0.155M uranyl nitrate solution drop-wise during a 2-hour period to 1.5 liters of 0.041M HDBP. The product was filtered and washed several times with water and finally with an aqueous acetone solution. The solid was then vacuum dried at 25° C. Chemical analysis of the product showed it to contain 33.6 per cent U and 9.3 per cent P; the theoretical values are 34.58 per cent U and 9.00 per cent P.

The thermal stability of this compound was investigated by use of a Chevenard thermobalance. A typical thermal decomposition curve is given in Figure 3. At an average heating rate of 3° C per

Fig. 3. Thermal Decomposition Curves for Uranium and Aluminum Dibutylphosphates

minute, decomposition begins at 192° C and is very rapid up to 275° C. A gradual weight loss continues until nearly 500° C; then there is a region of stability which extends to 675° C. Based on weight loss, the compound in this region corresponds to $\text{U}(\text{PO}_4)_2$. X-ray analysis shows this material to be amorphous. Beyond 675° C, the compound again slowly loses weight up to 830° C. Further heating to 1050° C produces no further weight changes. The compound which is produced by heating above 830° C has been established as UP_2O_7 by X-ray analysis. Measurement of weight loss confirms this analysis. Conversion of $\text{UO}_2 [(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_2$ to UP_2O_7 should give a final residue which amounts to 59.85 per cent of the starting compound. The average value obtained in this study was 59.64 per cent.

Aluminum Dibutylphosphate, $\text{Al} [(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_3$

The aluminum dibutylphosphate compound was prepared by adding, drop-wise, an aluminum nitrate solution to 1 liter of 0.044M HDBP. The precipitate was washed several times with water and finally with an aqueous acetone solution. The product was vacuum dried at 30° C. Chemical analysis of the product showed it to contain 14.5 per cent P compared to a theoretical value of 14.20 per cent P in $\text{Al} [(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_3$.

The thermal stability of this compound was investigated. A typical decomposition curve with a heating rate of 3° C per minute is shown in Figure 3. The initial decomposition temperature is about 220° C. Very rapid decomposition continues to 270° C; further rise in temperature causes a gradual weight loss which continues to at least 1050° C. X-ray analysis shows that at 500° C the product is completely amorphous. Samples heated to 1050° C contain only one crystalline compound, $\text{Al}(\text{PO}_3)_3$, along with some amorphous material. Thermal conversion of $\text{Al} [(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_3$ to $\text{Al}(\text{PO}_3)_3$ should give a residue which corresponds to 40.33 per cent of the original weight of the sample. Values in the range 28.3 - 33.2 per cent have been obtained, indicating that the decomposition is not simple.

Zirconium Nitrate Dibutylphosphate, $\text{Zr}(\text{NO}_3)_2 [(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_2$

As described by A. J. Moffat⁽⁶⁾, the compound formed from zirconium ion and HDBP in HNO_3 solution corresponds to the formula $\text{Zr}(\text{NO}_3)_2 [(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_2$. It is also formed during the decomposition of TBP in the presence of zirconium and nitric acid.⁽⁷⁾ An acetone solution of HDBP (0.091 moles in 20 ml acetone) was added, drop-wise, during the course of an hour to a 250 ml solution of 0.18M Zr and 2.0M HNO_3 at 0° C. The compound obtained was a waxy solid. Chemical analysis of this compound showed it to contain 9.79 per cent P compared to a calculated value of 9.78 per cent P.

Vacuum drying of the waxy solid slowly converted it to a glass-like material. Air drying of the sample at room temperature resulted in a clear viscous liquid. After 10 days in air at room temperature, nearly constant weight was achieved, and the residual liquid corresponded to 83.60 per cent of the original sample weight. If $\text{Zr}(\text{NO}_3)_2 [(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_2$ were converted to $\text{ZrO} [(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_2$, the residue should amount to 82.95 per cent of the original sample weight. The agreement may be fortuitous, since previous data⁽⁸⁾ indicate that the latter

compound is crystalline; however, the method of preparation was not stated. Further work is being conducted to establish the composition and behavior of zirconium dibutylphosphate.

b. Solubility of Uranium, Aluminum, and Zirconium
Dibutylphosphate Compounds in Amsco-125-90W

E. M. Vander Wall, Problem Leader; E. M. Whitener,
R. E. Ohlin

The solubilities of uranium, aluminum, and zirconium dibutylphosphate compounds were determined in Amsco-125-90W at 25° C and 35° C. One-gram samples of these compounds were placed in 100 ml of the Amsco, which had been washed with H_2SO_4 and dried with $CaCl_2$. Duplicate samples were agitated in their respective baths for four days. In the case of the uranium and aluminum dibutylphosphate compounds, the Amsco was separated from the solids by filtration. The samples with zirconium dibutylphosphate present contained two liquid phases. The Amsco phase was carefully withdrawn from the bottles and filtered to remove any solids which may have been present.

Then 50 ml. samples of the Amsco, saturated with the dibutylphosphate compounds, were placed in beakers and evaporated to dryness by gradual heating. The last traces of liquid were removed by heating the samples to 125° C under vacuum. The residues contained appreciable amounts of tar which had to be removed to determine the actual amount of dibutylphosphate compounds present. Removal of the tars, together with varying amounts of the dibutylphosphate, was accomplished by dissolution in acetone. The beakers were dried and weighed in the case of the aluminum and uranium dibutylphosphates, since they were not completely solubilized by the acetone. The beakers were then carefully wiped to remove the residues and weighed again to establish tare. The solids removed and weighed in this manner were recorded as a portion of the actual dibutylphosphate compounds.

In order to determine the amounts of the dibutylphosphate compounds washed from the beakers, the acetone solutions of the tars and compounds were transferred to porcelain crucibles. The acetone was evaporated from the samples at room temperature. The samples were then heated to 1000° C in the crucibles which had previously been heated to 1000° C until they achieved constant weight. It was assumed, on the basis of the thermogravimetric studies, that UP_2O_7 was formed when uranium(VI) dibutylphosphate was heated to 1000° C. Also on the basis of the thermogravimetric studies, it was assumed that the aluminum dibutylphosphate compound lost 71.7 per cent of its original weight when heated to 1000° C. This is the largest percentage loss that was observed; therefore, solubility data based on this assumption are the upper limits and the actual solubility may be somewhat less. There was sufficient residue in the case of the ignited zirconium dibutylphosphate samples to obtain X-ray data establishing the final compound as ZrP_2O_7 .

By combining the data obtained by weighing the beakers and that obtained from weighing the ignited residues, the solubilities listed in Table 8 were obtained. Since the solubility of the aluminum and uranium compounds is quite small, the limits of weighing prevented

any differentiation between solubilities at 25° C and 35° C.

TABLE 8
SOLUBILITY OF DIBUTYLPHOSPHATE COMPOUNDS IN AMSCO-125-90W

Compound	Molecular Weight	Solubility (Molar)	Temperature
$\text{Zr}(\text{NO}_3)_2[(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_2$ *	633.6	$(7.9 \pm 0.1) \times 10^{-3}$	25° C
$\text{Zr}(\text{NO}_3)_2[(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_2$ *	633.6	$(8.2 \pm 0.2) \times 10^{-3}$	35° C
$\text{UO}_2[(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_2$	688.4	$(4 \pm 2) \times 10^{-5}$	25-35° C
$\text{Al}[(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_3$	654.6	$(1.5 \pm 0.1) \times 10^{-4}$	25-35° C

* Impurities introduced during preparation of this compound may enhance the solubility considerably.

The uranium solubility reported in Table 8 is considerably less than that obtained by the U-233 tracer method described in the next section, $(4 \pm 2) \times 10^{-5}\text{M}$ U versus $(1.1 \pm 0.1) \times 10^{-4}\text{M}$ U, respectively. This discrepancy may arise from the fact that the solid compound was dried prior to use in the former instance, while it was prepared in situ in the latter. It is also conceivable that there is a species present in aqueous solution (besides the $\text{UO}_2[(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_2$) which is somewhat soluble in Amsco.

c. Distribution Coefficients for the Uranium(VI) Dibutylphosphate Complex Between Amsco-125-90W and 0.02M Uranium in 0.04M HNO_3 Solution

E. M. Vander Wall, Problem Leader; E. M. Whitener
R. E. Ohlin

A simulated stripping column solution was prepared which was 0.02M U and 0.04M HNO_3 . This solution contained approximately 5 mg of U-233 per 100 ml, and resulted in a specific alpha activity of 1.04×10^6 d/m/ml. The Amsco used was washed with H_2SO_4 and then dried over CaCl_2 before use. The extractions were performed in the following manner: Five ml of stripping column solution was placed in a 15-ml centrifuge tube. Then 1 to 100 μ of $5 \times 10^{-4}\text{M}$ HDBP was added to the aqueous solution. The two higher concentrations were prepared by adding the HDBP directly to the centrifuge tube and weighing it; then the aqueous strip solution was added to the tubes. Finally, 5 ml of Amsco was added to each tube. The mixtures were then stirred rapidly for 4 minutes; after about 30 minutes, samples were taken from each phase. The experiments which contained $1 \times 10^{-5}\text{M}$ HDBP or less were performed in duplicate. Counting of the samples was performed by the CPP Special Analysis Group.

The uranium distribution coefficients obtained from these experiments are given in Table 9.

TABLE 9

DISTRIBUTION COEFFICIENTS FOR URANIUM(VI) DIBUTYLPHOSPHATE
BETWEEN AMSCO AND 0.02M U IN 0.04M HNO₃

Initial Dibutylphosphoric Acid Concentration in the Aqueous Phase (M)	Uranium Distribution Coefficient E_a^0
1 x 10 ⁻⁷	~ 1 x 10 ⁻⁶
1 x 10 ⁻⁶	~ 1 x 10 ⁻⁶
1 x 10 ⁻⁵	~ 1 x 10 ⁻⁶
1.86 x 10 ⁻²	8.7 x 10 ⁻³
1.79 x 10 ⁻²	11.1 x 10 ⁻³

In the last two determinations listed in Table 9, there was some solid present at the phase interface after equilibration; therefore both phases were probably saturated. Based on this assumption, the solubility of the uranium(VI) dibutylphosphate compound in the Amsco was calculated to be $(1.1 \pm 0.1) \times 10^{-4}M$ on the basis of activity count of the tracer U-233. This value is considerably larger than that found by evaporation of the Amsco which had been equilibrated with solid $UO_2[(C_4H_9O)_2PO_2]_2$.

d. Distribution Coefficients for the Uranium(VI) Dibutylphosphate Complex Between 3.25 Per Cent Tributylphosphate-Amsco and 0.02M Uranium in 0.04M HNO₃ Solution

These experiments were performed in the same manner as those just described. All the solutions which contained more than $1 \times 10^{-5}M$ HDBP were prepared by weighing amounts of stock solutions into the centrifuge tubes before addition of the aqueous phase. The data obtained from this series of experiments are given in Table 10.

TABLE 10

DISTRIBUTION COEFFICIENTS FOR URANIUM(VI) DIBUTYLPHOSPHATE
BETWEEN 3.25 PER CENT TBP-AMSCO AND 0.02M U-0.04M HNO₃

Initial HDBP Concentration in Aqueous Phase (M)	E_a^0 for U Between 3.25 % TBP-Amsco	E_a^0 for U corrected for TBP Contribution *
0	5.6×10^{-3}	---
1×10^{-7}	5.1×10^{-3}	---
1×10^{-6}	5.0×10^{-3}	---
1×10^{-5}	5.1×10^{-3}	---
2.5×10^{-5}	7.3×10^{-3}	2.2×10^{-3}
1.2×10^{-4}	1.01×10^{-2}	5.0×10^{-3}
1.7×10^{-4}	1.17×10^{-2}	6.6×10^{-3}
1.8×10^{-4}	1.18×10^{-2}	6.7×10^{-3}
4.6×10^{-4}	2.30×10^{-2}	17.9×10^{-3}
3.9×10^{-4}	1.87×10^{-2}	13.6×10^{-3}
1.32×10^{-3}	5.54×10^{-2}	50.3×10^{-3}
9.8×10^{-4}	4.41×10^{-2}	39.0×10^{-3}
2.09×10^{-3}	5.95×10^{-2}	54.4×10^{-3}
4.38×10^{-3}	9.29×10^{-2}	87.8×10^{-3}
2.26×10^{-2}	6.67×10^{-1}	662×10^{-3}
1.61×10^{-2}	1.071	1066×10^{-3}

* Neglects any synergistic effect

Again, in Table 10, the last two determinations exhibited the presence of a solid uranium dibutylphosphate at the phase interface. Comparison of these two sets of experiments, where an excess of solid occurred, indicates that the presence of 3.25 per cent TBP in Amsco increases the capacity for uranium about 100-fold over that for pure Amsco. Examination of the data in Table 10 indicates that the average species extracted into the organic phase at total HDBP concentrations of 10^{-3} M or less contains less than two dibutylphosphate groups per uranyl ion. However, the known synergistic effect complicates the situation, especially as the HDBP concentration approaches the concentration of TBP in the organic phase.

