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CHEMICAL PROCESSING TECHNOLOGY

QUARTERLY PROGRESS REPORT

April - June, 1961

**PHILLIPS
PETROLEUM
COMPANY**

ATOMIC ENERGY DIVISION

**NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION**

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Printed in USA

IDO-14567
AEC Research & Development Report
General, Miscellaneous, and Progress Reports
TID-4500 (16th Ed.)
Issued: November 10, 1961

CHEMICAL PROCESSING TECHNOLOGY
QUARTERLY PROGRESS REPORT
APRIL - JUNE 1961

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Contract AT(10-1)-205

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U. S. ATOMIC ENERGY COMMISSION

Previous Quarterly Reports in the ICPP Series

1954

<u>Quarter</u>	<u>Number</u>
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1960

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4	IDO-14553

1961

<u>Quarter</u>	<u>Number</u>
1	IDO-14560

CHEMICAL PROCESSING TECHNOLOGY
QUARTERLY PROGRESS REPORT
APRIL - JUNE, 1961

SUMMARY

The Idaho Chemical Processing Plant did not operate on fuel recovery during this period, due to extensive renovation and modification of facilities. Principal modifications included replacement of remote diaphragm pulse units with direct air pulsers on all pulse columns, replacement of additional remote diaphragm pumps with air lifts, and replacement of the original first cycle product evaporator with a redesigned unit. Examination of a test specimen in the dissolver, used for sulfuric acid dissolution of stainless-steel fuels, indicated that the Carpenter-20 dissolver had probably suffered only moderate corrosion losses. A test specimen lost 2.3 mils/month, based on 1080 hours of exposure to batch dissolution service.

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, showed potassium fluoride to be an undesirable additive to the barium precipitating agent used in formation of barium fluozirconate, because of precipitation and loss of uranium, although essentially complete precipitation of zirconium was achieved. Addition of hydrofluoric acid with barium precipitant, to achieve a fluoride/zirconium mole ratio of 5.5, was found to give a total zirconium recovery of 95 percent, including approximately 10 percent recovered after concentration of the supernate from the original precipitation.

Removal of 97 percent of the zirconium and fluoride from zirconium-uranium dissolver solutions was achieved by precipitation with two moles of sodium formate per mole of zirconium. Uranium loss to the precipitate was of the order of 0.2 percent, provided the uranium was kept in the hexavalent state by use of chromic acid and the precipitate was properly washed. Uranium was readily recovered from the concentrated filtrate and wash solution by TBP extraction, provided the evaporation was done in the presence of nitric acid. Corrosion tests indicated that sodium formate-zirconium precipitation equipment could be constructed of type 316 stainless steel, Carpenter-20, or Hastelloy-F, but not of Monel.

In general aqueous studies, the preparation and characterization of zirconium nitrate dibutylphosphate are described, and the solubility in Amsco was found to be similar to that of the uranium dibutylphosphate complex (2 to 4×10^{-5} M); these compounds are of interest because of their influence on stripping operations and formation of gummy precipitates which impair operation of mechanical equipment.

Development of in-line instrumentation for detection of uranium in second and third cycle waste raffinate streams by optical measurements appears

possible because stability studies indicate very little, if any, oxidation of ferrous to ferric iron in a normal raffinate environment, and ferrous iron has a very low molar extinction coefficient (0.8) compared with that of uranium (15) in the spectral region near 415 m μ . The presence of ferric iron, with an extinction coefficient as high as 300, could not be tolerated in the process stream.

Pilot plant studies of the fluidized-bed calcination process for reduction of radioactive liquid wastes to the more-easily-stored solid form have continued in the two-foot-square calciner with production, for the first time over a prolonged period of continuous operation, of alpha alumina-free product from a feed containing substantial sodium. Sodium has been considered a promoter of alpha alumina growth, and no explanation of its lack of effect in this case has been developed. Intra-particle porosities ranging from 0.04 to 0.60 were obtained, emphasizing the effect of bed temperature (250 to 550°C), primarily, and feed concentration (0.8 to 1.95M aluminum nitrate), secondarily, on this property. Low temperatures and low feed concentrations favor low product porosity. Test of a single-fluid nozzle indicated severe erosion or corrosion of the orifice, with the orifice diameter increasing from 76 mils to 150 mils in nine days, and the production of a considerable amount of caked solids, even with the accompanying use of jet grinders to control average particle size.

Laboratory investigation of the conversion of amorphous alumina to alpha alumina, being conducted in an effort to find ways to inhibit formation of the friable alpha form, has demonstrated differences in alpha-forming tendency of amorphous aluminas with varied calcination histories, but attempts at correlation with known variables in fluid bed calciner operation have not been successful. Further studies on the effect of sodium on the conversion confirm the positive, but quantitatively unpredictable, influence of the material.

In studies aimed at converting the fluoride content of STR-type wastes into a form which will resist volatilization during subsequent calcination of the material, rapid (< 5 minutes) precipitation of the zirconium, fluoride, and aluminum was achieved by addition of calcium oxide (CaO/F ratio = 1.5) as a slurry at 60°C; the rapidity and completeness of the reaction indicate that a continuous precipitation step just prior to calcination might be feasible.

The second and third runs in the Demonstrational Waste Calcining Facility were conducted during this period, with Run No. 3 continuing for fifteen days and being shut down on a prearranged schedule to allow additional planned modifications by construction forces. These runs were not intended to provide significant calcination information, but provided operational experience and pointed out areas, both expected and unexpected, of potential operating difficulty.

Additional studies on removal of long-lived radioisotopes from waste solutions (a program directed at simplifying long-term storage and disposal problems) indicate that strontium can be removed from relatively acidic solutions (up to 1M) by adsorption on Amberlite 200 cation exchange resin. Salt cations at one molar concentration interfere seriously with the removal of strontium, and the concentration of aluminum in ICPP aluminum nitrate-nitric acid wastes would probably have to be reduced before efficient removal of strontium could be achieved.

A study of the anodic potential-current density relationships during the electrolytic dissolution of type 304 stainless steel, undertaken to define optimum

operating conditions, revealed that at a temperature of 60°C or higher, anode operation was practical over a wide range of solution compositions (1 to 10M acid) and high current densities (up to 2 amp/cm²), since passivation, limiting current density, and gas evolution were avoided. Similar information on cathode operation remains to be determined before optimum electrolytic dissolver operating conditions can be specified.

A new technique in electrolytic dissolution, Series Electrolytic Dissolution, has been demonstrated at the ICPP. This eliminates the problem of fuel contact with an anode basket and the requirement for high-current, low-potential power sources. Metal to be dissolved is placed in a tubular dissolver through which an acid dissolving solution is passed; electrodes, not in direct contact with the metal but immersed in the electrolyte, are located at the ends of the dissolver. A series of electrolytic cells is formed within the dissolver; one end of each fuel piece acts as a cathode reducing nitric acid, while the other end acts as the anode, going into solution. Dissolution rates of 2.5 mg/cm²/min at current efficiencies of 1000% have been demonstrated for stainless steel.

Additional corrosion tests on materials of construction for possible use in electrolytic dissolver systems indicate that titanium and niobium test coupons are resistant to corrosion in locations in an operating electrolytic dissolver where stainless-steel specimens were rapidly destroyed. Plastic specimens, which had previously been shown to be resistant to the chemical environment in an electrolytic dissolver, were exposed to gamma irradiation (up to 10⁹ R) while exposed to the dissolver solution; only polyethylene, in this group, adequately resisted the combined radiation and chemical conditions to warrant further testing as a possible insulating and supporting material for dissolver construction.

Application of the ARCO Process to niobium (dissolution in molten lead chloride through which chlorine is passed) appears feasible, the dissolution rate being readily controlled by chlorine rate and at least 99.9% of the dissolved niobium being sublimed from the melt as niobium pentachloride. In the absence of chlorine, only 40% of the niobium is volatilized from the melt, and the evidence suggests the formation of lower chloride than the pentachloride. In exploratory tests for further application of the ARCO Process, thorium was found to dissolve in molten lead chloride (550°C) at a rate of at least 8.9 mg/cm²/min, and Nichrome was found to dissolve in molten PbCl₂-CuCl-Cl₂ at a rate of at least 6.7 mg/cm²/min. Zirconium oxide was found to be completely resistant to PbCl₂-CuCl-Cl₂. Rate equations for the dissolution of uranium oxide in PbCl₂-CuCl-Cl₂ are presented with copper concentration and UO₂ form (area) as variables.

Chloride was readily removed, by refluxing, from 8M or stronger nitric acid leach solution used to extract uranium from the lead chloride matrix resulting from the ARCO Process, thus giving a solvent extraction feed solution compatible with stainless-steel equipment. Chloride vapor-liquid distribution coefficients are presented.

Corrosion tests indicated the possible usefulness of Haynes 21 or Haynes 25 alloys for structural use in an ARCO Process dissolver system; corrosion rates experienced were 2 to 3 mils/month in a lead-lead chloride-chlorine system at 520°C.

Analog simulation of the 1A column air pulser to determine theoretical operating curves showed a square wave to be a satisfactory representation

of the pressure input, and an average value of the friction factor to be an excellent substitute for a variable factor. A maximum change in orifice coefficient expected for flow through the column plates, or a 10% change in organic holdup in the column, changed the pulse amplitude less than 10% in the normal operating range.

A cascade control system was specified for the new first cycle product evaporator to provide rapid response to feed rate changes and to better maintain product quality. A study of the stability of the system is underway.

A systems study of pulsed extraction columns has been initiated as a first step in a program to improve present operation and the subsequent design of new process equipment and plants. As a preliminary trial, equations representing a five-stage simplified model for the nearly ideal system, water-acetic acid-hexone, were solved in the analog computer to determine the effect of composition and flow disturbances at constant holdup. At aqueous and organic flow rates of 200 gal/hr-ft², a sudden composition disturbance in the aqueous feed gave time constants ranging from 19 to 113 sec from top to bottom of the column. A 100% disturbance in aqueous flow gave time constants from 19 to 26 sec.

Gaseous ozone-oxygen dissolved in water (0.27 mg O₃/100 ml water) was found to be a suitable decontaminant for removing Ag-110 from samples of aluminum and stainless steel taken from the ETR circulating water loop, achieving a decontamination factor of 50 or greater. This reagent was found more effective than potassium persulfate or hydrogen peroxide in either acid (0.001N H₂SO₄) or neutral media, and is easily removed from the system by heating to 70°C.

Reported as supplemental information are partial molal volumes calculated from previously presented density data for some Zirflex-type solutions.

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I. ICPP OPERATIONAL SCHEDULE, PERFORMANCE, AND PROBLEMS

1. ICPP PROCESSING SCHEDULE

(J. R. Bower)

The Idaho Chemical Processing Plant did not operate on fuel recovery during this period since numerous repairs and modifications to the extraction and uranium-concentration equipment were being made. A discussion of the principal changes was presented in the preceding quarterly report [1]*. These changes include replacement of remote diaphragm pulse units with direct air pulsers on all extraction and stripping columns, replacement of diaphragm pumps with air lifts on in-cell process streams, and modification of product evaporators to minimize criticality hazards.

The Demonstrational Waste Calcining Facility was operated for the first prolonged period (15 days) during this quarter. A discussion of findings is included in Section III of this report, since developmental rather than production aspects are of prime concern at the present stage of operation.

Four barium 140 runs were completed yielding batches of 21,600 to 28,700 curies of product (45 to 51% of theory).

2. PLANT CORROSION STUDIES

(N. D. Stolica, Problem Leader; T. L. Hoffman)

2.1 Corrosion in the Sulfuric Acid Process Dissolver

A plant test corrosion measurement was made on an as-welded, 2-in. high by 2-in. cylindrical, Carpenter-20 (Cb) specimen which was exposed in the plant vessel of the same material to sulfuric acid dissolver solutions of the SIR and OMRE flowsheets. After 1080 hr of batch dissolution service the observed general corrosion was 2.3 mils/month, with mild interdendritic attack at weld areas. This information suggests that the ICPP dissolver used for reprocessing uranium-stainless-steel-clad fuels has suffered only moderate corrosion losses.

2.2 Location of Radioactive Source in Processing Equipment

A pinhole camera for gamma radiation proved very successful in locating accurately a region of insoluble residue of high radioactive content which formed in a feed adjustment vessel used for dissolver solutions from both the sulfuric acid and the hydrofluoric acid processes.

* Numbers in brackets refer to entries in Section X, References.

II. AQUEOUS PROCESSING STUDIES

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

In the current process for uranium recovery from fuel elements containing large percentages of zirconium, extraction capacity is limited by the amount of zirconium contained in the solvent extraction feed. The presence of zirconium also governs the volume of liquid waste which must be stored permanently. In addition, use of hydrofluoric acid as a dissolvent requires the introduction into the dissolver product of gross quantities of aluminum nitrate to complex the fluoride ion, in order to obtain stable, non-corrosive solutions with good uranium extraction properties.

Removal from the dissolver product of both zirconium and fluoride can serve to increase extraction capacity, decrease liquid waste volume, and minimize requirements for aluminum nitrate addition. Precipitation is one head-end method for accomplishing such removal. After precipitation of zirconium and fluoride by appropriate reagent addition the slurry is filtered and the precipitate washed to remove carried uranium. The filtrate and washes are combined and concentrated to suitable conditions for extraction feed, resulting in a volume very much less than that of the original dissolver solution.

Studies on the use of barium nitrate as a precipitant (to form barium fluozirconate) have continued, with results being reported on the effects of potassium fluoride and hydrofluoric acid as precipitation aids. Further results on the use of sodium formate as a precipitant are also reported, with emphasis on (1) the effects of the mole ratios of fluoride, zirconium, and sodium formate on the completeness of precipitation, and (2) the recovery of uranium from the filtrates and wash solutions by boildown and extraction.

Zirconium dibutylphosphate, a compound formed from zirconium in solution and dibutylphosphoric acid resulting from decomposition of TBP (tributylphosphate), is known to affect extraction column performance adversely and to form precipitates which can impair the function of moving mechanical parts. In order to study the behavior of zirconium dibutylphosphate under conditions in which uranium is stripped from the organic phase and tributylphosphate is stripped from the resulting aqueous phase, a quantity of the compound was prepared and characterized, and its solubility in Amsco was determined.

Study of the optical properties of uranium and iron in second and third cycle extraction raffinates indicates the possibility of development of an in-line instrument for detection of uranium in these waste streams. Effects of ferrous and ferric iron on uranium detection are discussed.

Uranium distribution data were determined for possible conditions existing in a stripping column in case of various kinds of process maloperation, in order to review the nuclear safety in the light of abnormal uranium concentrations. Distribution curves are presented for a 3.25% TBP-Amsco solution carrying uranium in contact with acid stripping solutions varying from 0.01M to 0.6M nitric acid.

1. AQUEOUS ZIRCONIUM FUEL PROCESSING

1.1 Barium Fluozirconate Precipitation Process (J. W. Coddington, Problem Leader; B. E. Paige)

Further studies of the precipitation of zirconium from zirconium-hydrofluoric acid dissolver product solutions have been made in an attempt to minimize the quantity of barium reagent and the concentration of residual acid required without decreasing the removal of zirconium. The precipitant solution used was barium nitrate and barium hydroxide at 22°C.

1.11 Effect of Potassium Fluoride or Intermittent Hydrofluoric Acid Addition. The addition of potassium fluoride in various combinations with barium solution produced essentially complete zirconium removal without increasing the hydrogen ion concentration; however, uranium losses, initially 2 to 5%, were not reduced to acceptable levels by washing. Excess oxidant added just prior to precipitation to prevent possible precipitation of potassium fluouranates did not decrease the uranium loss. According to X-ray diffraction analysis, the unidentified crystalline species produced by the addition of 12M potassium fluoride to the dissolver product did not match existing ASTM data for either potassium fluozirconates or potassium fluouranates. Studies of potassium fluoride addition for improved zirconium removal have been discontinued because of the high uranium losses. Uranium losses of only 0.1 to 0.2% are achieved by other barium fluozirconate precipitation techniques [1].

In dissolver product solutions containing 5 moles of fluoride per mole of zirconium, the fluoride/zirconium ratio in the supernate decreases continuously with the addition of increasing proportions of barium. Based on this fact, the addition of hydrofluoric acid at various stages during the additions of barium precipitant was investigated extensively. No improvement in zirconium removal was obtained by this technique; the degree of zirconium removal was shown to depend on the total moles of barium and fluoride in the system and not upon the order in which they were added.

1.12 Boil-down Studies. Supernates from three precipitations using barium solution with added hydrofluoric acid were evaporated in Teflon beakers 15 to 20% of the original dissolver product volume to determine the effect of the additional acid on further zirconium removal. In the first case, one mole of barium per mole of zirconium had been used as the precipitant, yielding a fluoride/zirconium mole ratio of 5; in the second, one mole of barium and one-half mole of fluoride per mole of zirconium were used, yielding a fluoride/zirconium mole ratio of 5.5; in the last case, one mole of barium and one mole of fluoride per mole of zirconium were added, yielding a mole ratio of 6. The additional hydrofluoric acid increased the zirconium removal during the boil-down and improved the filtering characteristics of the precipitate. However, in the last supernate, the acid concentration of the evaporator product was 7M after boil-down, which is too high for direct use in the extraction cycle. The second supernate, after concentration, gave the best over-all results. Ten percent of the zirconium was removed during the evaporation step resulting in a total zirconium removal of 95%. The addition of aluminum prior to boil-down, for corrosion inhibition, decreases zirconium removal suggesting that the minimum quantity of aluminum necessary should be established by additional studies.

1.2 Zirconium Precipitation with Sodium Formate (J. W. Coddington, Problem Leader; B. J. Newby)

The addition of sodium formate to zirconium-hydrofluoric acid process solutions under favorable conditions removes greater than 97% of the zirconium and fluoride as a precipitate [1, 2]. A removal of 91% can be accomplished from process solutions having a fluoride/zirconium mole ratio as high as 6. Uranium loss is of the order of 0.2% provided uranium is in the hexavalent state and the precipitate is properly washed. The volume of filtrate and wash solution can be reduced by evaporation to 20% of the volume of the original dissolver solution without the formation of a thick slurry; it can be reduced to 33% of the volume of the original dissolver solution with no solid formation at all. Providing the evaporations are done in the presence of sufficient nitric acid, uranium can be adequately removed by TBP extraction.

1.21 Effect of Fluoride and Zirconium Concentrations in the Dissolver Solution. Since the fluoride/zirconium mole ratio of dissolver solutions may vary, experiments were performed to determine whether an increase in this ratio would reduce zirconium and fluoride removal. Removal was decreased from about 97 to 91% as the fluoride/zirconium mole ratio was increased from 5 to 6 (see Table I). Increasing the fluoride/zirconium mole ratio also resulted in a precipitate with higher fluoride/zirconium and sodium/zirconium mole ratios even though the sodium formate concentration was held constant.

1.22 Wash Solution Studies. A study was conducted to determine the smallest volume of wash solution necessary for effective uranium removal from precipitates. These experiments were done both with and without the aid, during precipitation, of 6 ml of 0.1% flocculating agent (General Mill's Galactasol CAM). Precipitations were carried out at 60°C using 50 ml of dissolver solution (0.03M in chromic acid) and 50 ml of precipitant solution

TABLE I

EFFECT OF FLUORIDE/ZIRCONIUM MOLE RATIO IN DISSOLVER SOLUTIONS ON THE SODIUM FORMATE PRECIPITATION PROCESS

Conditions: Two moles of sodium formate added per mole of zirconium present; precipitation temperature = 60°C; dissolver solution composition = 1.6M Zr, 0.03M Cr⁺⁶, 3.7 g/1U; F varied by HF addition; precipitate washed 4 times with a volume of 0.1M NaNO₃ equal to 1/2 the dissolver solution volume used.

F/Zr Mole Ratio of Dissolver Solution	Precipitate Composition		% Zr loss to Filtrate	% F loss to Filtrate
	F/Zr Mole Ratio	Na/Zr Mole Ratio		
5.0	5.0	1.5	2.7	<3.0
5.5	5.2	2.1	5.4	5.8
6.0	5.7	2.4	6.9	9.0

containing 10.7 g of sodium formate. Wash solutions studied were 0.1M solutions of nitric acid, formic acid, sodium formate, and sodium nitrate. Uranium analyses of the liquid and solid phases, which were obtained when nitric acid was used to wash a precipitate formed without the aid of a flocculating agent, are plotted as the equilibrium curve in Figure 1. In the calculation of the operating line, the total weight of precipitate was corrected for the weight of the individual samples removed for analysis. The uranium loss, ie, retention of uranium in the precipitate, was about 2.4% with one wash equal in volume to one-half of the original dissolver solution. At the end of four such washes, the loss had decreased to about 0.2%, and the washing approached the limit of effectiveness as shown by the equilibrium curve.

Curves obtained with the other wash solutions, used on precipitates formed both with and without the aid of Galactasol CAM, were very similar. However, using either of the sodium washes results in about a 2% zirconium loss to the wash solution; the use of the acid washes resulted in an even higher loss.

Fig. 1 Uranium equilibrium curve for precipitate washings. Precipitate: 16 g from 50 ml of dissolver solution. Washes: 25 ml each using 0.1M HNO_3 at 22°C. Precipitate treatment: Filtered and dried at 105°C for analysis.

1.23 Effect of Sodium Formate Concentration. Previous studies [2] showed that a sodium formate/zirconium mole ratio of 2 was sufficient adequately to remove zirconium, while a ratio of 1 was not. The mole ratio range between 1 and 2 has now been investigated. Precipitations were done at 60°C in determining how zirconium removal from zirconium-uranium dissolver solutions (0.03M in chromic acid) was affected by varying the sodium formate/zirconium mole ratio from 1.5 to 2.0. The resulting precipitate compositions were also noted. Table II indicates that a sodium formate/zirconium mole rate of 2 is necessary for the most effective zirconium removal. In all cases, the sodium/zirconium mole ratio in the precipitate is about 1.5 and the fluoride/zirconium ratio is about 5.

1.24 Corrosion during Precipitation. Tests were performed to determine the corrosion resistance at 60°C of unwelded coupons of stainless steel 316 (extra low carbon), Carpenter-20, Monel and Hastelloy F, in two different systems: (1) slurries produced between dissolver solutions (0.03M in chromic acid) and sodium formate (both with and without flocculating agents) and (2), dissolver solutions which were 0.03M in chromic acid. These media should bracket all conditions found during precipitation. The expected corrosion rates for precipitation-vessel materials should be between that found using the slurry to which all precipitant had been added and that found using the solution prior to precipitant addition.

Sodium formate was added as an 8-molar solution; 2 moles were added per mole of zirconium present. The flocculating agent used was Stein Hall's Jaguar at a concentration of 6 ml of 0.1% Jaguar for every 50 ml of dissolver solution. Tests lasted 48 hr and coupons of each material were suspended within, at the surface, and above the solution. Monel was tested

in an inert atmosphere of nitrogen. Table III shows that all of these materials except Monel could be used in the construction of a precipitation vessel.

TABLE II
EFFECT OF SODIUM FORMATE CONCENTRATION ON THE
SODIUM FORMATE PRECIPITATION PROCESS

Conditions: Precipitation temperature = 60°C; dissolver solution composition = 1.6M Zr, 1.6M H⁺, 0.03M Cr⁺⁶, 3/7 g/l U, and 8.0M F⁻; precipitate washed 4 times, each with a volume of 0.1M NaNO₃ equal to 1/2 the dissolver solution volume used.

Moles of Sodium Formate Per Mole of Zr	Precipitate Composition		% Zr Removed from Filtrate
	Na / Zr Mole Ratio	F / Zr Mole Ratio	
1.5	1.5	5.1	89.6
1.6	1.6	5.1	92.6
1.7	1.6	5.4	95.8
1.8	1.5	5.0	96.2
1.9	1.5	4.9	97.1
2.0	1.5	4.9	97.4

TABLE III
CORROSION DURING THE PRECIPITATION OF ZIRCONIUM AND
FLUORIDE WITH SODIUM FORMATE

Conditions: Temperature = 60°C; 2 moles of sodium formate per mole of Zr; dissolver solution composition = 1.6M Zr, 1.6M H⁺, 8M F, 0.03M chromic acid, 3.7 g/l U; flocculating agent = 6 ml of 1% Stein Hall's Jaguar per 50 ml of dissolver solution; length of test = 48 hrs.

Construction Material (unwelded)	Corrosion in Slurry Containing Flocculating Agent (mils/mo)			Corrosion in Slurry without Flocculating Agent (mils/mo)			Corrosion in Dissolver Soln which is 0.03M Chromic Acid (mils/mo)		
	liquid	interface	vapor	liquid	interface	vapor	liquid	interface	vapor
Stainless Steel 316 (ELC)	0.03	nil	nil	nil	nil	nil	0.79	2.1	1.6
Monel	2.5	0.99	0.18	9.1	4.3	0.42	25 (a)	5.8	nil
Hastelloy F	0.03	0.04	0.02	0.07	0.08	0.07	0.52	0.63	0.32
Carpenter-20	nil	nil	nil	nil	nil	nil	0.53	0.33	0.24

(a) Pitted

1.25 Recovery of Uranium from Concentrated Filtrate and Wash Solutions. Preliminary boil-down and extraction experiments showed that uranium could not be extracted from the boiled-down filtrate and wash solutions with 10% TBP in Amsco. However, when the evaporations were done in the presence of nitric acid, extraction of uranium was accomplished easily. If sodium nitrate was substituted for nitric acid in the boil-downs, uranium was again difficult to extract. It was also noted that the presence of higher nitric acid concentrations in boil-downs resulted in an ability to concentrate to smaller volumes without the appearance of solids.

Using this information, studies have been directed toward the preparation of two different boil-down and extraction flowsheets. In one flowsheet the evaporation of filtrate plus wash solution is performed in the presence of the minimum concentration of acid. This will result in a boiled-down solution having good extraction characteristics. Concentration by boiling is carried to the smallest volume possible without formation of thick slurry; the solid is removed by filtration, then stabilizing, salting, and fluoride complexing agents are added. Such a flowsheet yields an extraction feed containing only a small amount of aluminum and practically no zirconium or fluoride, but requires two filtration steps. In the other flowsheet the boil-down is performed in the presence of enough nitric acid to prohibit precipitate formation and to yield a four molar acid product in the smallest possible volume. Aluminum nitrate can be added either before or after the boil-down. This latter flowsheet, with one filtration step eliminated, results in a higher concentration of aluminum nitrate, fluoride and zirconium, in addition to an extraction feed of greater volume.

1.26 Boil-Down with Solid Formation, Followed by Extraction. The volume of solution resulting from sodium formate precipitation of dissolver solution followed by evaporation of the filtrates and washes can be reduced to 20% of the original dissolver solution volume without the formation of a thick slurry.

Several experiments were performed to determine the amount of nitric acid in the boil-down which would lead to low fluoride and zirconium supernate concentrations, and also to uranium distribution coefficients of greater than 10 when the filtrate was contacted with 10% TBP in Amsco. In these experiments 50 ml of 3.2M sodium formate were added, at 60°C, to 50 ml of dissolver solution which was 0.03M in chromic acid. The slurry was stirred for about 1/2 hr at 60°C and filtered. Each precipitate was washed 4 times with 25 ml of either 0.1M sodium nitrate or nitric acid, and the wash solutions and filtrate were then combined. Various amounts of 15.7M nitric acid were added and the resulting solution boiled down to 10 ml and filtered. Some of these filtrates were extracted with no further treatment. In some cases, nitric acid and aluminum nitrate or aluminum nitrate alone were added prior to TBP extraction.

The addition of 4.6 ml of concentrated nitric acid prior to boil-down results in a 0.5M nitric acid solution that, when evaporated to the appropriate volume and filtered, yields a filtrate containing almost no zirconium and fluoride ions and from which uranium can be effectively extracted with TBP (See Table IV). However, addition of varying amounts of aluminum nitrate or aluminum nitrate and nitric acid is required to stabilize the solution. Making the solution 0.45M in aluminum nitrate or 1.6M in nitric acid and 0.045M in aluminum nitrate serves to stabilize it and provide good extraction

TABLE IV

BOIL-DOWN AND EXTRACTION CHARACTERISTICS OF FILTRATES PRODUCED DURING PRECIPITATION BY SODIUM FORMATE FOLLOWED BY A 0.1M NITRIC ACID OR SODIUM NITRATE WASH

Conditions: Precipitate was formed by adding 50 ml of 3.2M sodium formate solution to 50 ml of dissolver solution (0.03M in chromic acid) with stirring for 1/2 hr at 60°C; 16 g of sodium formate precipitate were washed 4 times with 25 ml of 0.1M NaNO₃; HNO₃ was added to the combined 80 ml of filtrate and 100 ml of wash solution and the resulting solution boiled down to 10 ml.

Wash Soln Used	ML of 15.7M HNO ₃ Added Prior to Boil-down	Reagents Added to 10 ml of Boil-down Product	Analysis of Boil-down Product after Reagent Addition				48-hr Stability of Boil-down Product	Extraction of Boil-down Product with 10% TBP in Amsco		
			Zr (M)	H ⁺ (M)	F ⁻ (M)	Na ⁺ (M)		U in Aqueous (g/l)	U in Organic (g/l)	E _g
HNO ₃	2.8	none	0.023	0.76	--	--	unstable	2.97	12.21	4.1
HNO ₃	4.1	none	0.021	0.46	--	--	unstable	1.01	12.55	12.4
HNO ₃	4.1	0.2 ml of 2.26M Al(NO ₃) ₃	0.007	0.62	<0.10	2.7	unstable	4.14	10.84	2.6
HNO ₃	5.5	none	0.20	0.63	--	--	unstable	0.66	11.97	18
HNO ₃	6.8	none	0.17	1.10	--	--	unstable	0.49	12.28	25
HNO ₃	8.1	none	0.16	1.81	--	--	unstable	0.42	9.50	23
HNO ₃	10.5	none	0.23	4.3	--	--	unstable	1.68	13.97	8.3
NaNO ₃	4.6	none	0.021	0.46	--	--	unstable	1.01	12.55	12.4
NaNO ₃	4.6	0.2 ml of 2.26M Al(NO ₃) ₃	0.005	0.69	<0.10	3.2	stable	4.24	10.40	2.5
NaNO ₃	4.6	0.05 ml of 2.26M Al(NO ₃) ₃	---	---	--	--	unstable	--	--	--
NaNO ₃	4.6	1 ml of 2.26M Al(NO ₃) ₃	<0.005	0.81	<0.10	--	unstable	2.03	11.69	5.8
NaNO ₃	4.6	2 ml of 2.26M Al(NO ₃) ₃	---	0.56	--	--	stable	0.92	9.27	10
NaNO ₃	4.6	3 ml of 2.26M Al(NO ₃) ₃	---	0.38	--	--	stable	0.22	10.16	46
NaNO ₃	4.6	4 ml of 2.26M Al(NO ₃) ₃	---	0.29	--	--	stable	0.20	8.75	44
NaNO ₃	4.6	0.2 ml of 2.26M Al(NO ₃) ₃ + 1 ml 15.7M HNO ₃	---	0.77	--	--	stable	0.33	11.71	35
NaNO ₃	4.6	0.2 ml of 2.26M Al(NO ₃) ₃ + 2 ml 15.7M HNO ₃	---	1.36	--	--	stable	0.34	10.84	32

characteristics. The combination of aluminum nitrate and nitric acid is preferable since it adds less non-volatile material to the system. Use of sodium nitrate as a washing solution is preferred over nitric acid; its use results in less solids formation during evaporation and still yields small zirconium and fluoride concentrations in the resulting supernate.