2. Density and Stability of Boric Acid Solutions

E. M. Vander Wall, Problem Leader; J. L. Teague, D. L. Bauer

A brief investigation was made of the density and stability to precipitation of aqueous solutions containing boric acid, nitric acid, and uranyl nitrate.

The density coefficients of boric acid were obtained from

measurements at $20 \pm 0.05^\circ \text{C}$. Solutions contained 0 or 1M HNO_3 ; 30, 60, or 120 g/l uranium (as $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$); and 2, 4, 6, or 8 g/l boron (as H_3BO_3). In 1M HNO_3 , the coefficient

$$d\rho/dB = 0.0021, \sigma = 0.0003 \text{ (g/cc/g/l B), from 6 data points.}$$

In 0.0M HNO_3 ,

$$d\rho/dB = 0.0021, \sigma = 0.0002 \text{ (g/cc/g/l B), from 8 data points.}$$

Density coefficients for uranium can also be calculated.

In 1M HNO_3 ,

$$d\rho/dU = 0.00132, \sigma = 0.00005 \text{ (g/cc/g/l U), from 6 data points.}$$

In 0.0M HNO_3 ,

$$d\rho/dU = 0.00136, \sigma = 0.00001 \text{ (g/cc/g/l U), from 8 data points.}$$

The relative stabilities of $\text{HNO}_3\text{-UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O-H}_3\text{BO}_3$ solutions at various temperatures are shown in Table 11.

TABLE 11

RELATIVE STABILITY OF $\text{HNO}_3\text{-UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O-H}_3\text{BO}_3$ SOLUTIONS
IN 1M HNO_3

Uranium, g/l	Boron, g/l			
	2	4	6	8
30	no ppt	{ no ppt after 4 hrs at 1° C	ppt 0-12° C	ppt 20-22° C
60	no ppt		ppt 0-12° C	ppt 20-22° C
120	no ppt		ppt 0-12° C	ppt 20-22° C
IN 0.0M HNO ₃				
30	no ppt	{ no ppt after 4 hrs at 1° C	ppt 0-12° C	ppt 0-12° C
60	no ppt		ppt 0-12° C	ppt 18-20° C
120	no ppt		ppt 0-12° C	ppt 22-24° C

IV. WASTE CALCINATION DEVELOPMENT AND DEMONSTRATION

Section Chiefs: J. I. Stevens, Waste Calcination Demonstration
J. A. Buckham, Technical Projects
D. W. Rhodes, Waste Treatment
R. A. McGuire, Pilot Plant Operations

Laboratory and pilot plant studies on the fluid bed calcination technique for reduction of aqueous aluminum nitrate waste solutions to solid alumina form have continued. The pilot plant two-foot-square calciner was operated to collect data on feed nozzle wear, calcine particle porosity as affected by temperature and feed concentration, alpha alumina content as a function of temperature and nozzle air rate, and the effect of the starting bed material on the evaluation of plant operating variables. A low temperature (400° C) was found to favor production of a low-porosity alumina with minimum alpha alumina formation; additionally, a low-concentration feed was found to favor low-porosity product, and a reduced nozzle air-to-liquid ratio resulted in lower alpha alumina formation.

Laboratory studies were continued on the factors affecting alumina structure, i.e., variables favoring the formation of amorphous vs alpha crystalline alumina, with emphasis during this period on the effect of sodium and heating on the phase transition. The optimum temperature for the conversion of amorphous alumina to alpha alumina was approximately 500° C.

Results of the first operation of the Demonstrational Waste Calcining Facility as an integrated unit are reported. The principal object of the first process test was investigation of the solids-handling and thermal capabilities of the system; control of the calciner bed temperature at 400° C appeared to be adequate, with a liquid feed rate of 60 gal/hr and a superficial fluidizing velocity of 1 ft/sec. Certain deficiencies were found and required correction before further tests could be undertaken.

A. Research and Development in the Pilot Plant

E. S. Grimmett, Problem Leader; B. R. Wheeler, B. P. Brown
D. R. Evans

The intra-particle porosity of alumina generated in the two-foot-square calciner unit is primarily determined by the concentration of aluminum nitrate in the feed and the bed temperature. Results from Runs No. 15, 16, and 17, performed during this quarter, together with those of previous Runs No. 11 through 14^(1,2), have established that the production of: (1) relatively high-porosity (0.55 - 0.60) alumina resulted when 1.40M or 1.85M aluminum nitrate feed solutions were calcined at a bed temperature of 500° C; (2) relatively low-porosity (0.42 - 0.49) alumina resulted when 1.22M to 1.50M aluminum nitrate feed solutions were calcined at bed temperatures of 400° C or 425° C; and (3) alumina with a medium-high porosity (oscillating between the values 0.52 - 0.58) resulted when 1.89M aluminum nitrate solution was calcined at a bed temperature of 400° C.

Other significant findings this quarter are that the use of a sand starting bed has numerous practical advantages, that under certain conditions bed temperature and nozzle air rate appear to affect the alpha alumina content of the bed, and that a condition of regular, undamped oscillation in the values of most observed parameters may be encountered under certain as-yet-unidentified operating conditions.

The equipment used for these studies was different in only two respects from that previously described⁽²⁾: A single Spraying Systems Company type 1/2 J feed nozzle with a flat-faced nozzle cap was substituted for the two pairs of opposed, smaller feed nozzles; and the dry fines return system was modified so that the dry fines separated from the off gas by the primary cyclone were introduced to the fluidized bed above the bed support plate rather than with the fluidizing gas below the support plate.

1. Intra-Particle Porosity of Calcine

A high intra-particle porosity (0.55 - 0.60) alumina has been generated in all past runs, including Run No. 11, during which 1.85 - 1.95M aluminum nitrate solution was calcined at a bed temperature of 500° C. A relatively low-porosity (0.42 - 0.49) alumina was generated for the first time during Runs No. 12, 13, and 14⁽¹⁾, when 1.22 - 1.34M aluminum nitrate solution was calcined at a bed temperature of 400° C. This quarter's Runs No. 15, 16, and 17 were designed to verify that bed temperature and aluminum feed concentration are primary factors in determining the porosity of alumina generated in a fluidized bed calciner. The intra-particle porosity of the alumina generated in Runs 11 through 17, together with pertinent run conditions, is given in Table 12.

The effect of a change in bed temperature on the alumina porosity was directly observed during the last portion of Run No. 15. An increase in bed temperature from 400° C to 500° C resulted in an increase in intra-particle porosity from 0.47 to 0.57, and the porosity was still increasing when equipment failure forced premature run termination. During an earlier period of operation at a bed temperature of 500° C on this run, the porosity of the alumina in the bed did not change appreciably from its initial value of 0.57.

The effect of feed aluminum concentration on porosity of the alumina is demonstrated by comparison of the high porosity (0.52 - 0.58) of the product generated in Run No. 16, made with 1.89M aluminum nitrate feed at a 400° C bed temperature, with the low porosity (0.42 - 0.49) of the alumina produced in Runs No. 12 through 15, made at the same temperature but with 1.22 to 1.40M aluminum nitrate feed. Aluminum concentration, rather than the concentration of mercury or nitric acid in the feed, appears to be responsible for the effect of feed composition on product intra-particle porosity. This is most vividly shown by a comparison of conditions for the second part of Run No. 15 and for Run No. 17, two runs in which relatively low-porosity alumina was generated. On these runs, both made at 400° C, the aluminum concentration was similar - 1.40M to 1.50M - but the concentrations of mercury and acid were vastly different, as shown in Table 12.

TABLE 12

FACTORS AFFECTING THE INTRA-PARTICLE POROSITY OF CALCINE PRODUCED
IN RECENT RUNS IN THE TWO-FOOT-SQUARE CALCINER

Run Number	11	12	13	14	15 ⁽¹⁾	16	17
Bed Temperature, °C	500	400	400	400	500-400-500	400	425
Feed Composition: (Average)							
Aluminum nitrate, M	1.85	1.22	1.34	1.31	1.40	1.89	1.50
Nitric acid, M	1.84	2.84	3.00	2.97	2.89	1.24	1.26
Sodium nitrate, M	0.103	0.078	0.084	0.081	0.086	0.103	0.088
Mercuric nitrate, M	0.0065	0.014	0.016	0.015	0.016	0.0061	0.0060
Superficial Fluidizing Gas Velocity ⁽²⁾ , ft/sec	0.78	0.90	1.0	1.0	1.0	1.0	1.0
Nozzle Air-to-liquid Volume Ratio ⁽³⁾	Varied from 590 to 120	300	Varied from 400 to 1060	Varied from 250 to 400	400	400	Varied from 300 to 450
Starting Bed	Alumina	Alumina	Alumina	Alumina	Alumina	Alumina	Sand
Feed Rate, l/hr	80	120	49 to 100	70 to 115	90	90	90
Intra-Particle Porosity of Product	0.55 to 0.60	0.42 to 0.44	0.45 to 0.49	0.42 to 0.45	0.57 at 500° C 0.46-0.49 at 400° C 0.57 at 500° C	0.52 to 0.58	0.46 to 0.49 ⁽⁴⁾

- (1) Run 15 was conducted in three distinct phases with respect to temperature, as indicated. Note the variation of intra-particle porosity with temperature.
- (2) The superficial fluidizing velocity is determined on the basis of the empty cross section of the calciner at the calciner bed temperature and vessel pressure, and includes the fresh air and dry fines return gas; it does not include the nozzle air, the water vapor, or decomposition products of the feed.
- (3) Air volume determined at the metered temperature and vessel pressure.
- (4) Values correspond to amorphous alumina. Slightly higher values were associated with product having a high alpha alumina content.

Intra-particle porosity of alumina is also somewhat dependent on the alpha alumina content of the product, as well as on the calcining temperature and feed concentration. A relatively low-porosity (0.46) alumina was associated with a semi-concentrated feed solution, 1.50M aluminum nitrate, being calcined at a bed temperature of 425° C during periods in Run No. 17 when predominantly amorphous alumina was generated. However, this varied as the alpha alumina content of the product changed. For example, during this run the porosity of the alumina increased from 0.46 to a value of 0.53, coincident with an increase in the alpha content of the alumina from 18 to 60 per cent. The porosity later declined to values between 0.45 and 0.50, along with a decline in the alpha content of the alumina to an eventual low of 8 per cent. Later, when the alpha content of the alumina once again rose to 52 per cent, the porosity simultaneously increased to a peak value of 0.55. The ensuing decline in alpha content of the alumina to 25 per cent was accompanied by a decrease in porosity to 0.48.

2. Alpha Alumina Behavior of Calcine

Effect of Temperature

Results of Runs No. 15 and 17 suggest that a reduced bed temperature and a reduced nozzle air-to-liquid volume ratio (NAR) result in less formation of alpha alumina in the calciner. A comparison of the transient behavior of the alpha content of alumina generated at a bed temperature of 500° C with that observed previously at a bed temperature of 400° C was an objective of Run No. 15. In direct contrast to the three preceding runs⁽¹⁾ (bed temperature 400° C) in which the alpha alumina content of the bed peaked at 36 to 48 per cent after about 18 hours and then declined to a value of 4 to 12 per cent, the alpha alumina content of the bed during Run No. 15 (bed temperature 500° C) continued to rise above 48 per cent, with no indication of any recession. Common calcining conditions for this and for the 400° C bed temperature runs were the concentration of alumina in the feed and the starting bed.

An additional study was made during Run No. 15 to identify the cause of this radical difference in the alpha behavior of alumina from that previously observed at the 400° C bed temperature. To do so, a deliberate attempt was made, at a bed temperature of 400° C, to cause the behavior of the alpha alumina to parallel that of the three previous runs. This time, after the alpha alumina content of the bed had peaked and declined to a value of 13 per cent, the bed temperature was increased to 500° C. Subsequently, the trend in alpha content of the bed reversed; the bed alpha content reached a value of 23 per cent by the end of the run, which occurred prematurely as a result of plugging of the scrubber cyclone effluent cooler — an event probably not related to the particular operating conditions at the time.