1.27 Boil-down without Solid Formation, Followed by Extraction. During the boil-down experiments described in Table IV, it was observed that the allowable concentration factor, before the onset of solids formation, increased with increasing nitric acid addition. Accordingly some experiments were done to study boil-down conditions leading to stable evaporator products in which no solids formed. Precipitation conditions were as described above; 11.4 ml of 15.7M nitric acid were added to the supernate before boil-down. Varying amounts of aluminum nitrate were also added, either before or after concentration.

The smallest stable boil-down volumes occurred when the addition of aluminum nitrate was made after evaporation and when a flocculating agent (Jaguar) was used during the precipitation. In experiments using 0.1M nitric acid as wash solution, slightly smaller stabilized volumes could be obtained than when 0.1M sodium nitrate was used under the same conditions. Optimum results were obtained for an evaporator feed composed of the following: 80 ml of filtrate containing a flocculating agent (Jaguar); 100 ml of 0.1M nitric acid washes; and 11.4 ml of 15.7M nitric acid. After concentration of such a solution, the addition of 8 ml of 2.26M aluminum nitrate before cooling produces an extraction feed of the following composition: $\text{Zr} = 0.25\text{M}$, $\text{F}^- = 1.0\text{M}$, $\text{H}^+ = 2.2\text{M}$, $\text{Na}^+ = 3.1\text{M}$, $\text{Al}^{+++} = 1.0\text{M}$, and $\text{U} = 8 \text{ g/l}$. Such a solution is stable for at least two weeks; a uranium extraction coefficient of 27 was achieved when it was contacted with 10% TBP in Amsco. This method of boil-down avoids any solids formation during the evaporation step, at the expense of a greater extraction volume.

2. GENERAL AQUEOUS STUDIES

2.1 Dibutylphosphate Chemistry (E. M. Vander Wall, Problem Leader)

The primary decomposition product of tributylphosphate is dibutylphosphoric acid (HDBP). The disposition of DBP 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 equipment parts. Of immediate interest is the behavior of zirconium dibutylphosphate under conditions in which uranium is stripped from the organic phase and tributylphosphate is stripped from the resultant aqueous phase. Preparation and characterization of zirconium dibutylphosphate is reported. The solubility in Amsco was found to be similar to that of the uranium compound reported earlier [1].

2.11 Preparation and Thermal Stability of Zirconium Nitrate Dibutylphosphate. $\text{Zr}(\text{NO}_3)_2[(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2]_2$ Attempts to prepare pure zirconium nitrate dibutylphosphate by addition of HDBP-acetone solution to a zirconium nitrate-nitric acid solution were not successful [1]. Removal of the reagents from the product was difficult and incomplete. As an alternative, this compound

was prepared by the decomposition of TBP in the presence of zirconium nitrate and nitric acid [3]. A solution which was 0.068M TBP, 0.062M Zr and 3.69M HNO₃ was refluxed for 30 hr. The solid which formed was washed with water, then air dried, and finally dried over P₂O₅ for a few days. An analysis of the product gave the following results: 14.79% Zr, 29.84% C, 5.58% H, 3.88% N, 10.00% P and 35.91% O by difference. The theoretical element analysis for the compound Zr(NO₃)₂[(C₄H₉O)₂PO₂]₂ is as follows: 14.40% Zr, 30.32% C, 5.73% H, 4.42% N, 9.78% P and 35.35% O.

The thermal stability of this compound was investigated using a Chevenard thermobalance. A typical thermal decomposition curve is given in Figure 2. The average heating rate was 2.7°C/min. Decomposition became noticeable at approximately 165°C, and very rapid above 210°C. There was a definite break in the curve between approximately 230 and 255°C, then another region of rapid decomposition between 260 and 280°C followed by a gradual decrease in decomposition rate until constant weight was achieved between 600 and 700°C. On the basis of the curve it appears that removal of the organic material occurs first, followed by the loss of nitrate. No analysis of intermediate products has been obtained; the final product is zirconium pyrophosphate.

2.12 Solubility of Zirconium Nitrate Dibutylphosphate in Amsco. The solubility of zirconium nitrate dibutylphosphate prepared by the decomposition of TBP in a zirconium nitrate-nitric acid solution was found to be $(2 \pm 1) \times 10^{-5}$ M at 25°C. The solubility was determined by igniting the evaporated zirconium pyrophosphate. This value is considerably less than that previously reported, $(7.9 \pm 0.1) \times 10^{-3}$ [1]. However, the material used in the original determination was impure and may have contained some acetone which could enhance the solubility considerably. The value $(2 \pm 1) \times 10^{-5}$ M is comparable to the solubility of uranyl dibutylphosphate in Amsco 125-90W [1].

2.2 Spectral Properties of 3rd Cycle Raffinate Solutions (J. W. Coddling, Problem Leader; R. D. Cannon)

The optical properties of uranium and iron in a synthetic second or third cycle raffinate were examined for use in the design of an in-line instrument for uranium detection. The process stream of interest, which may contain uranium as an extraction loss, contains 1.5M Al(NO₃)₃, 0.36M NH₄NO₃, 0.08M

Fig. 2 Thermal decomposition of Zr(NO₃)₂[(C₄H₉O)₂PO₂]₂.

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HSO_3NH_2 and 0.04M $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ and is 0.20M acid deficient. Measurements on synthetic raffinates of this type in the spectral region near $415\text{ m}\mu$ showed absorption only for uranium and iron. The measured molar extinction coefficient at $415\text{ m}\mu$ (ϵ_{415}) was 15 for uranium and 0.8 for ferrous iron. The extinction coefficient for ferric iron in this solution, however, can be as high as 300 depending on the acid deficiency of the system.

Colorless components of the system affect the optical properties of ferric iron. For example, the ϵ_{415} ranged from 17 to 40 in a series of synthetic solutions in which 0.04M ferrous iron (the amount normally present) was replaced by 0.001M ferric iron and the acid deficiency was varied from 0 to 0.3 NB . The concentration of sulfamic acid was 80 times that of iron in this system. A series of solutions was therefore prepared in which the sulfamic acid concentration was lowered to 2 times that of the iron. Under these conditions the value for ferric ϵ_{415} increased to as much as 100 in some cases. In solutions with constant pH (1.75), and 0.5, 1.0, and 1.5M aluminum, ϵ_{415} for ferric iron was 180, 25, and 15, respectively. These observations indicate the complexity of the chemical system.

An instrument with a very narrow pass filter will be affected only slightly by the normal flowsheet quantities of ferrous iron, since ϵ_{415} for uranium is a factor of 20 greater than for iron. The absorbance of ferrous iron increases rapidly below $400\text{ m}\mu$, however, and it will probably interfere with the measurement of uranium in this shorter wave length spectral region. Ferric iron has such a high ϵ_{415} (as much as 20 times that of uranium) that its presence in even small quantities could not be tolerated in the process stream.

In spite of the problems created by the possible presence of ferric iron in the process raffinates, the operation of an instrument of the type considered appears possible because stability studies indicate very little, if any, oxidation of ferrous iron to ferric iron in a normal raffinate environment. Synthetic solutions of flowsheet composition were observed over a four week period. Although the samples were in equilibrium with air, no darkening due to the appearance of ferric iron was noted at the end of this time. Samples containing no sulfamic acid showed a slight increase in optical density near the end of the period.

The apparent resistance to oxidation and the low molar extinction coefficient of ferrous iron indicate that the chemical problems due to the reagent iron should not be encountered in this system. Corrosion of stainless steel is the only apparent source of ferric iron in this system under normal operating conditions.

2.3 C-column Distribution Data (J. W. Coddling, Problem Leader; B. J. Newby)

During a study of nuclear safety in plant operation, the CPP Engineering Safeguard Committee considered the possibility of abnormal uranium concentrations occurring in the first cycle stripping column due to various kinds of process maloperation. Uranium distribution data in a strip column environment were required for an analysis of this problem; therefore laboratory data were taken for the distribution of uranium under stripping conditions. The organic phase was 3.25% TBP in Amsco, and the aqueous phase was uranyl nitrate in nitric acid. The data are shown in Figure 3. A number of the measurements were made at an aqueous acidity of 0.01M , since this establishes a "base line" for the system, ie, the equilibrium line for the case where acid

Fig. 3 Uranium X-Y diagram—IC system.

enters the column via the strip stream only. Further measurements were made at higher aqueous acidities to determine the effect of increased acid on column operation.

The values for uranium equilibria formed the basis for a study of the column system under abnormal operating conditions. The approach used was the McCabe-Thiele-type X-Y diagram method as outlined in KAPL-1543 [4],

Fig. 4 Effect of ICX flow and IBP acidity on uranium concentration in ICP.

Three conditions of column operation were chosen for examination, each involving normal organic feed flow with a gradual loss of strip flow. Condition I is for zero acid in the organic feed stream, such as would occur if fuel dissolution was carried to a zero acid product. Condition II considers normal organic feed acidity (0.013M). Condition III indicates the effect of a relatively large acid increase in the organic feed as might occur if the ammonium hydroxide were not added to the scrub. It was assumed that the stripping column is equivalent to three equilibrium stages for all conditions examined. The results of this study are shown in Figure 4. The "worst case" with respect to high strip column product uranium concentration occurs when organic feed acidity is zero, in which case the uranium concentration in the effluent stream can

be as high as 68 g/l. Increasing the acidity lowers the product uranium concentration, but a corresponding uranium waste loss occurs.

For various abnormal conditions, the aqueous phase within the column will have a higher uranium concentration than the column product. This occurs when the column is in reflux. No situation was found where this in-column uranium concentration exceeded 68 g/l, if the three-stage assumption is valid. However, the effect of lower HETS was considered, and this condition could lead to in-column concentrations as high as about 80 g/l.

III. 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)

Pilot plant studies of the fluidized bed calcination process for reduction of radioactive liquid wastes to the more-easily-stored solid form have continued. The studies are conducted in the two-foot-square calciner with production, for the first time over a prolonged period of continuous operation, of alpha alumina-free product from a feed containing substantial sodium. Sodium has been considered a promoter of alpha alumina growth, and no explanation of its lack of effect in this case has been developed. Intra-particle porosities ranging from 0.04 to 0.60 were obtained, emphasizing the effect of bed temperature, (primarily) and feed concentration, (secondarily) on this property. Low temperatures and low feed concentrations favor low product porosity. Test of a single-fluid nozzle indicated severe erosion or corrosion of the orifice and production of a considerable amount of caked solids, even with the accompanying use of jet grinders to control average particle size.

Laboratory investigation of the conversion of amorphous alumina to alpha alumina, being conducted in an effort to find ways to inhibit formation of the friable alpha form, has demonstrated differences in alpha-forming tendency of amorphous aluminas with varied calcination histories. Attempts at correlation with known variables in fluid bed calciner operation have not been successful. Further studies on the effect of sodium on the conversion confirm the positive, but quantitatively unpredictable, influence of the material.

In studies aimed at converting the fluoride content of STR-type wastes into a form which will resist volatilization during subsequent calcination of the material, rapid precipitation of the zirconium, fluoride, and aluminum was achieved by addition of calcium oxide as a slurry; the rapidity and completeness of the reaction indicate that a continuous precipitation step just prior to calcination might be feasible.

The second and third runs in the Demonstrational Waste Calcining Facility (DWCF) were conducted during this period. Run No. 3 continued for fifteen days and was shut down on a prearranged schedule to allow for additional planned modifications by construction forces. These runs were not intended to provide significant calcination information, but to provide operational experience and to point out areas, both expected and unexpected, of potential operating difficulty.

1. RESEARCH AND DEVELOPMENT IN THE PILOT PLANT

(E. S. Grimmer, Problem Leader; B. R. Wheeler, B. P. Brown, D. R. Evans, S. C. Hoff)

In continuing the development studies for the fluidized bed waste calcination process, three additional runs were completed in the two-foot square pilot plant calciner. Run No. 18 was made to study the effects of bed temperature

and aluminum concentration on the intra-particle porosity of calcined alumina. The primary objective of Run 19 was to obtain erosion data on an extended cone cap for a DWCF feed nozzle. In Run No. 20 a single-fluid liquid nozzle was used to introduce feed into the calciner bed. A summary of run conditions is given in Table V.

TABLE V
CALCINING CONDITIONS FOR RUNS 18, 19, AND 20
IN THE TWO-FOOT SQUARE PILOT PLANT CALCINER

Run No.	18	19	20
Starting Bed	Sand	Sand	Sand
Feed rate, 1/hr	90	90	40
Spraying Systems Nozzle No.	1/2 J	1/2 J	1/4 LN
Nozzle Air-to-liquid Volume Ratio	400	250 - 500	—
Bed Temperature (°C)	Var.	400	400
Superficial Fluidizing Velocity, ft/sec	1.0	1.0	1.0
Dry Fines Return from Primary Cyclone	Yes	Yes	Yes
Feed Composition			
Aluminum Nitrate, $\underline{M}$	Var.	1.29	1.29
Nitric Acid, $\underline{M}$	1.25	2.84	2.84
Sodium Nitrate, $\underline{M}$	0.089	0.078	0.000 (a)
Mercuric Nitrate, $\underline{M}$	0.006	0.015	0.015

(a) The actual sodium concentration was approximately 0.01M because the aluminum nitrate used in the feed preparation contains sodium nitrate as an impurity.

1.1 Porosity of Calcined Alumina

Results from earlier work [1] had shown that intra-particle porosities (Fraction Voids) ranging between 0.42 and 0.60 were obtained when calcining 1.3 to 1.95M aluminum nitrate feed solutions at bed temperatures of 400 to 500°C. The highest porosities were obtained at the higher aluminum nitrate concentrations or the higher bed temperatures. Run No. 18 was designed to explore the effect of a broadened range of these variables on intra-particle porosity. Bed temperatures were varied from 250 to 550°C and the aluminum nitrate molarities of the feed were varied from 0.8 to 1.95. The run was

divided into a series of 24-hr operating periods. Each run period was conducted at different bed temperature and feed concentration, and each started with a fresh bed of sand. One of the periods was extended for six days to produce a supply of low porosity alumina for special thermal conductivity tests.

Results of the run indicate that intra-particle porosities ranging between 0.04 and 0.60 can be obtained by an appropriate selection of bed temperature and feed aluminum concentration. The lowest porosity (0.04) was obtained when calcining a 1.80M aluminum nitrate solution at a bed temperature of 250°C. The highest porosity (0.60) was obtained when calcining 1.90M aluminum nitrate solution at a bed temperature of 500°C. As shown in Figure 5, higher

Fig. 5 Effect of aluminum feed concentration and bed temperature on the intraparticle porosity of alumina.

bed temperatures or aluminum nitrate concentrations produce a more porous product. Runs No. 19 and 20, which used bed temperatures of 400°C and aluminum nitrate molarities of 1.29, produced calcined product with porosity values from 0.36 to 0.46 and 0.39 to 0.47, respectively. These values are consistent with the results of Run No. 18.

1.2 Crystalline Structure of Calcined Alumina

X-ray diffractometry detected no alpha alumina in the product made during any of the 24-hr operating periods of Run No. 18. However, during the 6-day operating period, alpha alumina began to appear after 60 hr of operation and reached a value of 5% at the end of the 6-day period.

Gamma alumina was found in the product from the 6-day operating period of Run No. 18. No gamma alumina was detected in the product from the

24-hr operating periods; however, this does not mean that gamma alumina was entirely absent in the short runs, since the gamma pattern is blanketed by the X-ray pattern of sand.

No alpha alumina was found in the product of the nine-day Run No. 20 in which sodium was absent from the feed. Review of data from Runs No. 8, 9, and 10 reveals a similar occurrence, ie, when sodium was temporarily removed from the feed, the alpha alumina content of the product dropped to zero. This substantiates laboratory test data^[1] showing that sodium promotes the growth of the alpha alumina phase (See Section III, 2.1 of this report). No alpha alumina was found in the product of Run No. 19; interestingly, this run represents the longest period of continuous operation to date (10 days) in which sodium has been included in the feed and no alpha alumina has been formed. Apparently, other factors also affect the alpha alumina growth.

Two samples of the alumina obtained from Run No. 18 were heated at 1020°C for 200 hr to determine the effects of high temperature storage on the calcine properties. Table VI lists the properties of these samples before and after heat treatment.

It is evident that prolonged heating of the calcined product produces the alpha alumina phase. The bulk of the residual nitrate is driven off, leaving a more porous product. A completely valid reason cannot be given for the loss of sodium. Trace amounts of crystalline beta-sodium alumina were found by X-ray diffractometry after the heating period.

TABLE VI
COMPARISON OF PHYSICAL CHARACTERISTICS OF LOW POROSITY
ALUMINA BEFORE AND AFTER HEATING AT 1020° C
(Samples obtained from the bed at the end of the six-day
operating period of Run No. 18)

	<u>Sample 1</u>		<u>Sample 2</u>	
	<u>Initial</u>	<u>After Heating for 200 hr</u>	<u>Initial</u>	<u>After Heating for 200 hr</u>
Absolute density, g/cc	3.10	3.34	3.10	3.34
Particle density, g/cc	2.38	2.27	2.37	2.30
Bulk density (calculated), g/cc	1.41	1.34	1.40	1.36
Alpha alumina content, wt%	5	56	5	54
Nitrate content, Millimoles/gram	1.30	0.06	1.34	0.06
Intra-particle porosity, void fraction	0.23	0.32	0.24	0.31
Sodium, wt%	2.4	0.62	2.5	0.63

1.3 Nitrate Content of Calcined Alumina

The nitrate content of the amorphous alumina produced in Run No. 18 is shown in Figure 6 as a function of the bed temperature during calcination. As had been indicated in earlier studies [2], the nitrate content of the calcine is inversely related to the bed temperature.

Fig. 6 Effect of bed temperature on the nitrate content of alumina.

1.4 Feed Nozzle Performance

The erosion resistance of three flat-faced nozzle caps, each fabricated of a different material, was observed during Run No. 18. The amount of measured wear and other pertinent data are given in Table VII.

Run No. 19 was made to determine the performance of a Spraying Systems Co. type 1/2J feed nozzle with a re-designed 38° conical nozzle cap. A sketch of this nozzle cap is shown in Figure 7. The erosion rate measured for this cap during the 10-day run was roughly one

TABLE VII
NOZZLE CAP EROSION DURING RUN NO. 18

Cap Material	Hours in Operation	Measured Wear grams/year
Titanium	29	2.9
Type 347 ss	99	4.0
Type 440C ss	420	0.07

gram per year. This value must be compared to the erosion rates of 0.07 to 4 grams per year for flat-faced caps constructed of various materials and tested previously [1, 2, 5]. A similar but longer conical cap was used in Run No. 14, and from an erosion standpoint was found to be satisfactory. The various nozzle cap designs used on the Spraying Systems type 1/2J feed nozzle have been shown previously [2].

Fig. 7 Sketch of the 38° conical nozzle cap used on the Spraying Systems Company type 1/2J feed nozzle during Run No. 20.

In Run No. 20 a Spraying Systems Co. type 1/4LN No. 12, single-fluid, atomizing nozzle was used. At the completion of the 9-day run, the orifice of the single-fluid nozzle was found to be severely corroded or eroded. The feed orifice diameter had increased from 76 to 150 mils, and inspection of the feed nozzle indicated that some corrosion had taken place. Co-occurrence of erosion is speculative.

During the first five days of the run the mass median particle diameter increased from 0.3 to 0.8 mm. For the remainder of the run a jet grinder was used to control the mass-median particle diameter of the fluidized bed. The grinder consisted of five 1/8-inch ID orifices discharging horizontally into the fluidized bed just above the support plate. With proper adjustment of the air flow rate to the jet grinder, it was possible to maintain the mass-median particle diameter within a range of 0.4 to 0.6 mm. No wear around the orifices of the jet grinder was found at the end of the run. However, a considerable amount of caked solids was found in the bed. This was attributed to malfunction of the single-fluid nozzle as a result of the change in orifice geometry.

1.5 Service Test Corrosion Evaluation of the Two-Foot Square Waste Calciner Furnace (N. D. Stolica, Problem Leader; T. L. Hoffman)

Corrosion measurements were made on the liquid metal tube bundle in the oil-fired furnace associated with the 24-in. calciner. The bundle is made of type 316 stainless steel and has been in operation for 9,089 hr. As a result of this evaluation it was concluded that the rate of attack on the fired side of the tubes was low and that the bundle is suitable for continued use.

Liquid NaK (78% potassium - 22% sodium) is heated in a 316 stainless-steel bundle by an oil-fired furnace. During the period June 1958 through June 1961, the furnace was operated at 1000-1440°F for 6,359 hr, and at 200-999°F for 2,730 hr; a total of 9,089 hr use.

Visual examination of the 316 stainless-steel-metal bundle suggested that the alloy had suffered only minor corrosion damage. All tubes were coated with a porous, rather tenacious, non-uniform scale. Numerous pits, which were estimated to be less than 5 mils deep, were observed under the scale.

From micrometer measurements on 10 of the vertical connecting tubes, the over-all corrosion rate for 9,089 hr was 1.38 mils/month or 1.93 mils/month for the 6,359-hr service above 1000°F if one assumes that all the corrosion took place at the higher temperature.

The top and bottom 3.0 in. OD headers and 1.5 in. OD manifold tubes suffered maximum metal losses of 25 and 33 mils, respectively. These values represent over-all corrosion rates of about 2.0 mils/month and 2.6 mils/month during the 9,089 service hr, or 2.83 and 3.74 mils/month, respectively, if all attack occurred above 1000°F.

Accordingly, the remaining minimum tube wall thicknesses are: vertical connecting tubes, 92 mils; 3.0 in. OD headers, 163 mils; and 1.5 in. OD manifold tubes, 92 mils. The original wall thicknesses were 109 mils, 188 mils, and 125 mils, respectively.

Comparison of these data with a corrosion evaluation of the tube bundle after 6115-hr service [5] indicates a lower over-all rate of corrosion for

the extended period than that reported previously (2.0 mils/month for 6,115-hr total service).

2. LABORATORY INVESTIGATIONS

2.1 Calcination of Aluminum Nitrate Wastes (D. W. Rhodes, Problem Leader; R. F. Murray, D. R. Anderson)

The calcination of synthetic aluminum nitrate-nitric acid process waste solutions in a fluid bed calciner is known to produce both amorphous alumina and crystalline alumina species, such as alpha and gamma alumina, depending on the composition of the waste and the calcination conditions. Laboratory work was continued in an attempt to find calcination conditions which would minimize the amount of alpha alumina formation. The alpha alumina form (crystalline), undergoes severe attrition in a fluid bed calciner and results in excessive loading of alumina "fines" in the off-gas.

2.11 Experimental Methods and Equipment. The laboratory experiments consisted essentially of heating calcined alumina samples, which had been prepared and treated by various techniques, in a laboratory test unit for a specified time. The laboratory test unit consisted of a small tube containing 24 individual sample pots, each with a stainless steel wire-mesh bottom to support the solid sample and to expose the sample freely to the simulated calciner environment. The tube containing the sample pots was fitted into a larger tube in such a way that when the entire unit was placed inside of a combustion-tube furnace and nitric acid and air were introduced into the system, the decomposition products of the nitric acid were forced to pass through the sample holders. Samples were removed from the test unit periodically and subjected to X-ray diffraction to determine the crystal structure. This technique quantitatively identified alpha alumina in concentrations greater than 5% by weight when only alumina was present. However, in recent cold-pilot plant tests, using sand as the starting bed in the fluid bed calciner, determination of the amount of alpha alumina in the samples was somewhat more difficult. Emission spectroscopy was used to determine the concentration of added cationic materials such as sodium and potassium.

2.12 Experimental Results. The laboratory data indicated clearly that the conditions under which the aluminum nitrate was converted to amorphous aluminum oxide had a definite influence on the rate of conversion of amorphous alumina to alpha alumina in a calciner atmosphere. For example, alumina prepared in the laboratory by various methods, including thermal decomposition of aluminum nitrate in air and precipitation of hydrous aluminum oxide by ammonium hydroxide or sodium hydroxide, consistently failed to form alpha alumina when heated in the laboratory test unit. On the other hand, samples of amorphous alumina from two different runs in the cold-pilot plant calciner consistently formed about 65 and 10% alpha alumina, respectively, when heated in the laboratory test unit. Attempts at correlation of the marked difference in "alpha forming ability" of alumina prepared in different runs in the fluid bed calciner with specific calciner variables have not been successful. Differences in the rate of conversion of amorphous alumina to the alpha form during heating in the laboratory test unit are illustrated by comparing the laboratory and cold-pilot plant samples shown in Table VIII.

TABLE VIII
FORMATION OF ALPHA ALUMINA BY HEATING CALCINED
AMORPHOUS ALUMINA IN A LABORATORY TEST UNIT

Conditions: Heating temperature, 500°C; vapor feed to test unit: 510 l/h air at 5 psig, 0.2 l/h 6.8M HNO₃

Alumina Sample	Method of Preparation	Weight % Sodium	Weight Percent Alpha Alumina after Heating for the Indicated Number of Hours				
			0	5-10	18-22	90-95	140-165
IV-A	Pilot Plant Calciner, 400°C	2.3	~ 5	9	15	46	62
PB-2	Pilot Plant Calciner, 400°C	1.7	< 5	< 5	5	8	11
19-P-03-0830	Pilot Plant Calciner, 400°C	2.0	< 5	< 5	-	14	18
BB-2	Pilot Plant Calciner, 500°C	< 0.2	< 5	< 5	< 5	5	7
	Decomposed Al(NO ₃) ₃ ·9H ₂ O on a hot plate	< 0.2	< 5	< 5	< 5	< 5	< 5
NH ₄	NH ₄ OH Precipitation in Al(NO ₃) ₃ ·9H ₂ O Solution	< 0.2	< 5	< 5	< 5	< 5	< 5
20-PP-18-0430	Pilot plant calciner, 400°C using pressure nozzle	< 0.2	< 5	< 5	-	< 5	< 5

(a) Approximate value

Earlier work [1] established the fact that sodium was needed in the amorphous alumina to cause the formation of alpha alumina in the relatively low calcination temperature range of 400-500°C. Recent laboratory results indicated that the rate of change from amorphous alumina to alpha alumina during heating in a calciner atmosphere was different if solid sodium nitrate instead of a solution of sodium nitrate was added to the alumina. This effect is illustrated in Table IX.

The data in Table IX demonstrate that contacting the amorphous alumina with water or sodium nitrate solution prior to heating in the laboratory test unit definitely inhibited the formation of alpha alumina. This was true even though the 1M sodium nitrate solution actually resulted in a slight increase in the total sodium content. For example, contacting the IV-A sample, which contained 2.3% by weight of sodium, with water or sodium nitrate solution reduced the amount of alpha alumina formed during heating to about one-fourth of the value obtained without any pre-treatment.

Adding solid sodium nitrate to the PB-2 sample which contained 1.7% sodium and the BB-2 sample which did not contain sodium increased the amount of alpha alumina formed during heating by a factor of three to four. Thus, a positive effect of adding sodium is evident not only on a sample that was prepared originally without sodium but also on a sample which appeared to contain adequate sodium to effect the conversion to alpha alumina. For

TABLE IX

EFFECT OF PRETREATMENT WITH SODIUM NITRATE ON THE CONVERSION
OF AMORPHOUS ALUMINA TO ALPHA ALUMINA DURING HEATING
IN THE LABORATORY TEST UNIT

Conditions: Heating time, 164 hours; Heating Temperature, 500°C; Vapor feed
to test unit, 510 l/h at 5 psig, 0.2 l/h 6.8M HNO_3

Treatment Before Heating	IV-A $\% \alpha \text{Al}_2\text{O}_3$	Sample (a) PB-2 $\% \alpha \text{Al}_2\text{O}_3$	BB-2 $\% \alpha \text{Al}_2\text{O}_3$
None	62	11	7
Soaked in 1M NaNO_3	13	5	< 5
Soaked in 0.01M NaNO_3	16	< 5	< 5
0.1 g solid NaNO_3 added	50	35	30
Leached 3 times with water; then soaked in 1M NaNO_3	16	< 5	—
Leached 3 times with water; then soaked in 0.01M NaNO_3	13	< 5	—
Leached 3 times with water; then 0.1 g NaNO_3 added	25	< 5	—

(a) Sodium content of untreated sample given in Table VIII

reasons not yet established, the sodium that was already in the PB-2 sample was not effective in promoting the conversion to alpha alumina.

Sodium oxalate, potassium nitrate, and cesium nitrate also promoted the growth of alpha alumina, although to a lesser degree than sodium nitrate. Sodium sulfate was not effective in promoting growth of alpha alumina in the one experiment where it was used.

Laboratory data to date indicate the short residence time in the calciner and the removal of sodium from the calciner feed are the two most effective means of reducing the amount of alpha alumina formation in a fluid bed calciner. Neither of these approaches is very practicable for the calcination of stored process wastes in the ICPP fluid bed calciner although a better definition of the rate of formation of alpha alumina as a function of sodium concentration in the feed may show that some of the stored wastes are within the necessary limits. An attempt is currently being made to define these limits by preparing alumina under a variety of conditions in a small 2-in. laboratory calciner. An investigation will be made of the possibility of inhibiting the growth of alpha alumina by the use of additives in the calciner feed solution.

2.2 Preparation of Zirconium Fluoride Wastes for Calcination (D. W. Rhodes, Problem Leader; R. F. Murray, D. R. Anderson)

Laboratory investigations were continued on a precipitation-calcination method for the treatment of zirconium process wastes containing fluoride. The purpose of the precipitation step is to convert the fluoride to a compound or compounds that will retain the fluoride in the calcined product during calcination.

Previous experiments showed that calcium oxide added to a synthetic STR type waste precipitated the fluoride, if allowed to remain in contact with the solution for several hours. Studies conducted during this report period were aimed at determining the precipitation conditions which gave the most rapid precipitation of the fluoride. Conditions for rapid precipitation were found, indicating that it may be possible to design a continuous process in which precipitation occurs just prior to calcination, thus minimizing the need for slurry handling equipment.

2.21 Methods and Materials. The precipitation was carried out by adding calcium oxide to the synthetic waste contained in a beaker. A mechanical stirrer was used at a speed just fast enough (300 rpm) to prevent the precipitate from settling. The temperature was controlled by means of a water bath, hot plate, and a cooling coil through which a cooling liquid was passed on demand by a thermoregulator. Since the reaction of calcium oxide with the synthetic waste is exothermic, it was necessary to cool the system for the experiments conducted at 25°C. Samples of the slurry were removed periodically, centrifuged at 11,500 rpm, and the supernatant liquid was removed for analysis. The sampling times were measured from the first addition of the calcium oxide.

The synthetic zirconium fluoride waste was made up to approximate an STR type waste. The composition of the waste used in this set of experiments was: 0.48M Zr^{+4} , 0.51M Al^{+3} , 3.01M F^- , 1.64M NO_3^- and 1.00M H^+ . Calcium oxide was added in the chemical equivalent ratio, CaO/F , of 1.0 or 1.5. The calcium oxide was added either as a powder or as a water slurry (50 g CaO per 250 ml H_2O). Where the calcium oxide was added as a slurry the results were corrected back to the original solution volume.