Although the effect of temperature on the alpha alumina behavior during Run No. 15 is not conclusive in itself, the behavior of the alpha alumina during this run compared with that of the other three runs indicates that the higher bed temperature, 500° C, does promote the formation of alpha alumina. At a 400° C bed temperature, the relatively high alpha alumina content of the bed was transient, and declined after

a short period of operation; whereas at a bed temperature of 500° C, there was no indication that the alpha alumina content would recede to lower values.

Effect of Nozzle Air-to-Liquid Volume Ratio (NAR)

From an operating standpoint, it is of utmost importance to have some method of depleting a fluidized calciner bed of high alpha alumina during operation. Results of Run No. 17 clearly show that this may be done by utilizing the proper low setting of NAR, at least under some conditions. The discovery that variables associated with NAR affect alpha alumina formation occurred when an attempt was made to reduce the average particle diameter of the product by increasing the NAR from a value of 400 to 450. Unexpectedly, the alpha alumina content of the bed rapidly increased from 9 to 60 per cent, causing high product attrition. The resultant entrainment of product in the off gas caused the bed level to drop to a point near the elevation of the nozzle, in effect causing an approach to a spray drying-type of operation. The NAR was then reduced to a value of 300, just 24 hours after the previously mentioned change, in an attempt to override the effect of the high alpha alumina bed on the calciner operation and to stop bed losses. This was effective; the alpha alumina concentration of the bed declined, eventually to 8 per cent. Figure 4 shows the various values of NAR used during this portion of the run, together with the alpha alumina concentration of the product and of the off gas solids.

Fig. 4. Effect of Nozzle Air-to-Liquid Ratio on Alpha Alumina Content of Calciner Solids

The cause of this alpha alumina behavior was clouded (this was the first time that alpha alumina appeared to be associated with factors affected by a change in NAR), and therefore the NAR was increased to a value of 450 for a second time. The alpha alumina content of the bed started to increase some 30 hours later, after a forced calciner shutdown for maintenance work. The alpha alumina content eventually reached 53 per cent, at which point the NAR was reduced to a value of 300; a depletion of alpha alumina in the bed was again observed (Figure 4). The NAR was increased a third time during this run, after the alpha alumina content of the bed had dropped to 35 per cent. Some 18 hours later, the alpha alumina content of the bed reversed direction and increased to a peak value of 45 per cent by the time the run was terminated.

There is little doubt that a reduced value of NAR created conditions less conducive to alpha alumina formation on this run; both times the NAR was reduced, the subsequent depletion rate of the alpha alumina in the bed was similar. It also appears that, under the conditions of this run, an increase in NAR encourages the formation of alpha alumina; however, no completely credible reason has been advanced for the variation in response times.

Alpha alumina material balance considerations for the periods during which the rapid increase in alpha alumina occurred permit either the possibility that (1) the bed material was converted to the alpha state, or (2) the newly-generated material in the bed was primarily alpha alumina. It is considered significant that on two occasions, when the alpha alumina concentration of the product was rapidly increasing, there was a parallel increase in the concentration of the alpha alumina in the off gas, as is shown in Figure 4; however, each time the NAR was reduced, the alpha alumina decline of the product was more gradual than the rapid decrease in the concentration of alpha alumina in the off gas. Although numerous mechanisms can be postulated to explain this phenomenon, there are insufficient data to prove any postulate. Further studies in the pilot plant calciner to elucidate the cause of alpha alumina formation are being held in abeyance until additional bench-scale studies are completed.

A short period of Run No. 17 also marked the first observance of the generation of alpha-free alumina with sodium present in the feed. The only previous occasions on which conventional X-ray analyses of alumina have not indicated the presence of the alpha phase have been when sodium was absent from the feed.

3. Observed Cycling of Calcine Characteristics

A uniform cycling of all product and bed characteristics was evident during Run No. 16. The period between cyclic peaks in values of all the characteristics was approximately 38 hours (five cycles were completed), and the total variations in individual oscillating characteristics ranged from 10 to 100 per cent. The values of the alpha alumina content, the bulk and absolute densities, the solids leaving with the scrub solution, and the time required for 90 per cent bed replacement all passed through maxima at approximately the same time that the values

of the intra-particle porosity, the nitrate content, the product rate, the product mass median particle diameter, the bed height, and the bed weight passed through minima.

Although the cause of this uniform cycling has not been identified, it is felt to be related to the particular combination of operating conditions used rather than to any operating technique or fluctuation in independent variables. The main basis for this conclusion is that known perturbances in many operating conditions had no significant effect on the cycling; also, one shift of operators unknowingly doing something every 24 hours could hardly cause cycling with a 38-hour period.

4. Use of Sand as a Starting Bed

The use of a sand starting bed in Run No. 17 was the initial attempt to eliminate an undesirable variable, the history of the bed, which has disguised the characteristics of the newly-generated product. There is no known method to determine porosity, alpha alumina content, attrition index, or other similar product characteristics of only the newly-generated alumina if the starting bed consists of alumina generated under different calcining conditions; on the other hand, when a completely different material such as sand is used for a starting bed, the newly-generated alumina can be examined at any time and the desired product characteristics determined by eliminating the influence of the sand through proper analyses and calculations. During Run No. 17, the porosity, alpha alumina content, and other product characteristics of the newly-generated alumina were known within 24 hours after the run began, whereas in previous runs, at least 95 per cent of the bed had to be replaced (which ordinarily required from 50 to 100 hours) before there could be any significance attached to the values of these product characteristics.

A series of alumina-sand samples representing various periods of the early part of this run has been sectioned and photographed so that the growth rate uniformity of the alumina can be studied. The photomicrographs clearly show a gradual growth of alumina on the seeds of sand, and it is hoped that useful data may be obtained from measurements of this growth.

Some of the properties of the sand used for a starting bed, together with those of alumina, are given in Table 13 for comparison.

The rate at which a calciner bed is replaced is of considerable interest. Since sand was used as the starting bed in Run No. 17, the replacement of the sand by alumina was easily followed by chemical analysis of the bulk product; for the first time, the derived bed replacement or "washout" equation⁽⁹⁾ could be checked. The "washout" equation is based on the assumption that the fluidized bed is perfectly mixed. Careful consideration of the process indicates that bed replacement occurs basically in terms of volume instead of weight; therefore, the "washout" equation is expressed in terms of a volume fraction. When more than one component exists in a bed, and the weight fraction of one of the components is desired, the particle densities of the components involved must be used in the calculations. The calculated and analytical values

TABLE 13

COMPARISON OF VARIOUS PROPERTIES OF AMMON SAND AND ALUMINA

	Ammon Sand		Alumina (Typical)	
	Value	(Temp.)	Value	(Temp.)
Thermal conductivity BTU/(hr)(ft ²)(°F/ft)	0.19	(20° C)	0.08 0.17 0.20	(100° C) (400° C) (500° C)
Specific heat, BTU/lb	0.19	- - - - -	0.20 0.27	(100° C) (1500° C)
Absolute density, g/cc	2.62	- - - - -	2.62	- 3.95
Bulk density, g/cc	1.46	- 1.53	0.70	- 1.18
Particle density, g/cc	2.56		1.18	- 2.00
Intra-particle porosity, fraction	0.02		0.41	- 0.66
Mass median particle diameter, mm	0.26		0.26	- 1.20

for various alumina concentrations on this run were in excellent agreement, thus substantiating the assumptions made in deriving the "washout" equation.

The porosity of the alumina fraction of the alumina-sand product was calculated, in effect, by subtracting the particle volume and particle weight of the sand from those of the product. This information, together with the absolute density of the alumina fraction, was in turn used to calculate the intra-particle porosity values. A similar technique was used to calculate the bulk density of the alumina fraction of the product during the run.

5. Performance of Feed Nozzles

L. T. Lakey, Problem Leader; J. L. Lockard

A flat-faced titanium nozzle tip coated with 3 mils of alumina was tested for 10 days in the runs described earlier in the pilot plant calciner. The erosion rate was less than that experienced with a hardened type 440-C stainless steel tip, but was still unsatisfactory for long-term operation. Results are listed in Table 14. An additional 12-day period resulted in the alumina coating either eroding or breaking away to expose the titanium base metal, which eroded rapidly. A modified converging nozzle tip with a 38° cone was fabricated of aluminum and tested for 54 hours in a cold fluidized calciner bed. The weight loss of 1.3 milligrams out of a total nozzle weight of approximately 10 grams indicated a low erosion rate, and a stainless steel version of the nozzle was fabricated for future testing. Two flat-faced stainless steel nozzle tips were coated with alumina and boron carbide, respectively, by the

TABLE 14
FEED NOZZLE TIP EROSION RESULTS

<u>Nozzle</u>	<u>Hours Tested</u>	<u>Weight Loss (grams)</u>	<u>Volume Loss Rate (in³/yr)</u>	<u>Remarks</u>
Stainless Steel 440-C, Flat-Face, Hardened to 56 Rockwell	106	0.0315	0.0201	
Titanium, Flat-Face, 3-4 mils Alumina Facing	205	0.0124	0.00934	Losses assumed to be entirely alumina from facing

Plasmacote process and are awaiting future tests in the Demonstrational Waste Calcining Facility. Also, 5 flat-faced nozzle tips fabricated of boron carbide, in a modified design, will be purchased for future tests.

B. Laboratory Investigations

1. Calcination of Aluminum Nitrate Wastes D. W. Rhodes, Problem Leader; R. F. Murray

Calcined alumina prepared by the calcination of a synthetic aluminum nitrate-nitric acid waste solution is known to consist of amorphous and alpha crystalline alumina and sometimes several transition forms, depending on the calcination conditions and the characteristics of the waste from which it was formed. Laboratory work was continued to study the factors affecting the formation of these various phases as a function of the calcination variables and calcine composition. Earlier work⁽¹⁾ indicated that in an atmosphere containing the decomposition products of nitric acid, samples of calcined alumina containing sodium nitrate were readily converted to alpha alumina by heating at 400 to 500° C. Laboratory work was undertaken during this report period to better define the effect of sodium and of time of heating in this phase transition.

a. Methods, Equipment, and Techniques

Laboratory Test Unit

The experimental work in the laboratory was performed in a unit in which the composition of the atmosphere and the temperature were controlled. The equipment was described in IDO-14553⁽¹⁾. Briefly, it consists of a tube within the test unit, holding 24 small sample pots resting on top of each other in a vertical position, each having a screened bottom permitting gas flow through the series of samples from

top to bottom. In another portion of the unit, nitric acid is dropped onto a porous ceramic plate, where it is decomposed. The vapors of the decomposed acid are then carried by heated air through the series of samples. The whole unit is placed in a cylindrical furnace.

X-Ray Diffraction Analyses

Samples are submitted routinely for X-ray diffraction analysis to determine the crystal phases present. The results are checked against experimental conditions to determine the factors causing the phase changes. The concentrations of sodium nitrate in the samples are estimated by X-ray diffraction and also determined by means of the emission spectrograph.

Sample Preparation

Samples of alumina containing less than 5 per cent alpha alumina were used in the reactor. Sodium nitrate was added to the alumina either by soaking the alumina in a solution of sodium nitrate prior to calcination or by mixing solid sodium nitrate with the sample.

b. Experimental Results

Equipment Testing (Effect of Temperature)

Initial operation of the laboratory test unit indicated that a large thermal gradient existed between the top and bottom samples. Careful examination of the data indicated, however, that the following tentative conclusions could be made from this initial operation:

(1) The optimum temperature for the conversion of amorphous alumina to alpha alumina appeared to be near 500° C. Approximately 50 per cent of the amorphous alumina was converted to alpha alumina at 500° C, compared to about 5 per cent at 350° C or 650° C. (2) The rate of conversion from amorphous to alpha alumina was relatively rapid under favorable conditions; i.e., approximately 50 per cent was converted to the alpha form in 19 hours. (3) Iota alumina, a transition form between amorphous and alpha alumina, was identified in the treated samples for the first time.