2.22 Experimental Results. The results of the precipitation experiments are shown in Table X. It is obvious from these data that zirconium precipitated rapidly and completely under the conditions used. The aluminum remaining in solution at the shorter time intervals was nearly equivalent, chemically, to the amount of the fluoride. The aluminum and fluoride also precipitated in an amount chemically equivalent to each other, the total increasing with time; while the calcium concentration remained approximately constant or slightly increased. These data suggest that the precipitate is probably a mixture of hydrous oxides and fluo-hydroxy compounds of the metals together with some calcium fluoride. Positive identification of the compounds in the precipitate is not possible without a considerable amount of additional research effort.

The laboratory results definitely point out that a CaO/F ratio of 1.5, a temperature of 60°C and addition of the CaO as a slurry provided the best method for rapid precipitation of the fluoride. A secondary beneficial effect was the good dispersion and suspension of the precipitate obtained at 60°C. Good dispersion and suspension of the precipitate particles will simplify transport of the slurry from the precipitation vessel to the calciner.

TABLE X
PRECIPITATION OF FLUORIDE AND METAL IONS BY CALCIUM OXIDE
IN SYNTHETIC ZIRCONIUM FLUORIDE WASTE

Minutes After Addition of CaO	Conditions for Precipitation	Concentration in Supernatant Liquid, $\frac{M}{pH}$					
		F^{-}	Al^{+3}	Zr^{+4}	Ca^{+2}	NO_3^{-}	pH
(Run No. 1)							
15	CaO added as a solid $CaO/F = 1.0$ Temp 25°C	0.92	0.35	<0.01	0.94	1.48	3.25
30		0.32	0.14	<0.01	0.77	1.36	4.20
60		<0.10	0.04	<0.01	0.79	1.52	5.25
960		<0.10	0.04	<0.01	0.79	1.34	5.95
(Run No. 2)							
5	CaO added as a slurry $CaO/F = 1.0$ Temp 25°C	0.60	0.27	<0.01	0.66	1.05	4.15
15		0.34	0.13	<0.01	0.74	1.56	4.36
25		0.15	<0.06	<0.01	0.81	1.56	4.65
35		<0.01	<0.06	<0.01	0.89	1.65	5.02
45		<0.01	<0.06	<0.01	0.81	1.58	5.15
60		<0.01	<0.06	<0.01	1.23	1.65	5.35
(Run No. 3)							
5	CaO added as a slurry $CaO/F = 1.5$ Temp 60°C	<0.16	<0.06	<0.01	0.47	1.46	8.7
10		<0.16	<0.06	<0.01	0.68	1.48	8.0
15		<0.16	<0.06	<0.01	0.72	1.53	7.9
20		<0.16	<0.06	<0.01	0.72	1.50	7.8
25		<0.16	<0.06	<0.01	0.72	1.54	7.8
30		<0.16	<0.06	<0.01	0.72	1.56	7.8

The laboratory data indicate that a continuous precipitation just prior to the calcination step may be feasible, because the fluoride is precipitated rapidly. The success of the precipitation-calcination process will depend on how well the fluoride in the precipitate resists volatilization under calcination conditions. This phase of the process will be tested in a cold pilot plant fluid-bed calciner in the near future.

3. DEMONSTRATIONAL WASTE CALCINATION FACILITY (Section Chief, J. I. Stevens)

Program Planning and Correlation, B. M. Legler,
Problem Leader; G. E. Hohse

Technical Surveillance, L. T. Lakey, Problem Leader;
P. N. Kelly, J. L. Lockard, E. A. Travnicek

Two runs of the Demonstrational Waste Calcination Facility were completed this period. These runs (No. 2 and 3) were the first in which an aluminum nitrate feed solution and continuous product withdrawal were used. Starting conditions for both runs were (1) a feed rate of 60 GPH, (2) a bed temperature of 400°C, (3) a recycle rate of scrub solution to the feed of 20 GPH, (4) a nozzle air/liquid ratio of 300, and (5) a simulated-waste feed composition of 1.72M aluminum nitrate, 1.26M nitric acid, and 0.104M sodium nitrate.

Cold alumina produced in the two-foot square pilot-plant calciner was used for the starting bed of Run No. 2 which used a fluidizing velocity of 1.9 ft/sec and no product withdrawal. After five hours, feed was shut off because the transport air blower could not be started. The blower was finally started by lowering the calciner pressure and fluidizing velocity, which effectively reduced the blower discharge pressure. Fluidizing velocities for the remainder of Run No. 2 remained in the range of 1.5 to 1.6 ft/sec. A complete process shutdown occurred 22 hr later when the carbon bearings in the scrub circulation pump wore out and pump vibration became excessive. Process operation was resumed after installing (1) temporary piping to supply fresh water to the quench tower and venturi scrubber and (2) a temporary pump to transfer the scrub water from the quench surge drum to an outside disposal pit.

The final process shutdown was made when the off-gas filters were contacted by water. During the run the bed level dropped continually, thus uncovering the feed nozzles. In an effort to expand the bed and cover the nozzles, additional air was temporarily introduced into the calciner bed through a sparger, raising the fluidizing velocity to approximately 2.8 ft/sec. This apparently carried considerable water from the scrub system into the off-gas piping downstream of the venturi scrubber. Drains in the off-gas lines could not remove the rapid water accumulation and some water passed through the lines to contact the off-gas filters. The filters then disintegrated and blocked the strainers located in the suction lines of the off-gas blowers. Following shutdown of the process, inspection revealed plugs in the calciner cyclone and dip leg.

Prior to Run No. 3, new off-gas filters and blower suction screens were installed. A blast air line terminating below the cyclone dipleg outlet was installed for use in keeping the dipleg clear. All equipment was cleaned of caked solids and the solids storage bin was unloaded. Some of the material removed from the solids storage bin was used as a starting bed for Run No. 3. Air nozzle caps on two of the three feed nozzles were replaced, one by a cap coated with alumina and the other by a cap coated with boron carbide, in order to test the erosion resistance of different materials. Both surfaces were applied as flame coatings by the Plasmadyne Corporation of Santa Ana, California. One nozzle was left in place with its original titanium cap.

Plant operation was continuous during Run No. 3, with scheduled termination after fifteen days of operation. For the first ten days, off-gas scrubbing

was done with fresh water as had been done during the last phase of Run No. 2. During the last five days, a temporary pump circulated scrubbing solution to the quench tower and venturi scrubber. No significant changes in calciner product were noted while recycling 20 GPH of the scrub solution to the feed tanks. However, the total solids content of the scrub solution increased from 0. to nearly 30 wt% during this period. Simultaneously, the nitric acid concentration increased from ~0 molarity to 3.85 molarity. A sufficient amount of the alumina solids in the scrub solution dissolved to raise its aluminum concentration to 1.5M. While recirculating the scrub solution, it was possible to maintain the water balance, ie, no net gain or loss of water, by adjusting the venturi scrubber outlet temperature.

Calciner feed-rate control proved to be difficult; the rates reached 125 GPH or fell below 50 GPH. Because of this, temperatures in the calciner varied considerably ($\pm 75^{\circ}\text{C}$) from the control point, and consequently, control of the off-gas system temperatures was difficult to maintain. The nozzle air rate was reduced from an initial value of 1175 SCFH to a final value of 985 SCFH without any noticeable effects on the calcined product size. Solids losses with the calciner off-gases were excessive, resulting in a product recovery rate of only 40% of the equivalent solids entering with the feed. It is felt that a jet grinder action at the distribution plate may contribute to small bed particle size and resultant solid loss.

During the fifteen-day running period, the calcined product characteristics changed steadily. The bulk density increased from an initial value of 0.96 to a final value of 1.5 gm/ml. Over the period, the mass median particle diameter decreased from 0.4 to 0.2 mm while the alpha alumina content increased from 30 to 70%.

Post-run inspections revealed no evidence of solids caking in the calciner and no plugs in either the dipleg or primary cyclone. Evidence of moisture was found in the off-gas filters and aluminum nitrate crystals were found in the equipment vent system filter. The air side of the alumina-coated nozzle plugged completely after only 24 hr of operation, after which the spare titanium-capped feed nozzle was used. The alumina coating was found to have been broken in several segments and was completely separated from the base metal it was supposed to protect. The boron carbide coat on the other cap was intact, but had worn through exposing the base metal near the air orifice. The titanium cap, installed 6-in. higher than the two coated nozzle caps, showed little wear.

At the completion of Run No. 3, the facility was returned to construction forces for additional modifications, including a second NaK expansion tank, new quench circulation pumps, additional purge lines, and an off-gas sampling station.

IV. NEW WASTE TREATMENT METHODS

(Section Chief, D. W. Rhodes)

1. REMOVAL OF LONG-LIVED RADIOISOTOPES FROM SOLUTION

(M. W. Wilding)

Study of the removal of strontium from acidic waste solutions by adsorption on Amberlite 200 cation exchange resin was continued [1]. This investigation is part of a long-range waste treatment program to develop methods for separating the long-lived radioisotopes from the alloy metal ions and process chemicals. Results of the laboratory investigation indicated that salt cations at one molar concentration interfered seriously with the removal of strontium. For example, increasing the concentration of aluminum in solution from one-tenth molar to one molar decreased the amount of strontium adsorbed on a fixed bed column of the resin from about 126 to 2 column volumes. The laboratory results suggest that the concentration of aluminum in existing ICPP aluminum nitrate-nitric acid wastes probably will have to be reduced before efficient removal of strontium by ion exchange resins can be achieved.

1.1 Experimental Methods

Two approaches were used to study the effect of salt cations and acids on the removal of strontium from solution.

1.11 Equilibrium Experiments. One gram (dry weight) of resin was contacted with 20 ml of solution for 24 hr at 25°C. Carrier strontium was added to the solutions at approximately ICPP waste concentration (0.02 g/l) and Sr-85 was used as a tracer. The concentration of strontium in the liquid phase after 24 hr equilibration was determined with a well-type scintillation counter. Distribution coefficients were then calculated from the experimental data. The added salts were the nitrate salts of sodium, calcium, and aluminum. The acids used were sulfuric, hydrofluoric or hydrochloric acids.

1.12 Column Experiments. The feed solutions were passed through packed beds (7 ml) of Amberlite 200 ion exchange resin contained in a 0.7 cm diameter by 20 cm long glass tube. The solution was passed upflow at a constant rate of 25 gal/(ft²)(hr). The effluent was collected with an automatic fraction collector, and the concentration of strontium was determined with a well-type scintillation counter. The feed solutions contained aluminum nitrate and nitric acid at various concentrations and 0.02 g of strontium per liter traced with Sr-85. The solution temperature was 25°C.

1.2 Experimental Results

1.21 Equilibrium Experiments. The results of the equilibrium experiments are shown in Figures 8 through 15 with the distribution coefficient (K_d) plotted against acid concentration; the salt concentration is a parameter. Differences in distribution coefficients above 10^5 are not significant due to the low concentration of Sr-85 in the supernatant liquid.

A marked reduction in strontium removal is evident in Figures 8 through 15 at salt concentrations above 0.01M. The order of interference by the cations was $\text{Ca} > \text{Al} > \text{Na}$. This interference is considered to be due

Fig. 8 Effect of aluminum and sulfuric acid on strontium adsorption by Amberlite 200 resin.

Fig. 9 Effect of calcium and sulfuric acid on strontium adsorption by Amberlite 200 resin.

to competition by the relatively high concentration of sodium, calcium, and aluminum ions compared to strontium ions in the solution. A decreasing removal of strontium in acid concentrations above 0.01N is apparent although interference by hydrogen ions appears to be less important than interference by salt cations.

An attempt was made to reduce the interference of aluminum ions by adding complexing agents to the solutions prior to equilibration. The solutions used were 0.1M to 1.0M aluminum nitrate in 0.001N to 0.01N nitric acid. The complexing agents that were added to complex the aluminum were EDTA, potassium oxalate, oxalic acid, sulfosalicylic acid, citric acid, tartaric acid, sodium fluoride and a special decontaminating agent. No beneficial effect (increased strontium removal) was obtained by the addition of complexing agents. Apparently the complexing agents function effectively only in a less acidic system. Conversion of the aluminum nitrate to basic aluminum nitrate of the approximate composition $\text{Al}(\text{OH})(\text{NO}_3)_2$ did not improve the strontium removal.

1.22 Column Experiments. The results of the column experiments are shown in Figure 16. These results confirmed the equilibrium data, which indicated that high concentrations of salt ions interfered with the adsorption of strontium. For example, decreasing the concentration of aluminum nitrate in the feed solution from 0.1M to 0.01M, at 0.01M HNO_3 acidity, increased the column capacity ($C/C_0 = 0.5$) from about 125 to ~400 column volumes.

Fig. 10 Effect of sodium and sulfuric acid on strontium adsorption by Amberlite 200 resin.

Fig. 11 Effect of aluminum and hydrochloric acid on strontium adsorption by Amberlite 200 resin.

The laboratory data indicate that strontium can be removed from relatively acidic solutions without causing physical breakdown of the resin. However, the effectiveness of the ion exchange process for removing strontium from an aluminum nitrate-nitric acid process waste will be highly dependent on the concentration of aluminum. The concentration of aluminum nitrate in ICPP stored wastes, for example, is probably too high for removal of the strontium by ion exchange in Amberlite 200 resin without a pretreatment to reduce the concentration of aluminum in the solution.

Fig. 12 Effect of calcium and hydrochloric acid on strontium adsorption by Amberlite 200 resin.

Fig. 13 Effect of sodium and hydrochloric acid on strontium adsorption by Amberlite 200 resin.

Fig. 14 Effect of aluminum and hydrofluoric acid on strontium adsorption by Amberlite 200 resin.

Fig. 15 Effect of sodium and hydrofluoric acid on strontium adsorption by Amberlite 200 resin

Fig. 16 Breakthrough curve for strontium in an aluminum nitrate-nitric acid-Amberlite 200 resin system.

V. ELECTROLYTIC DISSOLUTION SYSTEMS

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

The operational behavior of an electrolytic dissolver is dependent upon the reactions which occur in the dissolver. A number of undesirable conditions (limiting current density, passivation, high polarization, and competing reactions resulting in low current efficiency) can be encountered. For efficient and convenient dissolver operation these effects should be avoided or minimized.

A study of the anodic potential-current density relationships during the electrolytic dissolution of type 304 stainless steel, undertaken to define optimum operating conditions, revealed that at a temperature of 60°C or higher, anode operation was practical over a wide range of solution compositions and at high current densities. Passivation, limiting current density, and gas evolution were avoided. Similar information on cathode operation remains to be determined before optimum electrolytic dissolver operating conditions can be specified.

A new technique in electrolytic dissolution, Series Electrolytic Dissolution, has been demonstrated at the ICPP. This eliminates the problem of fuel contact with an anode basket and the requirement for high-current, low-potential power sources. Metal to be dissolved is placed in a tubular dissolver through which an acid dissolving solution is passed; electrodes, not in direct contact with the metal, but immersed in the electrolyte, are located at the ends of the dissolver. A series of electrolytic cells is formed within the dissolver; one end of each fuel piece acts as a cathode, reducing nitric acid, while the other end acts as the anode, going into solution. Dissolution rates of 2.5 mg/cm²/min at current efficiencies of 1000% have been demonstrated for stainless steel. Using the same technique, aluminum can be dissolved to a basic nitrate solution, and zirconium can be oxidized to ZrO₂.

Additional corrosion tests on materials of construction for possible use in electrolytic dissolver systems indicate that titanium and niobium are resistant to corrosion in locations in an operating electrolytic dissolver where stainless steel was rapidly destroyed. Plastic specimens which had previously been shown to be resistant to the chemical environment in an electrolytic dissolver were exposed to gamma irradiation while immersed in dissolver solution; only polyethylene, in this group, adequately resisted the combined radiation and chemical conditions to warrant further testing as a possible insulating and supporting material for dissolver construction.

1. ELECTROLYTIC DISSOLUTION OF STAINLESS STEEL IN NITRIC ACID

1.1 Electrochemistry of the Dissolution. (J. R. Aylward, Problem Leader; E. M. Whitener)

For efficient and convenient electrolytic dissolver operation, the effects of limiting current density, passivation, high polarization and competing

reactions resulting in a low current efficiency, should be avoided or minimized. At the same time, acceptable operating temperatures (30°C to 80°C), current densities (0.1 to 2 amp/cm²), and product solution compositions (70 to 100 g/l of stainless steel and less than 3M H⁺), must be maintained.

The anodic potential-current density relationships for type 304 stainless steel were studied as a function of solution composition and temperature to (1) define the optimum operating conditions for electrolytic dissolution, and (2) to obtain a better understanding of the reactions taking place. Also, polarization data at very low current densities were obtained for use in predicting corrosion rates of the steel in highly oxidizing chromium (VI) solutions.

The general characteristics of the polarization curves are quite varied, showing regions of Tafel behavior, secondary passivation, and, in some cases, a limiting current density. These factors were found to be greatly dependent on the hydrogen ion concentration and temperature. Tafel behavior is observed at low current densities over a wide range of solution compositions and temperature. Secondary passivation occurs at low hydrogen ion concentrations and low temperatures while a limiting current density is observed at high hydrogen ion concentrations and low temperatures. The discussion of the polarization curves will be divided into two parts: dissolution above and below 5M acid.

1.11 Dissolution at High Acid Concentrations. Figures 17 and 18 show the polarization curves as a function of nitric acid concentration (6 to 14M) and temperature (25 to 55°C), respectively. Two Tafel regions and a limiting current density are evident. At low current densities the Tafel slope (0.065 volts)

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Fig. 17 Dissolution of 304 stainless steel in the transpassive region at 25°C in concentrated HNO₃ solutions.

Fig. 18 Effect of temperature on the anodic dissolution of 304 stainless steel in 10M HNO_3 .

is essentially independent of HNO_3 concentration and temperature up to and including 55°C . Data obtained at 70 and 85°C gives a Tafel slope of 0.045 volts. This may be due to the presence of Cr^{+6} which seems to be more slowly reduced at the higher temperatures. The potential at a given current density decreases with increasing temperature (Figure 18) and decreasing HNO_3 concentration. From Figure 17
$$\frac{\partial \phi}{\partial \log (\text{HNO}_3)} = + 0.16 \text{ volts.}$$

In the second Tafel region the slope increases with decreasing nitric acid concentration in such a manner that the potential at constant current density is nearly independent of HNO_3 concentration. It can be seen that the value of the limiting current density increases with decreasing acid concentration and increasing temperature.

1.12 Dissolution at Low Acid Concentration. A number of solutions other than straight nitric acid were used for the experiments at low hydrogen ion concentration. These included mixtures of HNO_3 and NaNO_3 , and mixtures of HNO_3 with Fe^{+3} , Cr^{+3} , Ni^{+2} nitrates in the proportion found in type 304 stainless steel. In both cases the nitrate ion concentration was held constant at 5M. Due to hydrolysis of the Fe^{+3} , Ni^{+2} , Cr^{+3} nitrates, the hydrogen ion concentration in these solutions was determined potentiometrically by comparison with HNO_3 , NaNO_3 mixtures.

In all these solutions, as in the concentrated solutions, the Tafel slope at low current densities was essentially constant at 0.065 volts. The most distinguishing feature of the potential-current density relationships at low acid concentrations is the phenomenon of secondary passivation which was

found to be strongly dependent on hydrogen ion concentration and temperature. Beyond the region of secondary passivation, oxygen evolution is observed.

Figure 19 shows data for solutions containing various amounts of HNO_3 and NaNO_3 at a constant nitrate ion concentration of 5M . The curves for solutions composed of $\text{HNO}_3 + \text{Fe}^{+3}$, Ni^{+2} , Cr^{+3} nitrates are shown in Figure 20. From these it is seen that the "S" shaped region corresponding to secondary passivation is more pronounced when NaNO_3 is substituted for the Fe, Ni, Cr nitrates. Also, in the Tafel region (low current densities), the variation of the potential at constant current density with hydrogen ion concentration is different. For Fe, Ni, Cr nitrates $\frac{\partial \phi}{\partial \log H^+} \cong 0$ and for NaNO_3 solution $\frac{\partial \phi}{\partial \log H^+} \cong +0.038$. From the data (not shown) obtained with plain nitric acid solutions in the same range of hydrogen ion concentrations $\frac{\partial \phi}{\partial \log H^+} = +0.16$. For the straight HNO_3 solutions, a hysteresis effect is observed in the secondary passivation region, ie, the current is higher on decreasing the potential. These differences in the secondary passivation region and the changes of potential in the Tafel region with hydrogen ion concentration, for the three solutions, are probably due to the different buffering capacities of the solutions and changes in the structure of the double layer.

Above the "S" shaped region the current density increases rapidly with increasing potential and oxygen evolution takes place simultaneously with metal dissolution. In this situation there is of course a decrease in current efficiency.

Fig. 10 Dissolution of 304 stainless steel at 25°C in solutions of low H^+ concentrations with a constant NO_3^- concentration of 5M .

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Fig. 20 Dissolution of 304 stainless steel at 25°C in solutions containing Fe^{+3} , Cr^{+3} , Ni^{+2} nitrates with various H^+ concentrations and a constant nitrate ion concentration of 5M.

To determine the effect of temperature on the polarization curves, a solution was prepared which contained 1M HNO_3 + 4M NO_3^- from Fe^{+3} , Ni^{+2} , Cr^{+3} nitrates. The hydrogen ion concentration of this solution was 2.8M due to hydrolysis of the Fe^{+3} , Ni^{+2} , Cr^{+3} salts. The results are shown in Figure 21. It can be seen that the effect of temperature on secondary passivation is similar to the effect of hydrogen ion concentration. In this solution, secondary passivation is absent above 50°C. The heat of activation $\Delta H^\ddagger$ for the dissolution in the above solution ranges from +14 to +15 Kcal/mole. Arrhenius plots at potentials of 1.0, 1.1, 1.2, 1.3, and 1.4 volts are shown in Figure 22.

1.13 Corrosion due to Chromium VI. It has been observed that corrosion of stainless steel in electrolytic dissolver solutions can be excessive when a large amount of Cr^{+6} is present in solution. This is due to the Cr^{+6} - Cr^{+3} couple which, under some conditions, has a positive-enough potential and sufficiently favorable kinetics to maintain a mixed potential in the transpassive region of the steel. Preliminary potential-current density curves obtained with solutions containing Cr^{+6} show that the mixed potential of the steel is made more positive especially at high hydrogen ion concentrations. It was also noted that during dissolution the Cr^{+6} formed at the anode is reduced to Cr^{+3} both at the cathode, and in solution, by the reduction products of nitric acid. However, this reduction is rapid and complete only in solutions of high acid concentration (>5M). Also, recent experiments have indicated that this reduction is favored by low temperatures, but this fact has not yet been firmly established. In any case, by use of anodic polarization data at very low current densities, the instantaneous corrosion rate of stainless steel can be determined from simple potential measurements. For example, from the data presented, it can be seen that at potentials less than +0.9 volts at 25°C and +0.8

Fig. 21 Effect of temperature on dissolution of 304 stainless steel in a solution containing 1M HNO_3 and 4M NO_3^- from Fe^{+3} , Ni^{+2} , Cr^{+3} nitrates (H^+ concentration = 2.8M).

volts at 70°C the corrosion rate of type 304 stainless steel is less than 10^{-5} amp/cm^2 .

1.14 Conclusions. From an analysis of the data it is obvious that the dissolver solution should be maintained at a minimum temperature of 60°C . At this temperature (or higher) anode operation is practical over a wide range of solution compositions (1 to 10M H^+) and high current densities (up to $2\text{ amp}/\text{cm}^2$) since passivation, limiting current densities and gas evolution are avoided. Also, at and above 60°C , the anode polarization changes little with solution composition. However, before the optimum dissolver operating conditions can be specified, similar information on the cathodic reactions must be obtained.

Additional anodic data are being obtained on temperature dependence, the effect of higher metal concentration, and the effect of Cr^{+6} on polarization and corrosion.

Fig. 22 Arrhenius plots for the dissolution of 304 stainless steel in 1M HNO_3 + 5M NO_3^- (Fe^{+3} , Cr^{+3} , Ni^{+2}) at 1.0 , 1.1 , 1.2 , 1.3 , and 1.4 volts.

2. SERIES ELECTROLYTIC DISSOLVER (J. W. Coddington, Problem Leader; M. R. Bomar)

Current designs for dissolvers to be used in electrolytic dissolution of nuclear fuels incorporate an inert basket which acts as the anode and as a container for the fuel pieces. A major operating difficulty with this arrangement is the maintenance of good electrical contact between the basket and the fuel to be dissolved. In addition, the use of a relatively high current to achieve reasonable dissolving rates has been considered essential for a basket dissolver, requiring low-potential power sources of high current capacity.

A new electrolytic dissolution technique which avoids these problems has been demonstrated at the Idaho Chemical Process Plant. Metal pieces to be processed are placed in a tubular dissolver into which dissolving solution can be continuously pumped. Current is then passed through the contents of the tube between electrodes placed at each end. The electrodes are immersed in the dissolver solution and need not be in physical contact with the dissolving pieces of metal. A series of electrolytic cells are formed within the dissolver; one end of each fuel piece acts as the cathode, reducing nitric acid, while the other end acts as the anode, going into solution. Dissolution rates of 2.5 mg/cm²/min at current efficiencies of 1000% have been demonstrated for stainless steel. Using the same technique, aluminum can be dissolved to a basic solution, and zirconium can be oxidized to ZrO₂.

A topical report in preparation [6] describes the apparatus in detail and gives operating characteristics for the dissolution of stainless steel and aluminum and the disintegration of Zircaloy-2.

3. MATERIALS OF CONSTRUCTION IN ELECTROLYTIC SYSTEMS

3.1 Corrosion of Specimens Suspended in an Electrolytic Dissolver (N. D. Stolica, Problem Leader, C. E. May)

Continuing the study of the corrosion of metals suspended in the vicinity of the electrodes in an operating electrolytic dissolver, coupons of niobium and titanium were tested in the equipment described in Section VI-C-3 of the last Quarterly Progress Report [1]. As in the earlier work an anode of type 304 steel was dissolved into a product solution, 1M in nitric acid and 75 g/l in dissolved stainless steel components. The exposure time in the current work was 98 hr at the solution boiling point. The titanium coupons were located in position I, behind a cathode; in position III, adjacent to a cathode; and position II, between the cathodes. The niobium coupons were placed in positions I and III and also in position IV, farthest from and shielded from the cathodes. The positions given here are exactly defined in Figure 39 of the last Quarterly Progress Report [1].

No corrosion was evident on any of the titanium or niobium specimens. There was, however, a slight increase in weight of the coupons during exposure suggesting the formation of a film. These results suggest that titanium and niobium components may be usable in positions in the electric field in the

dissolver where components of stainless steel would be rapidly destroyed by corrosion.

3.2 Plastics Irradiation Testing (N. D. Stolica, Problem Leader, L. A. Decker)

Plastic specimens that have been considered as possible electrical insulating and supporting materials for use in an electrolytic dissolver were tested by irradiating them at levels up to 10^9 R in the dissolver product environment in the Gamma Facility at the Materials Testing Reactor. The gamma flux level was about 10^6 R/hr. The plastics were immersed in dissolver product solution, 1M nitric acid and 75 g/l stainless-steel components as nitrates, at 101°C for the irradiation. The four materials tested, Saran, Kynar, Kel-F and Marlex-50, had passed earlier screening tests [1] which showed them to be essentially inert to the chemical environment. The changes in physical appearance of the irradiated specimens are shown in Table XI.

Only the Marlex-50, in this group, appeared to adequately resist the combined radiation and chemical conditions to warrant further testing.

TABLE XI
VISIBLE CHANGES IN PLASTICS SAMPLES AFTER GAMMA IRRADIATION

Conditions: 1M nitric acid, 75 g/l stainless-steel components, 101°C.				
Material	Original Appearance	Appearance after Irradiation		
		at 1×10^8 R	at 4×10^8 R	at 1×10^9 R
Marlex-50	white, opaque	pale yellow, no obvious damage	dark brown, lightly crazed surface	Severely crazed surface, no spalling or warping
Kel-F ^(a)	white, translucent	pale yellow, many parallel cracks	many parallel cracks, some samples disintegrated	Very deep parallel cracks, small pieces completely disintegrated
Kynar	lt. brown, opaque	dark brown, few parallel cracks	deep parallel cracking and crazing	Very severely crazed and warped, some spalling
Saran ^(b)	lt. brown, opaque	spalled, warped dark brown	severely spalled and warped	Not tested

(a) Kel-F Grade 300 molding powder, (unfilled) KF-3010
(b) Saran, blonde Saran B-115, unfilled

3.3 Electrolytic Dissolution Pilot Plant (D. K. MacQueen, H. V. Chamberlain, Problem Leaders; H. E. Stelling, A. P. Roeh)

A flowsheet and a proposal to install an Electrolytic Dissolution System in Cell "C" of the ICPP instead of in the Hot Pilot Plant were prepared.

Fabrication of the dissolver, overflow vessel, recirculation cooler, and the two off-gas condensers is expected to be completed in the near future. Purchase contracts have been awarded for most of the required instruments. Specifications for fabrication of dummy SM-1 fuel elements are being prepared to obtain cost estimates.

VI. 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 [7]. Zirconium and aluminum alloys dissolve readily in the molten salt, and the respective chlorides are volatilized; uranium and thorium also dissolve readily, but exhibit no volatility. Dissolution of stainless steel requires the addition of chlorine to the melt in order to effect dissolution. The $\text{PbCl}_2\text{-Cl}_2$ system also dissolves chromium and niobium at feasible rates. Addition to copper to the $\text{PbCl}_2\text{-Cl}_2$ system permits dissolution of uranium oxide in the same temperature range as the alloys [2], 500 to 530°C; nichrome will also dissolve readily in this system.

During this quarter, the study of niobium behavior in fused lead chloride was completed; the dissolution rate was readily controlled by chlorine addition rate, and the dissolved niobium was almost quantitatively sublimed from the melt as niobium pentachloride. Additional work was performed on the dissolution mechanism of UO_2 in the $\text{PbCl}_2\text{-Cu-Cl}_2$ system, and rate equations are presented. Scoping experiments resulted in determination of dissolution rates of thorium and nichrome under certain conditions, but zirconium oxide was found to be resistant to the process.

Chloride was readily removed, by refluxing, from 8M or stronger nitric acid leach solution used to extract uranium from the lead chloride matrix resulting from the ARCO Process, thus giving a solvent extraction feed solution compatible with stainless-steel equipment. Chloride vapor-liquid distribution coefficients are presented.

Corrosion tests indicated the possible usefulness of Haynes 21 or Haynes 25 alloys for structural use in an ARCO Process dissolver system.

1. NIOBIUM BEHAVIOR

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

1.1 Molten Lead Chloride

A kinetic study of niobium dissolution in lead chloride has been completed. The rate of weight loss was linear at each temperature from 30 min to 4 hr. The initial parabolic period was too short in duration to obtain meaningful data by the experimental technique used. The rates in the linear region, determined by a least squares treatment of the data, are given in Table XII.