Following the initial runs, the test unit was modified to provide a more nearly uniform temperature for all samples. In addition to temperature measurements, the production of nearly equal amounts of alpha alumina in all sample positions was considered to be indicative of a nearly uniform temperature in the sample zone of the test unit. The results of a run made after modification of the equipment, with all sample holders containing the same type of amorphous alumina as the starting material, are summarized in Table 15. These results show approximately the same amount of alumina formed in each sample position. Apparently, variation in alpha alumina content due to the large temperature gradient was eliminated by the equipment modifications. The reason for the variation in the measured sodium concentration for similar samples has not been explained as yet.

TABLE 15

PHASE CHANGES OCCURRING IN AMORPHOUS CALCINED
ALUMINA DURING HEATING

Conditions: Feed Solution - 6.6M HNO_3
 Temperature - 500° C
 Heating Time - 21.5 Hr
 Treatment - Alumina soaked in 1M
 NaNO_3 solution before
 heating

Sample Position (from top to bottom)	Alumina Phases			NaNO_3 (by Spectrometer Analysis)	
	Alpha	Gamma	Iota	(by X-ray)	
1	40	present	present	present	5.1
6	40	present	present	present	2.7
12	35	present	present	present	3.7
18	36	present	present	present	3.8
24	35	present	present	present	3.4

Effect of Different Starting Materials

An attempt was made to determine the effect of using alumina prepared under different conditions or by different techniques, and subjected to different treatments, on the rate of formation of alpha alumina when heated in the laboratory test unit. Four different starting materials were obtained, three of which were very low in alpha alumina; unfortunately, they also contained appreciable amounts of sodium. The materials used were:

- (1) CA - Consisted of calcined alumina prepared in the pilot plant two-foot-square calciner at 500° C. This material contained ~ 52 per cent alpha alumina and about 1.9 weight per cent sodium, and trace chemicals to simulate fission products.
- (2) IV A - Consisted of calcined alumina prepared in the pilot plant two-foot-square calciner at 400° C. This material contained about 5 per cent alpha alumina and 2.3 weight per cent sodium.
- (3) PB-2 - Consisted of calcined alumina prepared in the pilot plant calciner at 400° C. This material contained less than 5 per cent total crystalline material consisting of alpha and possibly gamma and alpha monohydrate alumina. Contained ~ 1.7 per cent Na.

- (4) AN - Consisted of alumina prepared by decomposition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ on a hot plate in the laboratory. Consisted of amorphous alumina and < 0.5 per cent Na.

Samples of these materials were treated by soaking in sodium nitrate solution and were then heated in the laboratory test unit in a nitric acid atmosphere. Samples were removed at three different time intervals to measure the rate of formation of alpha alumina. In addition, an attempt was made to determine the presence of gamma alumina and crystalline sodium nitrate. The total sodium concentration was measured by emission spectroscopy. The results of these experiments are summarized in Figures 5, 6, and 7.

Fig. 5. Phase Changes in Alumina (Prepared in the Pilot Plant at 400° C) During Heating in the Laboratory Test Unit at 400° C and 500° C

Fig. 6. Phase Changes in Alumina (Prepared in the Pilot Plant at 500° C) During Heating in the Laboratory Test Unit at 400° C

Fig. 7. Phase Changes in Alumina (Prepared in the Pilot Plant at 400° C) During Heating in the Laboratory Test Unit at 400° C

The relatively large amounts of sodium in the samples as received from the pilot plant calciner prevented any meaningful interpretation of the effect of added sodium nitrate on the rate of formation of alpha alumina. Nevertheless, treating the calcined samples by soaking in sodium nitrate solution prior to heating in the laboratory test unit had an apparent effect on the rate of formation of alpha alumina, although it did not correlate with the amount of sodium in the sample. Figure 5 (II) shows the duplicate samples plotted for one run. The close agreement between duplicates suggests that the variation in alpha alumina content was not due to analytical error but to some as-yet-unknown factor. Additional experiments, beginning with sodium-free samples and the heating of more samples receiving the same treatment, will be necessary to determine the reason for the wide variation in alpha alumina after soaking in sodium nitrate solution.

The effect of time of heating was evident in all samples tested, as shown in Figures 5, 6, and 7. Even samples which contained 52 per cent alpha alumina prior to heating in the laboratory reactor unit (Figure 6) increased in alpha alumina content with increasing time of heating. Of particular interest were the relatively large amounts of alpha alumina produced in some of the samples with heating times less than 24 hours (Figure 5). These data suggest that under conditions favorable for the formation of alpha alumina, residence time of the alumina particles in the fluid bed calciner can be very important in determining the amount of alpha alumina formed. Also, the different amounts of alpha alumina formed in the laboratory test unit at 400° C (Figures 5-I and 7) by heating samples IV-A and PB-2, both of which were prepared by calcination at 400° C, indicated that the calcination conditions existing during the initial formation of the alumina in the calciner might be a major factor in determining the rate of conversion from amorphous to alpha alumina.

The AN sample (aluminum nitrate converted to alumina by heating on a hot plate) showed very little tendency to form alpha alumina regardless of the amount of sodium nitrate added. After exposure in the laboratory test unit for one week, only 5.0 per cent alpha alumina had formed, although numerous transition forms such as gamma, iota, kappa, and theta were identified in small amounts. Apparently the rapid drying of a fine spray in a calciner atmosphere produces alumina that is properly seeded with crystal nuclei, or otherwise "conditioned", to make it readily convertible to the alpha alumina form under the proper conditions.

Effect of Irradiation

Alumina samples were submitted to Stanford Research Institute for irradiation with 1 Mev electrons in the resonant transformer. The dose rate requested was 7.2×10^5 rad/(hr)(g. Al_2O_3), based on the beta irradiation expected in the calciner. Dosages equivalent to 10 and 100 hours in the calciner at ambient and liquid N_2 temperatures were examined. Alpha and amorphous alumina samples were submitted. From the results, it was concluded that the electron beam irradiation did not produce any phase changes of a permanent nature that could be detected by X-ray diffraction or with the X-ray powder camera.

C. Demonstrational Waste Calcining Facility, Section Chief, J. I. Stevens

1. Program Planning and Data Correlation
B. M. Legler, Problem Leader; G. E. Lohse
2. Technical Surveillance, L. T. Lakey, Problem Leader
P. N. Kelly, J. L. Lockard, E. A. Travnicek

Functional testing of the process components in the Demonstrational Waste Calcining Facility was completed. Using water as the feed to the calciner, an integrated process operation was undertaken. A discussion of individual component performance and deficiencies follows.

Construction Additions and Modifications

Excessive vibration in one of the transport air blowers was found to have been caused by a shaft which was out of alignment by 0.018 inches. This blower performed satisfactorily after a new shaft was installed and was accepted for operation. Vibrational and bearing heatup problems in other blowers throughout the system were minimized following grease replacement and alignment in the thermally hot condition.

Process Testing

The object of the first integrated process test was to investigate the solids-handling and the thermal capabilities of the system, as well as provide additional operator training. For this purpose it was deemed advisable to use water as the feed solution. The 4-foot diameter calciner was charged with alumina which had been produced in the pilot plant, and was operated for a period of 20 hours during which water was fed for a period of 2 hours.

The calciner charging rate was 5,000 lb/hr at a solids loading of 11 pounds per pound of transport air when the charging hopper was pressurized to 30 psig. A 1 ft/sec superficial velocity was chosen as the fluidizing velocity for the test. To attain this velocity, which is 44.5 per cent of the design rate⁽¹⁰⁾, required considerable manual manipulation of the fluidizing air supply control valving. Even this low rate of fluidization resulted in an average bed loss of 100 lb/hr from attrition and elutriation; however, this attrition rate is expected to be reduced materially when aluminum nitrate feed solutions are used. At no time during the test period could either of the solids samplers be made to function. Further, it was apparent early in the run that the single indicating instrument available for the eight pressure taps in the calciner was incapable of following, as rapidly as necessary, all of the pressure differentials that are required. This system will have to be revised, since the measurement and observation of these pressures are critical in controlling the operations.

At the outset of the run, intermittent cycling of the off gas temperature downstream from the off gas heater led to the discovery that water had been carried over from the venturi scrubber de-entrainment separator. After draining the water from the off gas line and raising the off gas heater outlet temperature to 80°C, no further temperature control difficulties were encountered.

Control of the calciner bed temperature at 400° C appeared to be adequate at the 60 gal/hr water feed rate. The NaK heat transfer system performed satisfactorily, with the NaK pump operated at 68 per cent of capacity, at the water feed rate of 60 gal/hr. To determine if it would be possible to refluidize the calciner, should an extended power outage cause the loss of fluidizing air, the process was deliberately shut down for 35 minutes, during which time approximately 20 per cent of the bed flowed through the holes in the distributor plate into the conical bottom section of the calciner. Upon establishing the fluidizing air flow rate at the design velocity of 2.2 ft/sec, the level in the calciner rose to its previous value, indicating that the solids had been refluidized through the plate. Except for a short period after the initial charging of the calciner, it was impossible to determine if the primary cyclone dipleg had functioned satisfactorily because of plugs in the differential pressure taps.

Unloading the calciner to the solids storage system via the pneumatic transport lines proved to be a sensitive operation requiring continual readjustment of the valve in the line from the distributor plate. After partially dumping the bed at a maximum rate of 1500 lb/hr, the system was shut down overnight; the remainder of the calciner bed was subsequently transferred to solids storage at a rate of 900 lb/hr. While it would be desirable to have a higher transporting rate, it is not believed that the demonstrated rates are prohibitively low.

At the end of the test period, the quench system contained a slurry of approximately 8 per cent by weight of alumina solids. This slurry caused the quench pump bearings and packing to wear appreciably, and at a much higher than anticipated rate. The pump discharge pressure dropped from 45 psig to 30 psig during the first half of the run and held

at that pressure during the remainder of the run.

At the end of the run the calciner was inspected internally through two nozzle ports. It was found that the distributor plate was covered with an irregular layer of solids. The cyclone dipleg was plugged by solids held up in the 4-inch space between the bottom of the dipleg and the dipleg baffle; however, these finely-divided solids, when disturbed with a probe, flowed from the dipleg into the bottom of the calciner. Inspection of the off gas filters revealed a small amount of dust on the inlet surface, but none on the outlet surface. These solids undoubtedly reached the filters during a period when the silica gel adsorbers just upstream were bypassed.

Following the first run, proposals and cost estimates were prepared for correction of major deficiencies, while minor defects were corrected and certain expedient changes were made to permit resumption of testing on a temporary basis. Attempts to make a second run during this period were halted by discovery of a leak in the outside service waste piping and a crack which developed in the bellows of a NaK drain valve, permitting an estimated 50 ml of NaK to leak to the atmosphere. Upon repair of these items, plant operation will be resumed.

V. NEW WASTE TREATMENT METHODS

Section Chief: D. W. Rhodes, Waste Treatment

The long-range program in radioactive waste management at the ICPP aims to reduce waste volumes to a minimum, store wastes as non-leachable solids, separate the non-radioactive alloy components from the fission products, and follow tank corrosion where liquid wastes are stored in temporary tanks. Toward these goals, results are presented on the specific removal of cesium and strontium from gross waste by adsorption on ammonium phosphomolybdate and resins, respectively, and on the process chemistry of the mercury cathode removal of iron, nickel, and chromium from stainless steel wastes.

A. Removal of Long Lived Radioisotopes from Waste Solutions M. W. Wilding

The laboratory work to investigate the removal of cesium from acidic waste solutions by adsorption on ammonium phosphomolybdate (APM) was completed and the results reported in IDO-14544.* Results obtained in this report period indicated that increasing the flow rate of the solution and decreasing the particle size resulted in a higher capacity of the APM for cesium. This higher capacity was attributed to the fact that more cesium was loaded on the column with less dissolution of the APM by the waste solution.

Experimental work was also continued to study the removal of strontium from acidic waste solutions by ion exchange with Amberlite 200 cation exchange resin. Equilibrium distribution data in salt-free 0.1N nitric acid solution indicated that the distribution coefficient was essentially constant at about 1×10^4 from tracer concentrations of strontium up to values above the concentration of strontium in ICPP waste (0.02 g/l). Increasing nitric acid concentrations above 0.003N and increasing concentrations of sodium nitrate, calcium nitrate, or aluminum nitrate from 0.001M to 1M decreased the K_d value for strontium. The order of interference for the salt ions was $\text{Ca} > \text{Al} > \text{Na}$.