The values shown in Table XII reflect the use of only the linear region and are somewhat lower than earlier results [2] averaged over the entire

TABLE XII
NIOBIUM DISSOLUTION RATES IN PbCl_2 AS A FUNCTION OF TEMPERATURE
(Linear Region)

<u>Temperature, °C</u>	<u>Rate, mg min⁻¹ cm⁻²</u>	<u>Standard Deviation</u>
550	0.020	0.001
600	0.046	0.005
650	0.115	0.008
700	0.180	0.008
800	0.569	0.023

period of observation. The Arrhenius activation energy calculated from data in Table XII is 23.4 kcal/mole.

A possible explanation for the decrease from the initial rate may involve the formation of a rate-limiting product layer. This is substantiated by a series of stirred dissolutions at 650°C. As shown in Table XIII, stirring considerably increased the dissolution rate, which would seem to indicate that the reaction mechanism is diffusion controlled.

TABLE XIII
NIOBIUM DISSOLUTION RATE IN
 PbCl_2 AT 650°C AS A FUNCTION OF STIRRER SPEED

<u>Stirrer Speed, rpm</u>	<u>Rate, mg min⁻¹ cm⁻²</u>
0	0.115
620	0.197
1280	0.412

Experiments with various volumes of lead chloride present indicated that the reaction rate increases with an increasing amount of lead chloride present.

Approximately 60% of the niobium dissolved in lead chloride is retained in the melt phase, the remainder being volatilized. Aqueous dissolution of the salt matrix yields niobium (IV) oxide which indicates that niobium (IV) or a lower oxidation state of niobium is present in the melt. Attempts to characterize the species present have been unsuccessful.

Of the niobium dissolution products which volatilize from the melt, about 90% are present as niobium pentachloride. The remaining 10% is less volatile and condenses nearer the furnace. The compound is crystalline according to its X-ray pattern; however, the X-ray patterns of lower niobium chlorides are not available in the ASTM files, so characterization of the less volatile sublimate materials is inconclusive.

1.2 The PbCl₂-Cl₂ System

The behavior of niobium in the lead chloride-chlorine system is apparently less complicated than in the lead chloride system. The niobium dissolution rate at 550°C for 30 min periods increases with the chlorine flow rate according to the equation

$$y = 5.28x - 0.018x^2,$$

where y = Nb weight loss (mg cm^{-2}) and x = Cl₂ flow rate (mg min^{-1}). A reaction rate, several orders of magnitude greater than that obtained in the lead chloride system, is possible in the lead chloride-chlorine system. No time dependency of the reaction rate was observed in this system. The metal surfaces which came directly in contact with the chlorine stream during the dissolution exhibited considerable etching. Therefore, the effective dissolution rate appears to be strongly dependent on the amount of surface in contact with chlorine vapor.

The niobium dissolved exhibited nearly complete sublimation from the melt and was in the form of niobium pentachloride. Only 0.1 wt% or less of the dissolved niobium remained in the melt. This negligible interaction between the lead chloride and niobium pentachloride further substantiates the fact that the niobium remaining in the melt of the lead chloride system is a lower chloride than the pentachloride.

The preceding data indicate the feasibility of dissolution of niobium based fuels in the lead chloride-chlorine system. The dissolution rate can be readily controlled by varying the chlorine flow rate and the alloying constituent is essentially removed completely from the uranium in the melt phase.

2. DISSOLUTION OF UO₂ IN THE PbCl₂ - Cl₂ SYSTEM CATALYZED BY COPPER (E. M. Vander Wall, Problem Leader; D. L. Bauer)

The effect of the copper concentration on UO₂ dissolution in the PbCl₂ - Cu - Cl₂ system has been investigated [2]. In those experiments, the PbCl₂ - Cu melt was chlorinated to dissolve the copper completely before the UO₂ was introduced. It was discovered that under these conditions a very rapid dissolution of UO₂ occurred immediately, before any additional Cl₂ was supplied.

Since, under these circumstances, a false value is obtained for the copper concentration in the rate equation, it appears that a valid appraisal of copper concentration effect could be obtained by using cuprous chloride instead of the copper metal. It has been established previously that UO₂ dissolution in the PbCl₂-CuCl system is not appreciable [2]. The procedure used was as follows: the molten salt solutions were prepared; the UO₂ introduced; then the chlorine flow started. The experiments were performed at 550°C.

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Fig. 23 Effect of CuCl concentration on the dissolution of UO_2 pellets in the PbCl_2 - CuCl - Cl_2 system.

Since the copper concentration effect was of primary interest in these experiments, an excess of chlorine was always used. Two forms of UO_2 were employed: pellets with a calculated initial surface area of 3.82 cm^2 and weighing approximately 5.8 g; and -35 to -40 mesh UO_2 with 5.0 g being used in each experiment. The data obtained from these experiments are presented in Figures 23 and 24, respectively. The large amount of scatter in Figure 23 is probably due to the fact that all the pellets shattered, with one exception, when introduced into the melt. The pellet which remained intact was used in the experiment which contained 0.67 molal CuCl .

The rate equation obtained from the experiments involving the use of pellets and where there was a chlorine excess is: $\frac{-d(\text{UO}_2)}{dt} = k(\text{CuCl})$.

The value for the rate constant k is $530 \text{ mg } (\text{UO}_2) \text{ min}^{-1}/(\text{CuCl molality})$. If one assumes that the pellets split in half with an average surface area of 5.44 cm^2 and that the area function is first order, then another rate equation can be written:

$$\frac{-d(\text{UO}_2)}{dt} = k' (\text{area of } \text{UO}_2)(\text{CuCl}).$$

k' is then equal to $98 \text{ mg } (\text{UO}_2) \text{ cm}^{-2} \text{ min}^{-1}/(\text{CuCl molality})$.

There is much less deviation from the line plotted in Figure 24. This may be due to two factors: (1) the finely divided material is much less subject to shattering by thermal shock, and (2) there is initially at least a 10-fold greater surface area available with the 35 to 40 mesh material than with the pelleted UO_2 and therefore the reaction rate may be insensitive to area changes. The rate equation obtained from these experiments is identical to that obtained with pelleted UO_2 , but the rate constant k is equal to $1350 \text{ mg } (\text{UO}_2) \text{ min}^{-1}/(\text{CuCl molality})$.

CPP-S-2005

Fig. 24 Effect of CuCl concentration on the dissolution of UO_2 (-35 to -40 mesh) in the PbCl_2 - CuCl - Cl_2 system.

3. VAPOR-LIQUID EQUILIBRIA IN THE NITRIC ACID-LEAD CHLORIDE SYSTEM

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

One method of uranium removal from the lead chloride matrix resulting from the ARCO process is a nitric acid leach which is followed by a solvent extraction step for the final decontamination [7]. In order to make the solvent extraction feed solutions compatible with stainless-steel equipment and to utilize present solvent extraction technology, it is necessary to remove the chloride from the nitric acid leach product. Chloride and nitric acid vapor-liquid equilibria data have been reported for systems which contain no metals [8, 9] and one study has also been made in which ferric nitrate was present [10]. However, no vapor-liquid equilibria data appear to be available for the nitric acid-lead chloride system.

Previous experiments have established that 8 to 10M HNO₃ is the most satisfactory concentration for leaching [7]. The vapor-liquid equilibria were studied in the range of 4.5 to 11.2M HNO₃. The experiments were conducted in a modified Gillespie still [10], however, no cold trap was used to condense vapors. In each experiment 75 ml of nitric acid was placed in the still along with 2 g of lead chloride. The still pot solutions were saturated with lead chloride in all instances. The system was allowed to reflux for ~4 hr before the system was sampled. Under reflux conditions, an average of 67.5 ml (20°C) of liquid remained in the still pot while the remainder was either vapor or condensed vapor in the system. Both the liquid and the condensed vapor phases were analyzed for hydrogen ion and chloride ion. The liquid phase analyses were corrected to values which would be observed at 20°C by taking into account the condensed vapor analyses and material balances. The chloride analyses (corrected to 20°C) of the solution in the still pot are given in Table XIV. The solubility products of lead chloride are calculated on the assumption that all the chlorine remains in the system and is present as chloride. At the higher acid concentrations some decomposition gases were observable in the system. Therefore, the respective solubility products are subject to greater error.

TABLE XIV
SOLUBILITY OF LEAD CHLORIDE IN REFLUXING NITRIC ACID

(Values corrected to 20°C)			
Atmosphere pressure ~640 mm (Hg)			
<u>HNO₃(M)</u>	<u>Temperature °C</u>	<u>Cl⁻(M)</u>	<u>K_{sp} PbCl₂</u>
4.51 ± 0.01	103	0.0187 ± 0.0002	(3.3 ± 0.1) × 10 ⁻⁶
6.75 ± 0.03	106	0.0167 ± 0.0003	(2.4 ± 0.0) × 10 ⁻⁶
8.71 ± 0.11	109	0.0102 ± 0.0012	(7.8 ± 1.8) × 10 ⁻⁷
9.59 ± 0.03	110	0.0109 ± 0.0009	(11.1 ± 3.1) × 10 ⁻⁷
11.22 ± 0.00	113	0.0061 ± 0.0007	(3.3 ± 0.6) × 10 ⁻⁷

Fig. 25 Chloride vapor - liquid equilibrium curves in nitric acid systems. CPP-S-2006

The chloride vapor-liquid distribution coefficients are plotted versus the still pot nitric acid concentration in Figure 25. The curve exhibits smaller distribution coefficients than those observed in acid systems with no metal present; however, these curves tend to merge at the higher acid concentrations. On the other hand the $\text{PbCl}_2\text{-HNO}_3$ curve and the $\text{Fe}(\text{NO}_3)_3\text{-HNO}_3\text{-HCl}$ curve diverge as the nitric acid concentration increases.

The chloride vapor-liquid distribution coefficients obtained in this study demonstrate that ohloride can be readily removed from the nitric acid leach product solution by refluxing if the nitric acid used is 8 molar or greater.

4. OTHER WORK

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

An experiment was performed to determine the feasibility of thorium dissolution in molten lead chloride. A small thorium rod weighing 4.49 g was immersed in 14.8 g of molten lead chloride at 550°C. The reaction mixture was chilled after 5 min to stop the dissolution. The dissolution rate during this period was $8.9 \text{ mg cm}^{-2} \text{ min}^{-1}$.

The $\text{PbCl}_2 - \text{CuCl} = \text{Cl}_2$ system was investigated as a possible dissolution medium for both nichrome and zirconium oxide. A nichrome ribbon (analysis 79.3% Ni, 20.5% Cr) was immersed in molten lead chloride through which 105 mg of chlorine were passed per min. The resultant dissolution rate was $0.25 \text{ mg cm}^{-2} \text{ min}^{-1}$. Then a melt containing 96 mole percent PbCl_2 - 4 mole percent CuCl was prepared and chlorine was passed through the melt at a rate of 26 mg min^{-1} . The average dissolution rate was $6.7 \text{ mg cm}^{-2} \text{ min}^{-1}$; a 25-fold increase over that obtained in the $\text{PbCl}_2 - \text{Cl}_2$ system.

The dissolution of zirconium oxide was attempted in a melt which was 80 mole percent PbCl_2 - 20 mole percent CuCl . Chlorine was passed through the melt at a rate of 50 mg min^{-1} . After two hours, there was no evidence that any dissolution had occurred.

5. ALLOY CORROSION TESTS

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

Since a number of fuel cladding materials can be readily dissolved in molten lead chloride if chlorine is present, a series of corrosion tests was

performed to establish the resistance of several alloys in the lead-lead chloride-chlorine system. Duplicate metal samples were placed concentrically around a glass dispersion ring which was placed in the center of a Pyrex glass vessel. A glass cover on the vessel retained a chlorine atmosphere in the system during the experiments. Approximately equal volumes of lead and lead chloride were placed in the vessel. Chlorine was admitted through the dispersion ring at the lead-lead chloride interface at a controlled rate. The temperature was maintained at 520°C. The coupons were held upright in the melt by glass support rods with ~1/3 of the coupon surface projected above the lead chloride melt into the chlorine atmosphere. The data obtained are given in Table XV.

On the basis of the data presented in the table it appears that both Haynes 21 and Haynes 25 alloys would make satisfactory structural material for this system. In all instances corrosion in the vapor phase was more severe than in either of the liquid phases.

TABLE XV
CORROSION OF SELECTED ALLOYS IN THE
LEAD-LEAD CHLORIDE-CHLORINE SYSTEM AT 520°C

<u>Alloy</u>	<u>Exposure, (Days)</u>	<u>Coupon Distance (mm) from dispersion ring</u>	<u>Corrosion Rate (Mils¹/Month)</u>	<u>Cl₂ Rate (mg/min)</u>
Incoloy 804	4	26.5	12.33 ± 0.10	25
Haynes 25	10	9.	2.66 ± 0.25	30
	10	26	2.30 ± 0.23	30
	10	41	2.21 ± 0.16	30
	10	16	9.75 ± 0.23	31
Hastelloy B	10	39	7.58 ± 0.18	31
	10	15.5	3.52 ± 0.07	29
Haynes 21	10	33	1.78 ± 0.47	29
	10	15	6.23 ± 0.11	31
INOR-8	10	35	3.37 ± 0.88	31

VII. BASIC PROCESS STUDIES AND 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 ICPP mechanical hydraulic pulsers with air pulsers [1]. Design and prediction of behavior of the first-cycle extraction-column air pulser was done by a series of analog computer runs. It is shown that a square wave is a satisfactory representation of the pressure input, and an average value of the friction factor is an excellent substitute for a variable factor.

Control of the first-cycle product evaporator originally installed in the ICPP was inadequate; major upsets required that the evaporator be operated manually; and damping action, built in to keep the recorder on scale, made it impossible to interpret the results. A cascade control system has been specified for a newly installed evaporator [1], and a study of the evaporator dynamics is underway.

A systems study of chemical processing operations at the ICPP has been initiated in order to improve present operations and the subsequent design of new process equipment and plants. The key unit chosen for the first such study was the pulse extraction column; results of preliminary investigations are discussed.

Requirements for shielding exposed air pulser lines, subject to possible contamination by backup of process solutions, are discussed.

1. AIR PULSER OPERATING CHARACTERISTICS

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

Theoretical operating curves for the air pulser on the 1A pulse column [1] were determined by simulation on the analog computer. The equation for the system was expressed in terms of flow in the 2-in.-diameter pulser leg of the 10-in.-diameter column. It included a variable friction factor for flow in the pulser leg and auxiliary piping, and an average orifice coefficient for flow through the perforated plates in the column. A square-wave pressure input and the friction factor as a function of Reynold's number were put into the computer by function generators.

The equation used to express the performance was of the form:

$$(a + b)\ddot{x} + (c_1 N_{Re}^f x + c_2 N_{Re}^f + d |\dot{x}|) \dot{x} + ex - F = -q(P,t)$$

The first term represents the pressure to accelerate the fluids in the system; the second, the pressure to overcome friction; and the last terms on the left side of the equation, the static pressure. The right side is the square pressure-wave driving function. The displacement length in the pulser leg is denoted

by x , the velocity by $\dot{x}$, and the acceleration by $\ddot{x}$. The friction factor, f , is a function of Reynold's number, N_{Re} , which is in turn proportional to the absolute velocity, $|\dot{x}|$. The other terms are constants defining the physical system.

Pulse amplitudes in the column were determined from computer data, as functions of applied pressures, for pulse frequencies in the 30- to 100-cycle/min range at 30% organic holdup. Amplitudes for 40, 60, and 80 cycles/min were obtained for 20 and 40% holdup, also. The resulting curves are shown in Figure 26. In the normal range of operation, at about 1-in. pulse amplitude in the column, a change of 10% in holdup causes less than a 10% change in amplitude at constant applied pressure.