Experimental Methods

The APM-silica gel granules were prepared for use in the fixed bed column by dissolving APM in 8N ammonium hydroxide, soaking the silica gel in the APM solution until the gel was saturated with liquid, and precipitating the APM in the gel by the addition of nitric acid. The APM-silica gel was washed thoroughly with distilled water and air-dried for use in the columns. The granules were approximately 20 weight per cent APM.

The feed solution contained 0.1N nitric acid, 2M aluminum nitrate, 0.06 g Cs/liter added as cesium nitrate with cesium-137 as a tracer. This feed solution was passed upward at a constant rate through a column 76 cm long and 2.2 cm diameter. Approximately 100 ml fractions of the column effluent were collected by means of an automatic fraction collector.

* To be issued

The concentration of cesium in the effluent was determined by a gamma counting technique and the concentration of APM by X-ray fluorescence analysis.

The strontium experiments were batch equilibrium experiments using 1 gram of solid per 20 ml of solution and mechanical agitation for 24 hours. The concentration of strontium was approximately equal to the concentration in ICPP waste (0.02 g/l), and strontium-85 was used as a tracer. The solid used in these experiments was Amberlite 200 resin in the sodium form. Amberlite 200 is a sulfonated styrene-divinyl-benzene copolymer having good resistance to oxidative attack and physical fracture. Aliquots of the supernatant liquid were removed, and the concentration of strontium in these samples was determined by a gamma counting technique.

Experimental Results

1. Cesium

The apparent capacity of the APM column to remove cesium from synthetic ICPP waste was increased from 65 to 78 column volumes by increasing the flow rate of the waste solution from 5 to 70 gal/(ft²)(hr) through the fixed bed column. To achieve adequate cesium decontamination factors at the faster flow rate, however, it was necessary to reduce the average particle size to about 1 mm diameter, approximately 1/4 the diameter of the particles used at the slower flow rate. The break-through curve for this experiment is shown in Figure 8. The apparent increase in column capacity was attributed to the fact that less APM was dissolved from the column at the faster flow rate. The amount of APM dissolved from columns at the two flow rates is shown in Figure 9.

Optimum conditions for the removal of cesium from acidic waste solutions would require the fastest flow rate consistent with adequate cesium removal and equipment performance.

2. Strontium

Effect of Concentration

Equilibrium data for strontium in 0.1N nitric acid at concentrations varying from tracer levels to 1.0 g Sr/liter are shown in Figure 10. Distribution coefficients (K_d) calculated from these data indicate an average distribution coefficient of $1.14 \pm 0.09 \times 10^4$, where ± 0.09 refers to the maximum deviation from the average value for strontium concentrations up to 0.1 g Sr/l. Above this value, the K_d values gradually decreased.

Effect of Time of Contact

The effect of time of contact for the removal of strontium from 0.1N nitric acid solution is shown in Figure 11. Measurements were made at time intervals between 1 minute and 24 hours. The data shown in Figure 11 indicate that approximately 90 per cent equilibrium was attained in 1 minute, and nearly complete equilibrium was achieved within 2 hours.

Fig. 8. Break-Through Curve for Cesium in an APM-SiO₂ Column

Fig. 9. Concentration of APM in Column Effluent (0.1N HNO₃) at 25°C

Fig. 10. Equilibrium Distribution of Strontium in the System:
Amberlite 200 Resin - Nitric Acid

Fig. 11. Effect of Time on Strontium Adsorption by Amberlite 200 Resin

Effect of Acid Concentration

Solutions of nitric acid of various concentrations containing 0.02 g strontium/liter were equilibrated with Amberlite 200 resin for 24 hours. The equilibrium distributions in these systems, which are reported in Figure 12, indicate that nitric acid at concentrations less than 0.003N has a negligible effect on the removal of strontium from a salt-free solution. Above 0.003N acid concentration, the acid definitely inhibits the exchange reaction with the strontium. Apparently the hydrogen ion competes directly with the strontium ion for the exchange sites.

Effect of Interfering Cations

The nitrate salts of sodium, calcium, and aluminum were used in nitric acid solutions to represent the effect of monovalent, divalent, and trivalent cations on the adsorption of strontium by the resin. The results are shown in Figures 13, 14, and 15, with a curve representing the effect of nitric acid in a salt-free solution included in each figure for comparison purposes. It is apparent from these data that all three types of cations at one molar concentration interfered seriously with removal of strontium. Even for the most seriously interfering cation (calcium), however, the K_d value was still approximately 10. One-tenth molar concentrations of aluminum or calcium still interfered seriously with the strontium exchange, but at 0.01 molar concentration or less, interference by the salt cations was greatly diminished. The order of interference for the three cations was $\text{Ca} > \text{Al} > \text{Na}$. The greater interference by calcium presumably was due to the chemical and physical similarities of the strontium and calcium ions.

Fig. 12. Effect of Nitric Acid on Strontium Adsorption by Amberlite 200

Fig. 13. Effect of Sodium Nitrate and Nitric Acid on Strontium Adsorption by Amberlite 200

Fig. 14. Effect of Aluminum Nitrate and Nitric Acid on Strontium Adsorption by Amberlite 200

Fig. 15. Effect of Calcium Nitrate and Nitric Acid on Strontium Adsorption by Amberlite 200

For a 1M solution of aluminum nitrate in 0.1N nitric acid, a condition readily attainable for aluminum nitrate-nitric acid process wastes by a formaldehyde kill, the K_d value for strontium was approximately 40, although a value as high as 66 was obtained in a previous experiment. The addition of a complexing agent to reduce aluminum interference should increase the K_d value for this system appreciably. The effect of complexing agents on the exchange reaction of strontium will be investigated in the near future.

Fig. 16. Removal of Strontium from Amberlite 200 by Elution with Nitric Acid

Elution of Strontium

A single experiment was performed to obtain preliminary information on the elution characteristics of strontium adsorbed on Amberlite 200 resin. A sample of resin from the equilibrium experiments was equilibrated with successive portions of 5N nitric acid, and the concentration of strontium in the supernatant liquid was determined. The results of this experiment are shown in Figure 16. Two successive elutions removed about 83 per cent of the adsorbed strontium, but two more elutions removed only an additional 4 per cent. No appreciable physical breakdown of the resin was observed. Regeneration with sodium will be attempted in future experiments.

B. Mercury Cathode Electrolysis of Stainless Steel Wastes, D. R. Anderson

The use of mercury cathode electrolysis as a method for separating the alloy metal ions iron, nickel, and chromium from the fission products in stainless steel-type wastes has been investigated on a laboratory scale at the ICPP. Recent results indicated that increasing the temperature of the aqueous solution to 35° C during electrolysis avoided an apparent inhibiting effect by the ion species formed from the so-called "powder" chromic sulfate in solution.

Experimental Methods

The electrolysis was carried out in a conventional Dyna-Cath electro-analyzer in the manner described previously.⁽¹⁾ The temperature of the aqueous solution was controlled to $\pm 1^\circ$ C.

Experimental Results

Work during this report period involved a brief investigation of the apparent interference by chromium ions in the electrolysis reaction.

The so-called "crystal" and "powder" forms of chromic sulfate (both of which were amorphous to X-ray diffraction) exhibited different characteristics during electrolysis at -1.80 V vs S.C.E. and $25 - 27^\circ$ C.

Examples of the rates of removal of iron, nickel, and chromium from solutions of identical chemical composition at 27° C, using "powder" and "crystal" chromic sulfate as a source of chromium, are shown in Figure 17. Not only was the rate of removal of chromium very slow from the solution containing the "powder" form of chromic sulfate, but also the rate of removal of iron and nickel was inhibited seriously.

Fig. 17. Effect of Crystal Form of Chromium on Removal of Alloy Metal Ions from 1N Sulfuric Acid Solution at 27° C

Electrolysis of the individual metals in sulfuric acid revealed that nickel and iron removal essentially followed the curves shown in Figure 17-II. Electrolysis of the two forms of chromic sulfate is shown in Figure 18. Polarographic, emission spectrographic, and X-ray diffraction data indicated that both forms of chromic sulfate were amorphous and essentially identical with respect to any impurities present. Therefore, it was concluded that the difference in the electrolysis rates was a result of the existence of different ionic species in solution from the two forms of chromic sulfate.

Chromic ions are characterized by the ability to form aquated ions such as $Cr(H_2O)_6^{+++}$ and coordination complexes such as $(Cr_4O(SO_4)_4)SO_4$ in solution. Apparently the ion species formed by the "powder" chromic sulfate when dissolved in sulfuric acid at room temperature inhibited the electrolysis reaction. Increasing the temperature of the aqueous solution to 35° C or above eliminated the apparent inhibiting effect of the chromium

Fig. 18. Removal of Chromium from 1N Sulfuric Acid Solution at 27° C as a Function of Form of Chromium

ions, and the rate of removal curves were essentially the same as those for the "crystal" form of chromic sulfate.

This temperature effect suggested that the aquated or coordination complex that was formed from the "powder" type chromic sulfate was altered by increasing the temperature, at least to the extent that electrolysis proceeded in a fairly rapid manner. The inhibiting effect of the chromic ions near room temperature also suggests that possibly cobalt, which forms ions in solution similar to those of chromium, may be prevented from undergoing electrolysis by proper adjustment of the electrolysis conditions if contamination by cobalt-60 should become a serious problem in a waste process involving electrolysis of metal ions.

VI. ELECTROLYTIC DISSOLUTION SYSTEMS

Section Chiefs: H. T. Hahn, Chemical Research
K. L. Rohde, Process Chemistry

The operational behavior of an electrolytic dissolver is considerably dependent upon the reactions which occur in the dissolver. An analysis of these reactions and their mechanisms may be made by a combination of polarization measurements and product analysis. From an understanding of the electrode reaction, it will be possible to select optimum operating conditions. Also important to both cell design and operation is the effect of cell and electrode geometry upon current density distribution. Since most dissolver-fuel configurations are too complex for theoretical treatment, the use of conductive rubber sheeting for analog simulation has proved very useful in solving the design problem of current distribution.

Demonstration and evaluation of the effects of stray currents in the vicinity of electrodes, with particular concern for corrosive situations in electrolytic process equipment, was pursued both with direct measurements by means of Luggin probes in an operating test cell and by determination of lines of equal potential on conductive sheet analogs. An extensive pictorial presentation of results is included with the discussion of the findings. As a result of a search for means of determining and controlling the conditions existing in an electrolytic dissolver, the comparison of electrical conductivity measurements of original and diluted dissolver solution was found to give promise of simultaneous determination of acid and stainless steel concentrations by instrumental analysis.

Investigation of electrolytic disintegration of Zircaloy-2 fuel in nitric acid, a process in which the Zircaloy undergoes oxidation and disintegration to form a sludge, while the uranium is dissolved to effect a separation of the fuel components, has been continued in an effort to define the most favorable conditions for the process. The effects of temperature, voltage, and acid concentration were investigated, and findings on uranium losses, zirconium solubility, cathode corrosion, and current efficiency are reported.

In order to evaluate possible materials of construction for use in an electrolytic dissolver system, a variety of stainless steels, special alloys, and plastic materials were subjected to exposure in boiling nitric acid-stainless steel dissolver solution. Results ranged from good resistance to complete failure. Exposure of other specimens to the environment of an operating electrolytic dissolver indicated existence of severe corrosion due to current paths far removed from the electrodes, emphasizing the limitations to be placed on the use of stainless steel near the active parts of the dissolver.

A. Electrolytic Dissolution of Stainless Steel in Nitric Acid

1. Electrolytic Dissolution Mechanisms and Current Paths

Work presented this quarter concerns the demonstration and evaluation of stray currents in the vicinity of electrodes, with particular concern for corrosive situations in electrolytic process equipment. Both conductive sheeting and Luggin probes were used to evaluate the magnitude of the effect as a function of distance and geometry. Data are also presented which pertain to the polarization of chromium and iron in nitric acid at 25° C.

a. Polarization of Stainless Steel and Its Components in Nitric Acid

J. R. Aylward, Problem Leader; E. M. Whitener

Studies of the electrolytic dissolution of stainless steel and its individual components (iron, nickel, chromium) were continued. The potential-current density curves for a pure chromium electrode in nitric acid of various concentrations at 25° C are shown in Figure 19. A Tafel relationship with a slope of 0.047 volt is observed over a wide

Fig. 19. Anodic Polarization of a Pure Chromium Electrode in Nitric Acid at 25° C

range of current densities. The slight deviation from Tafel behavior at high current densities is probably due to an IR drop error. There also appears to be some concentration polarization in the case of the higher acid concentrations. Complicating factors such as the secondary passivation observed for stainless steels are not present.

Preliminary experiments with pure (99.95 per cent) iron have revealed that the passive region extends to potentials above that at which oxygen evolution becomes appreciable. A more detailed study of pure iron in nitric acid appears warranted. Pure nickel and various iron-chromium-nickel alloys other than the 18-8 stainless steels should also be investigated.

The potential-current density relationships for 304 stainless steel have been studied extensively as a function of nitric acid concentration, hydrogen ion concentration at constant nitrate ion concentration and in buffered and unbuffered solutions. From this it became evident that the phenomenon of secondary passivation recorded in the last quarterly report⁽¹⁾ is predominantly a function of hydrogen ion concentration. At concentrations above 4M, this secondary passivation is absent. Details of this work will be described in a later report after the data are completely analyzed.

b. Stray Current Effect, J. R. Aylward, Problem Leader
R. E. Ohlin, E. M. Whitener

Two approaches were used to study the behavior of a metal in an electric field set up in a conducting medium (electrolyte). One involved the determination of equal potential lines on conductive sheet analogs. The second approach made use of an electrolysis cell, and the measurement of potential changes with a Luggin probe at various points on a test coupon, arranged at different positions with respect to anode and cathode.

Fig. 20. Electrolytic Cell for Measuring Stray Current Effects

In the first experiment of the latter type, the electrodes and test coupon of 347 stainless steel sheet were arranged as shown in Figure 20. All but the front face of the electrodes were masked from the solution (6M HNO_3) to give an exposed area of 2.25 cm^2 . The test coupon was placed between, and equidistant from, anode and cathode. By means of reference electrodes provided with Luggin probes, the potential on each side of the coupon could be measured as a function of the cell current. The difference between these potentials and the potential at zero cell current will be referred to as an overvoltage in that which follows.

From this experiment, it was found that the side of the coupon facing the anode acquired a negative (cathodic) overvoltage, and that facing the cathode a positive (anodic) overvoltage. The magnitude of the overvoltage increased with increasing cell current and decreasing distance between coupon and electrodes. Also, the overvoltage was a maximum at the center of the coupon, decreasing to zero at the edges. Some results at electrode-to-coupon distances (D) of 1 and 3 cm are shown in Figure 21. The latter overvoltage values were obtained from measurements at the center of the coupon.

Fig. 21. Coupon Polarization vs Field Intensity

Experiments with other coupon-to-electrode configurations show that the relative magnitude of the overvoltage at any point on a coupon depends upon the current flux at that point of the solution in the absence of the coupon, and the relative magnitudes of polarization resistance and solution path resistance. The sign of the overvoltage (anodic or cathodic) at any point on the coupon is determined by the direction of current flow at that point.

A simple example may serve to illustrate the above points. If one considers the stainless steel electrodes and coupon in Figure 20 replaced by copper, and the solution by copper sulfate, the steady state current through the solution is carried by the transport of Cu^{+2} from anode to cathode. The copper

coupon between anode and cathode increases the current path for the transport of Cu^{+2} through the solution, but at the same time offers a very low resistance path to the flow of electrons. However, the conversion of current from a flow of ions (Cu^{+2}) to a flow of electrons and back again can, in this case, be accomplished by the mechanism $\text{Cu} \rightleftharpoons \text{Cu}^{+2} + 2e$. Therefore, on the side of the coupon facing the anode, the cathodic reaction $\text{Cu}^{+2} + 2e \rightarrow \text{Cu}$ takes place, and on the opposite side, the anodic reaction $\text{Cu} \rightarrow \text{Cu}^{+2} + 2e$. This is shown pictorially in Figure 22. In this simple example, deposition occurs on one side of the coupon and dissolution (corrosion) on the other. The same principle holds for stainless steel in nitric acid, but the reactions are much more complex. Some aspects of the stainless steel-nitric acid system will be discussed later.

Any reaction taking place at a metal-solution interface is accompanied by polarization. This polarization will be balanced by the effective increase in solution path IR drop due to the presence of the metal coupon. Thus, current will travel both around and through the coupon to a degree depending upon the relative magnitudes of these two effects. In the above illustration, the current through the coupon is

Fig. 22. Representation of Stray Current Mechanism

greater at the center, decreasing to zero at the edges because of the decrease in solution path length. If the polarization resistance for either the anodic or cathodic reaction on the coupon is very large, as would be the case for a valve metal such as niobium, then current would flow only through the solution. In the opposite case, e.g., high solution resistance and low polarization resistance, current would tend to funnel through the metal coupon. Figures 23-A and 23-B show the form of the equal potential lines for these two cases in a cell having various coupon orientations with respect to the electrodes. These were obtained by the use of conductive sheet analogs.⁽¹⁾ To simulate a highly-

polarized coupon, a corresponding piece was cut from the sheeting; to simulate low polarization, the resulting hole was covered with a copper plate.

As seen above, the process by which current passes through a metal coupon placed in an electric field results in an oxidation reaction at one point and a reduction reaction at another. However, depending on the metal and oxidizable species in solution, the oxidation reaction need not necessarily be one of metal dissolution. For stainless steel in nitric acid, increased corrosion will occur only if the polarization is

Fig. 23. Conductive Rubber Sheet Analogs

A. Coupon with High Polarization Resistance

B. Coupon with Low Polarization Resistance

sufficient to hold the metal-solution interface at a potential lying in the active or transpassive regions.

It is important to remember that corrosion due to stray currents is possible only when the metal is oriented in the electric field so that current can enter at one point and leave at some other point. With a dissolver design consisting of anode, cathode, and electrically-"floating" container, as shown in Figure 24-A, corrosion of the container due to stray currents is impossible because a return path does not exist. This is not the case, however, for a design of the type shown in Figure 24-B, as can be seen by the arrows which indicate current paths. These two geometries were simulated with conductive sheet analogs (Figures 25-A and 25-B), and the shape of the equal potential

Fig. 24. Dissolver Design With (A) and Without (B) Stray Currents

lines confirms the above reasoning. The design represented by Figure 24-B was also studied in an electrolytic cell, Figure 26. The back and edges of the coupon were insulated from the solution, and the potential with and without cell current measured as before. These measurements were made at various vertical distances above and below the top of the cathode. From the results given in Figure 27, it can be seen that the part of the coupon above the cathode is polarized to a more cathodic potential, and

Fig. 25-A. Analog of Cell Design 24-A

Fig. 25-B. Analog of Cell Design 24-B

that below to a more anodic potential. The equipotential lines for the type cell in Figure 26 were also determined by a conductive sheet analog and are shown in Figure 28.

One other situation that could possibly result in stray currents in an actual dissolver is the point at which metal pipes connect to the dissolver. These, of course, will be insulated from anode and cathode. An analog simulation of this is shown in Figure 29, from which it can be concluded that stray currents do not exist or are negligible in this situation.

CPP-S-1898

Fig. 26. Electrolytic Cell

CPP-S-1899

Fig. 27. Coupon Polarization vs Distance from Top of Cathode in Cell of Figure 26

CPP-S-1900

Fig. 28. Analog of Electrolytic Cell of Figure 26

CPP-S-1901

Fig. 29. Analog of Simulated Dissolver with Lead-in Pipe

2. Electrolytic Conductance in Electrolytic Dissolver Solutions H. T. Hahn, Problem Leader; D. P. Pearson

The use of electrical conductivity measurements has been proposed as a basis for instrumental analysis of electrolytic dissolver solutions. The conductances of simulated dissolver solutions, in the ranges 0 - 6N HNO_3 and 25 - 150 g/l stainless steel as nitrates, have been measured at 25 and 80° C to determine whether this approach holds any promise. There appears to be a reasonable basis for simultaneous determination of HNO_3 and stainless steel concentrations, but a proved method has not yet been developed.

First consideration was given to the possibility of determining either stainless steel or HNO_3 concentration by means of conductance, and the other component by an independent method. Specific conductance values at 25° C and 1000 cycles/sec are presented in Figure 30 as a function of stainless steel concentration and in Figure 31 as a function of HNO_3 concentration. Values obtained at 4 and 6N HNO_3 were essentially identical, and hence offer no chance of acid analysis in solutions of 4 - 6N HNO_3 concentration. However, the region would be useful for stainless steel analysis. At the other extreme, in the region of little or no acid, the conductance passes through a maximum and the stainless steel concentrations are no longer unique at a given acid concentration. This region could be useful for acid determination if the stainless steel concentration were known from some property such as density (which is under study).

The sensitivity of the method depends on the concentrations involved. To determine this sensitivity, it is estimated that conductance measurements can be made with a precision of + 1 per cent. From this value, and tangents to the curves in Figures 30 and 31, isosensitive regions were calculated. It was found that if an uncertainty of 0.2N HNO_3 is permissible, the working range extends up to 3.7M HNO_3 and 50 g/l stainless steel or 3.2M HNO_3 and 100 g/l stainless steel. However, if the acidity must be known to 0.05N, then the working range is restricted to the 1 - 2M HNO_3 range.

If a sensitivity of 1 g/l stainless steel is required, most of the practical range of conductivity is excluded. The region of exclusion narrows as the permitted uncertainty increases. However, at low acid concentrations the uncertainty is still greater than 3 g/l stainless steel over the 60 - 80 g/l region, due to the maximum in Figure 30.

The possibility of obtaining both stainless steel and HNO_3 analyses from two conductance measurements at differing temperatures or dilutions was investigated. Conductances were measured at 80° C and plotted as a function of the specific conductance at 25° C (Figure 32). Very precise measurements would be required to define both the nitric acid and stainless steel compositions from conductance measurements at these two temperatures.

Figure 33 shows the specific conductances, at 25° C, of solutions diluted 1 : 1 with water as a function of the specific conductances of the undiluted solutions. In this case, the various compositions have

Fig. 30. Specific Conductance of Stainless Steel-Nitric Acid Solution at 25° C as a Function of Stainless Steel Concentration

Fig. 31. Specific Conductance of Stainless Steel-Nitric Acid Solution at 25° C as a Function of Acid Concentration

Fig. 32. Specific Conductance of Stainless Steel-Nitric Acid Solution at 80° C as a Function of the Specific Conductance at 25° C

Fig. 33. Specific Conductance of Stainless Steel-Nitric Acid Solution Diluted 1 : 1 with Water as a Function of the Specific Conductance of the Undiluted Solution

much more unique positions on the plot. If an absolute uncertainty of 0.01 in the conductance measurements (1 per cent of the maximum conductance, where $I_{\max} \sim 1.0$) is assumed, the uncertainty in the nitric acid concentration ranges from 0.04N (1N HNO_3 , 0 g/l stainless steel) to 0.2N (6N, 75 g/l and 1N, 150 g/l), and the uncertainty in stainless steel composition ranges from 1 g/l (6N, 25 g/l) to 8 g/l (1N, 150 g/l).

If a higher sensitivity is required where the conductance is less than $1.0 \text{ ohm}^{-1} \text{ cm}^{-1}$, the error may be reduced by amplification. For conductances determined to 1 per cent of the measured conductance (rather than 1 per cent of the maximum conductance), the maximum composition uncertainties are 0.1N HNO_3 (6N, 75 g/l) and 3 g/l stainless steel (0N, 25 g/l). The amplification is equivalent to magnifying the area near the origin of Figure 31.

The dilution of 1 : 1 was arbitrary; it is entirely possible that a different dilution would open the grid in Figure 33 still further. There would therefore appear to be a reasonable basis for simultaneous stainless steel and HNO_3 determination by conductance measurements of both the original and diluted dissolver solutions.

B. Electrolytic Disintegration of Zirconium-Base Alloys
J. W. Coddington, Problem Leader; M. R. Bomar

Efforts have continued to develop methods for electrolytically processing zirconium alloy fuels. When treated anodically in hot nitric acid, Zircaloy-2 undergoes oxidation and disintegration, forming a sludge of zirconium oxide. Distinct advantage could be shown for processing zirconium fuels in this manner if the uranium could be dissolved simultaneously, since a head end separation of the uranium and the alloying constituents would be effected. The resulting solution would be relatively non-corrosive, and it could be evaporated to achieve high uranium concentrations for subsequent recovery by solvent extraction. The tests herein reported were intended to show optimum conditions primarily for the zirconium disintegration process.

The experiments were performed in a one-liter beaker for which a special plastic top was fabricated. The top was prepared to hold two electrodes, a Luggin probe, a stirrer, a temperature controller, a cooling coil, and a reflux condenser. The Carpenter-20 Cb cathode was shielded by a Teflon holder so that only the side facing the anode was exposed. The electrodes were separated by 1/4 inch.

Zirconium penetration rates were measured by weight loss of the anode; cathodic corrosion rates were similarly determined. Zirconium solubility was determined by solution analysis. The uranium lost to the ZrO_2 precipitate was measured by dissolving the solid in an HF-HNO_3 mixture and submitting the resultant solution for uranium analysis. Total current passed during each experiment was measured with a copper coulometer.

1. Effect of Temperature, Voltage, and Acid Concentration

Temperature

The electrolytic oxidation of zirconium in nitric acid is notably temperature dependent. Figure 34 shows this effect for both Zircaloy-2 and STR fuel. The lowest temperature at which an appreciable reaction will take place is about 45° C. As the temperature is increased from 45° C, the rate of reaction increases rapidly until a maximum rate is reached at about 70° C. As the temperature is increased further, the rate of reaction decreases, and at the boiling point is only about 65 per cent of the maximum. This effect was demonstrated with STR fuel as well as with pure Zircaloy-2.

The temperature is difficult to control because the reaction is very exothermic. For this reason, the optimum temperature is very dependent on the stirring speed. In all tests herein reported, a stainless stirrer with a 2-inch diameter propeller having three 45° blades was used. The stirring speed was 600 rpm in all tests.

Voltage

The rate of the reaction is not a linear function of the voltage. Limited data shown in Figure 35 indicate that the oxidation rate increases in a logarithmic fashion as the voltage is increased from

Fig. 34. Effect of Temperature on the Rate of Oxidation of Zircaloy-2 and STR Fuel in 8M Nitric Acid

Fig. 35. Effect of Voltage on the Rate of Oxidation of Zircaloy-2 in 8M Nitric Acid

0 to 13 volts. The rate-voltage relationship has not been determined for voltages greater than 13 volts, but it has been observed that upon rapidly increasing the voltage to 25 volts, the reaction will stop. If the cell potential is supplied by a powerstat, both voltage and current fluctuate considerably as the zirconium oxide sloughs off in a somewhat irregular manner.

Acid Concentration

The oxidation rate for STR fuel as a function of nitric acid concentration was determined. All experiments were performed at 70° C and 13 volts. Of the concentrations studied, 8M HNO₃ produced the highest rate of oxidation. Data for 4, 8, 10, and 12M HNO₃ are shown in Table 16.

TABLE 16

EFFECT OF NITRIC ACID CONCENTRATION ON THE RATE
OF ELECTROLYTIC OXIDATION OF STR FUEL

<u>HNO₃ Concentration (M)</u>	<u>Oxidation Rate (mg/cm²-min)</u>
4.0	4.6
8.0	6.9
10.0	5.5
12.0	4.6

2. Process Development Information

Uranium Dissolution

The uranium contained in the zirconium oxide residue has typically constituted 6 to 25 per cent of the total uranium in the alloy. This uranium retention remains the most serious problem in the development of the potential process. Washing, oxidation, and complexing techniques, which may not have been explored completely in the past, will be tried to secure an adequate uranium recovery.

Cathode Corrosion

A Carpenter-20 Cb cathode was used in all tests. Corrosion rates for the cathode as well as half-cell potentials were measured. Corrosion rates during the oxidation of Zircaloy-2 in 8M nitric acid were 24 to 51 mils/month for the Carpenter-20 Cb cathode. Oxidation of STR fuel in 4M HNO₃ caused extremely severe cathode corrosion at a penetration rate of 2400 mils/month, while treatment of STR fuel in 8, 10, and 12M HNO₃ was accompanied by cathode corrosion rates of less than 3 mils/month. No useful correlation between cathode corrosion rates

and half-cell potentials has been made with the data presently available.

Current Efficiency

The current efficiency is generally of the order of 100 per cent, but there are some variations. Figure 36 shows the current efficiency for the oxidation of Zircaloy-2 in 8M HNO_3 at various temperatures. No explanation presently exists for the high current efficiency achieved at nearly the same temperature as that of optimum disintegration rate.

Zirconium Solubility

For the oxidation of Zircaloy-2 in 8M HNO_3 , the per cent of zirconium present in solution decreases with increasing temperature. Figure 37 shows this effect. It is noted that the variation in zirconium solubility is less than 5 per cent. Data so far collected do not indicate any correlation between zirconium solubility and the rate of oxidation or the amount of uranium retained by the residue. The per cent of zirconium dissolved ranged from 13.9 to 18.1 per cent of the total zirconium which reacted; the remainder was solid ZrO_2 .

Fig. 36. Current Efficiency as a Function of Temperature for the Electrolytic Oxidation of Zircaloy-2

Fig. 37. Effect of Temperature on Zirconium in Solution from the Electrolysis of Zircaloy-2 in 8M Nitric Acid

C. Materials of Construction in Electrolytic Systems

N. D. Stolica, Problem Leader; C. E. May

1. Corrosion of Alloys and Titanium in Electrolytic Dissolver Solution

The stainless steels types 304L, 316, 347, Carpenter-20 and Inconel and titanium were evaluated in boiling electrolytic dissolver product solution to determine their suitability for the construction

of portions of electrolytic dissolver systems. The dissolver product solution was prepared by the electrolysis of type 304 stainless steel in 8M HNO_3 . The resulting solution was 1M in HNO_3 and contained 75 g/l of dissolved stainless steel.

The testing of Inconel was discontinued after 2 days because it showed an excessively high corrosion rate, and the testing of titanium was discontinued after 50 days, when the rate had stabilized at a very low value. Testing of the other alloys was continued for a total of 78 days. The corrosion rates are plotted in Figure 38 as a function of time. Microscopic examination showed severe pitting on the edges of the coupons, which probably explains why the rates rose sharply after 60 days. Grain boundary attack was found on the face of the coupons, with only slight

Fig. 38. Corrosion of Metals in Boiling Electrolytic Dissolver Solution (Period Rates)

attack in the case of stainless steels 347 and Carpenter-20. With the exception of titanium, none of the metals tested should be used without restriction for the handling of boiling electrolytic dissolver solutions. Titanium-built evaporators are in use for the concentration of aluminum nitrate-nitric acid wastes at the ICPP.

2. Stability of Plastics in Electrolytic Dissolver Solution

Eleven plastics which were being considered for construction material for electrical insulators in an electrolytic dissolver were tested in boiling electrolytic dissolver solution, as described in the preceding section. The exposure time was 96 hours. The fluorocarbon plastics (Kel F, Kynar, Armalon 410L), the polyethylene plastic Marlex, and the polyvinyl chloride plastic Saran were found to resist the dissolver solution. The results of the tests are given in Table 17.

TABLE 17

STABILITY OF PLASTICS IN BOILING ELECTROLYTIC DISSOLVER SOLUTION

<u>Trade Name</u>	<u>Plastic Type</u>	<u>Results</u>
Kel F (KF3010)	Fluorocarbon	No weight loss
Kynar (RC2525)	Fluorocarbon (vinylidene fluoride)	Slight weight gain
Armalon 410L	Fluorocarbon (fiber glass impregnated Teflon)	Absorbed water which was driven off by prolonged heating in oven
Beetle	Urea formaldehyde (cellulose filled)	Dissolved
Cymel-1077	Melamine formaldehyde (cellulose filled)	Dissolved
Catalin	Phenol formaldehyde (unfilled)	Dissolved
Haveg 41	Phenol formaldehyde (asbestos filler)	Disintegrated
Marlex	Polyethylene	No weight loss
Duracite	Furan resin	Dissolved
Saran (B-115)	Polyvinyl chloride	Slight weight loss. Darkened.
CR39	Allyl resin (allyl diglycol carbonate)	Dissolved

3. Corrosion of Specimens Suspended in an Electrolytic Dissolver

Several stainless steel and Carpenter-20 specimens were suspended at various positions in a laboratory electrolytic dissolver during the dissolution of type 304 stainless steel. The electrolytic dissolver vessel consisted of a 1-liter resin reaction kettle equipped with a type 304 anode, two niobium cathodes, and two types of Teflon specimen holders. A top view of the apparatus is shown in Figure 39. Solution was continuously pumped out of the vessel and replaced by acid so that the concentration of the dissolver solution was maintained constant at $1M$ HNO_3 and 75 g/l of dissolved stainless steel. The exposure time for each run was 95 hours.

Fig. 39. Electrolytic Dissolver

No corrosion was found on the niobium cathodes, and localized attack was found on the suspended specimens. The data are given in Table 18. It is seen that all specimens, with the exception of the one in the position farthest from the cathodes, suffered much greater corrosion when the Teflon shields were removed from the cathodes. Figures 40 and 41 show specimens of type 304L stainless steel which were shielded and not shielded from the cathode. The side of the coupon facing the cathode corroded; i.e., it was anodic to the other side of the coupon. According to measurements made on suspended specimens between an anode and a cathode by the Electrochemistry Group (Section A-1-b, preceding), the specimens located in the path of current lines between the anode and cathode will function as anodes on the side facing the cathode and as cathodes on the side facing the anode. These studies confirm the observations described above.

TABLE 18
CORROSION IN AN ELECTROLYTIC DISSOLVER

<u>Location</u>	<u>Position **</u>	<u>Specimen</u>	<u>Overall Corrosion Rate (mils/month)</u>
Behind cathode (shielded from cathode).	I-a	347	10.6
	b		5.4
	a	316	8.0
	b		7.4
	a	Carpenter-20	4.5
	b	304L	8.5
Behind cathode (not shielded from cathode)	I-a	C-20	162.0 *
	b	304L	159.0 *
Between cathode assemblies	II	316	1.7
		347	4.1
		304L	3.3
		C-20	13.0 *
Adjacent to cathode assembly	III-a	316	8.8
	b		8.5
	a	347	15.3
	b		7.6
	a	C-20	4.8
	b		35.2 *
	a	304	8.0
	b		37.3 *
Position farthest from cathodes	IV	316	1.3
		347	2.4
		C-20	2.4 *
		304	1.4

* Samples were part of the same run.

** Refers to Figure 39.

Side Facing Cathode

Side Away from Cathode

Fig. 40. Specimens of Type 304L Stainless Steel Shielded from Cathode

Side Facing Cathode

Side Away from Cathode

Fig. 41. Specimens of Type 304L Stainless Steel Not Shielded from Cathode

These results indicate that:

- 1) In this system, at typical current densities, there are current paths far outside the direct path between anode and cathode.
- 2) In this particular geometry, and with the cathode back unshielded, approximately 1 per cent of the total cathode current was intersecting the coupon located directly behind the cathode in Position I.
- 3) Coupons in positions adjacent to the active cathode suffered severe corrosion under certain conditions. (Positions II and III.)
- 4) Only the coupon completely shielded by the anode, Position IV, showed normal corrosion, uninfluenced by the current field.
- 5) In the particular experimental arrangement of the dissolver used here, the corrosion-accelerating effects of short-lived chemical species, chromium VI, for example, were not observed. Comparison of the data from Table 18 and Figure 38 for the four stainless steels suggests that the corrosion in the freshly-prepared dissolver media, but outside the current field (Position IV of Table 18), is comparable to that experienced with equivalent exposure to aged dissolver product solution.

In general, these results should help to define the limitations to be placed on the use of stainless steel anywhere adjacent to the active region of the dissolver.

VII. THE ARCO PROCESS - DISSOLUTION OF FUEL ALLOYS IN MOLTEN CHLORIDES

Section Chief: H. T. Hahn, Chemical Research

The ARCO Process employs molten lead chloride as a solvent for reactor fuel alloys.⁽¹⁾ Zirconium and aluminum alloys dissolve readily in the molten salt, and the respective chlorides are volatilized. Stainless steel requires the addition of chlorine to the melt in order to effect dissolution. The $\text{PbCl}_2\text{-Cl}_2$ system also dissolves chromium and niobium at feasible rates. Addition of copper to the $\text{PbCl}_2\text{-Cl}_2$ system permits dissolution of uranium oxide in the same temperature range as the alloys⁽¹⁾ (500 - 530° C).

During the past quarter, the study of niobium behavior in fused lead chloride has continued. Factors affecting the volatilization of ferric chloride from lead chloride were investigated briefly, and it would appear that both temperature and minor element concentration are significant. Work in progress, which has not been completed, concerns the mechanism of dissolution of uranium dioxide powder in the $\text{Cl}_2\text{-Cu-PbCl}_2$ system.

A. Niobium Behavior in the $\text{PbCl}_2\text{-Cl}_2$ System

E. M. Vander Wall, Problem Leader; J. L. Teague

Studies of the behavior of niobium in ARCO Process systems have been extended to $\text{PbCl}_2\text{-Cl}_2$ melts.

The apparatus consisted of a 3-inch crucible furnace, with a Wheelco temperature controller. The molten PbCl_2 (7.5 g in each experiment) was contained in a Pyrex tube and supported on a 20 mm-diameter, medium-porosity glass frit through which the chlorine was introduced. Excess chlorine passing through the melt was collected in a potassium iodide scrubber, with the liberated iodine titrated with sodium thiosulfate solution. The amount of chlorine reacted was determined from the niobium dissolved, assuming the product to be niobium pentachloride. This assumption is justified in a subsequent paragraph. All experiments were carried out at a temperature of $550 \pm 5^\circ \text{C}$, with uniform-sized samples of niobium being used.

An increasing reaction rate with increasing chlorine flow rate is observed (Figure 42). The points shown in Figure 42 are for a 30-minute contact time. Limited experiments at other contact times show no significant time dependence of the reaction rate. It is of interest to note that extremely small rates are observed in the chlorine-free system at this temperature.⁽¹⁾

Analysis of the volatile reaction product for niobium and chlorine indicated NbCl_5 to be the only significant species present. A small uncertainty was introduced due to the extreme sensitivity of the product to hydrolysis. Analysis of the melt phase showed that volatilization of NbCl_5 was essentially complete (as would be expected from its 240° C boiling point), with 0.01 per cent or less niobium being detected in the

Fig. 42. Niobium Dissolution in PbCl_2 as a Function of Cl_2 Flow Rate

melt. Hence, very little complexing action of lead and niobium chlorides is indicated.

Some additional experiments designed to determine product species in PbCl_2 at 650°C revealed that 8 to 10 per cent of the melt phase appeared to be niobium metal in the form of small particles associated with lead. This may require a downward revision of previous dissolution rates⁽¹⁾, since the latter were based upon coupon weight loss.

B. Volatilization of Type 347 Stainless Steel Chlorides in the $\text{PbCl}_2\text{-Cl}_2$ System

E. M. Vander Wall, Problem Leader; D. L. Bauer

Dissolution rates greater than $30\text{ mg}/(\text{cm}^2)(\text{min})$ had been reported for type 347 stainless steel in the $\text{PbCl}_2\text{-Cl}_2$ system.⁽¹¹⁾ However, no effort was made in these experiments to establish the distribution of the iron chlorides in the system. Therefore, a brief study of iron chloride volatilization was initiated.

The reaction apparatus consisted of a Pyrex glass tube containing a 20-mm sintered glass disc which served both as a support for the lead chloride melt and to disperse the chlorine into the melt. A collection chamber was attached to the top of the reaction tube and fitted with a glass wool plug to retain any particulate material. The exit gases were washed by a series of acidified aqueous solutions before they were vented to the atmosphere. These wash solutions were also included in the analysis for volatile iron products.

The stainless steel samples were in the form of $1/4$ -inch rods. The sample was placed in the salt; the lead chloride was melted; and the chlorine flow started. The experiments were performed at approximately 550°C (with one exception which was allowed to reach red heat) and continued for varying lengths of time, as indicated by the final melt composition. The data obtained are given in Table 19.

TABLE 19

VOLATILIZATION OF IRON (III) CHLORIDE FROM THE MELT DURING DISSOLUTION
OF TYPE 347 STAINLESS STEEL IN THE $\text{PbCl}_2\text{-Cl}_2$ SYSTEM AT 550°C

Experiment Number	Final Melt Composition (mole per cent)				Per Cent of Dissolved Iron Which Volatilized
	Fe	Cr	Ni	Pb	
1	20.5	7.9	3.2	68.5	11.0
2	48.6	7.1	3.4	41.0	18.0
3	27.9	11.1	5.7	56.4	18.6
4	28.0	(11.0)*	(4.8)*	56.2	17.6
5	31.9	19.7	7.8	40.6	45.6

* Values are based on original 347 stainless steel composition and the average distributions in similar experiments.

In Experiment 2, pure iron wire was dissolved in the PbCl_2 melt by reaction with chlorine before the stainless steel was introduced. Even though the iron concentration was more than double that of Experiment 1, the amount of iron volatilized was increased only 64 per cent. The phase diagram for the $\text{FeCl}_3\text{-PbCl}_2$ system contains only one eutectic at 178°C and 63.1 mole per cent FeCl_3 .⁽¹²⁾ Therefore, one would expect a large percentage of the FeCl_3 to volatilize from the melt only at very high iron concentrations and at high temperatures. On the basis of Experiments 3, 4, and 5, it appears that an increase in the chromium and nickel content of the lead chloride melt has a significant effect on the amount of iron which is volatilized. They probably reduce the solubility of ferric chloride in lead chloride by an appreciable amount.

In Experiments 1 through 5, an average of 8 per cent of the nickel and from < 1 to 6 per cent of the chromium volatilized from the melt.

In another experiment, the dissolution was performed at red heat. The 6.86 g sample completely dissolved in 18 minutes. Based on the initial sample area, the dissolution rate was $63.5\text{ mg}/(\text{cm}^2)(\text{min})$, and the actual rate is considerably greater than this. After the dissolution, chlorine was passed through the melt at the rate of 1 g/hr for about 2 hours in an attempt to volatilize as much material as possible. Besides 78.9 per cent of the iron, 15 per cent of the nickel and 5 per cent of the chromium were collected in the overhead.

Considerable investigation remains to be done in this system. Phase studies involving the components would enable one to determine whether it may be possible to effect nearly 100 per cent volatilization of iron from the melt. The effect of uranium on the solubility of iron in the melt must also be determined.

VIII. EQUIPMENT DEVELOPMENT

Section Chief: M. E. Weech, Process Engineering

Successful performance of the ICPP first cycle direct air pulsed extraction column has led to replacement of all of the ICPP mechanical-hydraulic pulsers with air pulsers. The theoretical advantages cited earlier⁽¹⁾ for these units were reinforced by the results of the test run.

In continued study of large vessel criticality control, through use of boron stainless steel inserts, neutron multiplication tests have been run on a test vessel. Analysis of the results is not yet available.

A. Direct Air Pulsing of Extraction Columns

D. K. MacQueen, Problem Leader; R. S. P'Pool

The direct air pulsed extraction column has performed satisfactorily in full-scale plant operation, and it is therefore planned to replace the remaining mechanical-hydraulic pulsers in the ICPP with air pulsers by mid-1961. This project is proceeding simultaneously with the development effort using the experimental 10-inch air pulser unit.

The air pulser installation on the 10-inch diameter column in the ICPP was completed, cold tests were made, and a limited amount of operating experience with hot feed was obtained. The operating range of the air pulser and the column extraction efficiency were investigated during the cold runs. A summary of general operational observations concerning the air pulser system, column behavior, and raffinate uranium concentration is presented in Table 20.

From these cold test results, the maximum pulse energy input to the "A" column for satisfactory column operation was defined as approximately 100 cycles per minute at 0.7-inch pulse amplitude for 3/4 rate, or 90 cycles per minute at 0.75-inch pulse amplitude for full-rated plant capacity. The following generalizations were also obtained from results of the test program:

- 1) Extraction efficiency was at least as good with the air pulsers as with the mechanical-hydraulic pulse system.
- 2) A much wider range of pulser energy input was available than with the existing pulsers. Forty-five to 60 cycles per minute had represented the entire controllable frequency range for pulse amplitudes of 0.75 to 1.0 inch.
- 3) Operating conditions were simpler and faster to set and maintain than with the existing mechanical pulsers.
- 4) Initial installed costs for air pulser equipment were about 12 per cent of those for the mechanical pulsers.

TABLE 20

COLD TEST AIR PULSER OPERATIONS
ICPP 10-inch Diameter "A" Column

Pulser Control Settings			U Conc. in Raffinate (gm/l)(2)	Duration (hrs)(3)	Per Cent of Full Flow	General Column Behavior
Frequency (Cycles/ min)	Air Pressure (psig)	Column Pulse Amplitude (in)(1)				
45	9.2	1.0	6.3×10^{-4}	4.5	75	Steady
70	15.3	1.0	4.4×10^{-4}	1.0	75	Steady
100	18.5	0.75	9.7×10^{-5}	1.5	75	Fair ⁽⁴⁾
100	18.5	0.75	$< 5.0 \times 10^{-5}$	3.0	75	Flooded ⁽⁴⁾
60	13.0	1.0	$< 5.0 \times 10^{-5}$	6.0	75	Steady
75	14.5	0.8	$< 5.0 \times 10^{-5}$	6.0	75	Steady
90	17.0	0.75	$< 5.0 \times 10^{-5}$	6.5	75	Steady
100	17.0	0.60	$< 5.0 \times 10^{-5}$	3.0	75	Steady
100	18.3	0.70	$< 5.0 \times 10^{-5}$	13.0	75	Steady
100	18.3	0.70	$< 5.0 \times 10^{-5}$	1.5	100	Flooded ⁽⁵⁾
90	17.0	0.75	$< 5.0 \times 10^{-5}$	(6)	100	Steady

(1) Amplitudes taken from analog computer data for given frequency and pressure (Figure 43).

(2) Minimum detectable uranium is 5.0×10^{-5} g/l.

(3) Tests shown were run in sequence without an intermediate column shutdown.

(4) A gradual decline in the interface liquid level was indicated during this 4 1/2-hour operating period. Flooding occurred 4 1/2 hours after control settings were changed.

(5) Flooding occurred 1 1/2 hours after flow changed.

(6) Steady operation on continuous basis after last change at 100 per cent feed rate.

Following the cold tests, the plant started up on normal feed from irradiated fuel. The air pulser operated satisfactorily all through the ensuing 10-day run.

Design and prediction of behavior of the plant air pulser was done by a series of analog computer runs. Equation parameters and coefficients for the design equations were based upon the available data from the

experimental air pulser column. Figure 43 illustrates the air pulser ranges that are of interest in ICPP plant operations. The lower operating limit shown in this figure is not an inherent limitation in an air pulser system, but is determined by entrance of the organic fluid from the pulse leg to the air supply line for this particular ICPP "A" column installation. The equations used are not applicable for this special situation; the air pulser itself would operate well outside the ranges shown if other installation piping geometries were used.

The effect of changes in column organic holdup on pulse amplitude was also calculated on the analog, and the results of these calculations are shown in Figure 43. As a check on the calculations, points from the experimental column were plotted on the figure. In spite of geometrical differences between the experimental and plant columns, the agreement is quite good.

The successful demonstration of an air pulsed extraction column in routine ICPP operation has led to the acceptance of such a system as a substitute for the trouble-ridden mechanical-hydraulic pulsers currently in use. Design of an air pulser installation for the "B" and "C" columns in the high-capacity aluminum first cycle extraction system and all three pulsed first cycle STR-SIR columns is proceeding. All five of these new air pulsers will utilize equipment components similar to those installed for the 10-inch "A" column, with minor revisions and improvements. Differences in physical size and geometry between the STR-SIR columns and the 10-inch "A" column, plus the delay in procurement of final design data from the experimental unit, will necessitate the derivation of pressure-frequency-amplitude curves for the STR-SIR columns during the cold tests, and amplitude measurements will be made directly through transparent sections of the pulse leg. The transparent sections will be replaced by stainless steel pipe of the same inside diameter before processing of irradiated fuels begins.

B. Large Vessel Criticality Control, D. K. MacQueen

Neutron multiplication tests are under way by Dow Chemical personnel at Rocky Flats on an experimental cartridge supplied by Phillips Petroleum Company.⁽¹⁾ This cartridge consists of a series of stainless steel plates containing 1.1 weight per cent natural boron placed vertically in a 3-foot diameter by 4 1/2-foot high vessel. The spacing between the plates can be varied from 1 inch up to 3 inches. Data from these tests will permit the design of large vessels for the storage of concentrated, highly-enriched uranium solutions. One of the first uses of such a cartridge will be in the disengaging head of the first cycle product evaporator (H-110). Results from these tests are expected in early April.

Fig. 43. ICPP Extraction Column Air Pulser Settings

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