The effect, on the curves, of using an average value for the friction factor is insignificant. A change in average orifice discharge coefficient from 0.68 to 0.60, which is greater than would be expected, changes the curves only about as much as does a 10% change in organic holdup. The use of transient pressure peaks at the ends of the pressure waves to more closely simulate actual pressure conditions gives the same pulse amplitude as does the square wave, and is therefore an unnecessary complication in the computation.

Derivation of the pulser equation, the results of the computations, and the details of the computer program are given in a forthcoming report.

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

Control of the first cycle product evaporator originally installed in the ICPP was inadequate. Consequently, a cascade control system has been specified for a new evaporator being installed because of failure of the original [1]. In the cascade system, the flow of steam to the evaporator is proportioned to the evaporator feed rate by a magnetic flowmeter and controller. The set point of the steam controller is readjusted by a specific-gravity controller. Thus, a feed-forward control will reduce the time lag in response to feed-rate changes, and feed-back control will maintain product quality.

The ratio of recycle rate to product rate was estimated to be as high as 120:1. Calculated heat-transfer rates indicated that 10 psig steam will be adequate for average requirements, and about 20 psig will be needed for maximum expected loads. Under normal operating conditions, the present 35 psig supply can thus be reduced to about 20 psig for best control.

In addition, a study is partially completed of the evaporator dynamics in order to determine the system stability and to specify controller settings.

3. PROCESS DYNAMICS - PULSE EXTRACTION COLUMN PERFORMANCE (E. E. Erickson, Problem Leader; L. A. Jobe, E. L. Rowe)

In order to improve the present operations and the subsequent design of new process equipment and plants, a systems study of chemical processing

Fig. 26 Operating curves for ICPP first cycle extraction column.

operations used at the ICPP has been initiated. Past designs generally have been based on the assumption of steady-state operation, which is an inadequate basis for the design of a processing plant which is under optimum control. A systems study requires breaking the entire system into individual parts and determining the dynamic characteristics of each part. The key unit chosen for the first such study was the pulse extraction column.

Theoretical equations to describe several mathematical models of a pulse column have been written. Classically, these equations are (1) difference equations, (2) partial differential equations, and (3) ordinary differential equations. Difference equations would be used with digital computer solution. Partial differential equations cannot be handled on the analog computer without first converting to ordinary differential equations by the separation of variables or finite-difference techniques. Since analog computer simulation was desired, the third approach appeared to be the most direct, and was selected for a stagewise operation. Inventory (for the unsteady-state), equilibrium, holdup-interaction, and transport-lag relationships, which could be solved exactly on the analog computer, were written. As a preliminary trial, one particular combination of equations, representing a five-stage, simplified mathematical model for the nearly ideal system, water-acetic acid-hexone, was programmed for the analog computer. The effect of a composition disturbance and that of a flow disturbance at constant holdup were checked on the computer. Organic holdup was assumed to vary from 33 to 67%. Summary plots on an X-Y plotter following a sudden aqueous feed composition change showed effective time constants of 19, 48, 76, 97, and 113 sec for the top (5th) to the bottom (1st) stages, respectively. The time constants for composition change on a flow disturbance in the aqueous stream were 26, 25, 24, and 19 sec for fifth, third, second, and first stages, respectively. It will be noted that the order of time constants was reversed. The two sets of transient curves are shown in Figures 27 and 28.

To provide information for further computer simulation, a limited series of steady-state experimental runs was made on an existing 1 1/2-in.-diameter pulse column for a water-continuous hexone-water system at 60 cycles per min and 1-in. amplitude. Organic-phase holdups were measured at a total flow rate for both phases of 300 gal/hr-ft² and for organic/aqueous flow ratios of 0.5 and 2. The holdup ranged from 5% at the bottom to 10% on the sixth plate and above for the low organic to aqueous ratio; it varied from 5% at the bottom to 15% on the tenth plate and above for the high ratio.

4. RADIATION SHIELDING

(E. E. Erickson, Problem Leader; W. G. Morrison)

Liquid sensing units and quick acting valves have been incorporated in the individual air-pulser supply lines of the revised F-cell columns to prevent liquid backup and contamination of the lines in the cold process solution make-up (PM) area in case of equipment malfunction. The effectiveness of these devices has not been completely established, so the Engineering Safeguard Committee recommended that the lines be shielded from the PM floor, through and including the safety and poppet valves. Shielding calculations, based on 200-day cooled S1W fuel assemblies and an arbitrary shield-design point of one R/hr at 1 ft from the pipe, showed that shielding was required on the extraction column lines only. One-half and one-in. lines require 0.9 and 1.3 in. of lead, respectively. However, additional shielding will be required if solution backup in the lines should become a regular occurrence.

CPP-S-2007

Fig. 27 Effect of step change in feed concentration upon aqueous tray compositions: Analog computer solution for a five-stage extraction column.

CPP - S - 2008

Fig. 28 Effect of 100% step increase in aqueous feed rate upon aqueous composition on each tray: Analog computer solution for a five-stage extraction column.

VIII. SPECIAL STUDIES

The ETR circulating water loop has shown increasing radioactive contamination with Ag-110 constituting the source of over 90% of the gross activity present on samples of stainless steel and aluminum immersed in the water. A number of oxidants were evaluated as possible decontaminants, with gaseous ozone-oxygen found to be one of the most satisfactory from the standpoint of decontamination effectiveness, compatibility with the system, and ease of removal.

Reported as supplemental information are partial molal volumes of aqueous ammonium fluoride-ammonium nitrate solutions calculated from previously presented density data. No further work on these Zirflex-type solutions is underway.

1. EVALUATION OF DECONTAMINANTS FOR Ag-110 IN ETR COOLING SYSTEM (C. M. Slansky, E. M. Vander Wall)

A number of oxidants were evaluated as possible decontaminants of the circulating water loop at ETR. The major contaminant under consideration was Ag-110 which constituted over 90% of the gross activity on samples of stainless steel and aluminum that had been immersed in the circulating water. These studies were made in an effort to locate a simple and safe chemical decontaminant for Ag-110 which would require the least effort to apply to the ETR system. The reagents selected were gaseous ozone in oxygen, 0.01M potassium persulfate, 0.01M hydrogen peroxide, and 0.05% by weight hypochlorite. These studies were performed between 20 and 40°C, in both distilled H₂O and 0.001N H₂SO₄, and with either little or vigorous agitation.

The experiments, in which hydrogen peroxide, potassium persulfate, and hypochlorite solutions were used, were conducted in a 2 liter, round bottom, Pyrex flask. The solutions were stirred vigorously with a three bladed polyethylene stirring rod. The coupons were ~1 x 3/4 x 1/8 in. and immersed in a liter of solution. The flask in turn was immersed in a constant temperature bath and maintained at 40.0 ± 0.1°C.

The coupons were marked before counting so that a reproducible geometry was established. In most cases, the samples were placed 10 cm from the scintillation detector. Analyses of the coupons by gamma spectrometry was performed by the CPP Special Analysis Group; the 0.91 mev peak of Ag-110 was integrated for comparison purposes. Since the number of coupons available was limited, each coupon was used repeatedly in these studies.

The experiments which involved the use of ozone-oxygen mixtures were conducted in a special apparatus which is shown in Figure 29. The ozone

Fig. 29 Ozonator assembly.

was produced by passing a stream of dried oxygen past the tip of a Tesla coil in a glass chamber which was covered with a layer of aluminum foil to serve as a ground. The foil was surrounded by a water jacket in order to prevent a temperature rise. The ozone-oxygen mixture then entered the solution through a dispersion ring which required a gas pressure only slightly higher than atmospheric (640 mm Hg) to be operable. During operation approximately 10 mg of ozone was produced per hr and the solubility was found to be 0.27 ± 0.02 mg/100 ml H_2O in the oxygen saturated solution. In these experiments 100 ml of solution was used and gas flow was the only source of agitation. The sample coupons were placed on the bottom of the reaction vessel below the dispersion ring so

that any decontamination which occurred was due to dissolved gases in the solution.

The data obtained in these experiments are given in Table XVI, and are listed chronologically so that the effect of repeated contact with various solutions can be evaluated properly. Of the various reagents investigated, the neutral aqueous ozone-oxygen solution is the best reagent for silver removal. The potassium persulfate solutions were found to be ineffective in neutral solution, but useful in the presence of 0.001N sulfuric acid. Hydrogen peroxide was less effective than the persulfate solutions in acid media. The hypochlorite solution, even at the low concentration used, appeared to be promising as a decontaminant; however, due to the presence of chlorine it is incompatible with the ETR coolant system.

The effectiveness of ozone for removal of silver is probably due to the fact that silver is a catalyst for ozone decomposition. The following reactions may be occurring: [11]

The decontaminating effectiveness of ozone decreased with increased acidity. The acidic ozone solution treatment in experiment 8 caused an increase in the silver activity of two coupons while a considerable decrease was observed for the coupon which originally exhibited the greatest radioactivity. However, on the basis of the total activity present, there was a definite reduction ($D_F = 1.48$) if one considers all the surfaces present. In experiment 13, the solution was sampled periodically and the results are shown in Figure 30. After an initial rapid rise, the rate of activity removal appears to remain constant. Final silver decontamination factors of 50 or greater were observed for both aluminum

TABLE XVI
SILVER REMOVAL FROM ALUMINUM AND STAINLESS-STEEL COUPONS
BY VARIOUS REAGENT SOLUTIONS

Experiment Number	Coupon	Solution	Decontamination factor	Reaction times (hr)
1	SS#1	0.01M $K_2S_2O_8$, 0.001 N H_2SO_4	1.65	7.0
	SS#2		1.78	
2	SS#1	0.01M H_2O_2 , 0.001 N H_2SO_4	1.25	4.0
	SS#2		1.02	
3	SS#1	0.01M $K_2S_2O_8$	1.06	4.2
4	SS#2	0.01M $K_2S_2O_8$, 0.001 N H_2SO_4	1.50	4.1
5	SS#2	0.001N H_2SO_4	1.04	4.0
6	Al#2	O_3-O_2 sat'd 0.001 N H_2SO_4	1.94	4.0
7	Al#1	O_3-O_2 sat'd H_2O	7.58	4.0
8	SS#1	O_3-O_2 sat'd 0.001N H_2SO_4	15.03	4.0
	SS#2		0.71	
	Al#2		0.90	
9	SS#2	O_3-O_2 sat'd H_2O	1.98	4.0
	Al#2		3.85	
10	SS#3	O_3-O_2 sat'd H_2O	7.06	4.0
11	SS#3	O_3-O_2 sat'd H_2O	1.47	1.8
12	SS#3	0.005 w/o OCl	1.32	4.0
13	SS#1	O_3-O_2 sat'd H_2O	1.51	4.0
	SS#2		1.27	
	Al#1		2.67	
	Al#2		2.13	
14	SS#4	O_2 sat'd H_2O	1.13	4.5
	SS#5		1.07	
15	Al#1	O_3-O_2 sat'd H_2O	2.32	25.5
16	Al#1	O_3-O_2 sat'd H_2O	1.16 (Ag)	23.3
			1.06 (Zr-Nb)	
17	Al#1	O_3-O_2 sat'd H_2O	1.02 (Cr)	4.0
			0.98 (Ru) (Zr-Nb)	

and stainless-steel coupons which received the ozone treatment repeatedly. At this point, the peaks of other contaminants were present in the spectra to a sufficient degree to make possible a brief evaluation of ozone as a decontaminant for zirconium-niobium, chromium, and ruthenium; very little change in the activity of these constituents was observed after treatment. However,

Fig. 30 Activity buildup in ozone - oxygen decontamination solution.

only a slight amount of activity was present on these coupons by this time so no definite conclusion can be drawn. To yield significant results, these elements should be present at higher activity levels.

Ozone is in all probability compatible with the ETR coolant system. Ozone removal from the system can be accomplished by raising the water temperature, eg, it can be completely destroyed in distilled water by heating to 70°C [12].

2. MOLAL VOLUMES OF AQUEOUS AMMONIUM FLUORIDE-AMMONIUM NITRATE SOLUTIONS AT 25°C (D. P. Pearson and J. L. Teague)

Partial molal volumes of Zirflex-type solutions have been calculated from previously presented [13] density data. The experimental density data (48 solutions) can be represented by the equation $d(\text{g/cc}) = 0.9971 + 0.03157 C_3 + (0.02046 - 0.002659 C_3)C_2 - (0.003346 - 0.000703 C_3)C_2^{3/2}$ where C_2 and C_3 represent moles/liter of NH_4F and NH_4NO_3 , respectively. This equation reproduces the observed density of 46 solutions within 0.0003 g/cc. In the range covered (0-1.0M NH_4NO_3), the calculated densities of pure ammonium nitrate solutions are within 0.0002 g/cc of those given by Gucker's more precise equation [14], which is based on the data of Adams and Gibson [15]. The linear dependence of the density on the ammonium nitrate concentration is a result of the somewhat more limited precision and range of our ammonium nitrate data. This linearity implies an invariance of apparent molal volume of ammonium nitrate with nitrate concentration. The dependence of the density of pure ammonium fluoride solutions on the salt concentration is of the form derived by Root [16].

Apparent and partial molal volumes were calculated by means of the following equations, which were derived from the definitions:

$$\phi_{v2} = \frac{M_2 C_2 - 1000 (d - d_2)}{C_2 d_2} \quad \bar{V}_2 = \frac{M_2 - 1000 A}{d - AC_2 - BC_3}$$

$$\phi_{v3} = \frac{M_3 C_3 - 1000 (d - d_3)}{C_3 d_3} \quad \bar{V}_3 = \frac{M_3 - 1000 B}{d - AC_2 - BC_3}$$

where M_2 and M_3 are the molecular weights of NH_4F and NH_4NO_3 , respectively,

$$d_2 = \frac{d_o (1000d - M_2 C_2)}{1000d - M_2 C_2 - 31.57 C_3}$$

$$d_3 = \frac{d_o (1000d - M_3 C_3)}{1000d - M_3 C_3 - 20.46 C_2 + 3.346 C_2^{3/2} F}$$

$$F^2 = \frac{1000d_3}{1000d - M_3 C_3}, \quad A = \left(\frac{\partial d}{\partial C_2} \right)_{C_3}, \quad \text{and} \quad B = \left(\frac{\partial d}{\partial C_3} \right)_{C_2}.$$

In Figure 31, the apparent and partial molal volumes of ammonium fluoride are plotted as a function of ionic strength at constant nitrate concentrations of 0 and 1.0M. In contrast to observations on alkali halides [17], the partial molal volumes depend on the solution composition as well as the ionic strength. Further ϕ_{V2} is linear in $C_2^{1/2}$ at constant C_3 , which follows from the density equation.

In Figure 32, the limiting partial molal volume of ammonium nitrate ($\bar{V}_3^\circ$) in ammonium fluoride solutions is shown as a function of ionic strength (fluoride concentration). For comparison, $\bar{V}_3$ in pure nitrate solutions is shown, as derived from Gucker's equation [14]. The discrepancy in $\bar{V}_3^\circ$ values in water ($\mu = 0$) is a result of the simplified dependence of the density of C_3 , which should not affect significantly the dependence of $\bar{V}_3$ on C_2 .

Fig. 31 Molal volumes of ammonium fluoride in water and aqueous ammonium nitrate solutions at 25°C as a function of the ionic strength.

From the figures, it is apparent that the replacement of F^- by NO_3^- at constant ionic strength decreases both $\bar{V}_2$ and $\bar{V}_3$, possibly because the NO_3^- disrupts the water structure, allowing either ion to fit into it more readily.

Fig. 32 Partial molal volumes of ammonium nitrate at 25°C.

If $\bar{V}^\circ$ for KF is combined with $\bar{V}^\circ$ values for the ammonium and potassium salts of a common anion [18], a value of $\bar{V}^\circ$ for NH_4F of about 16.0 cc/mole is obtained, which may be compared with the present value of 16.6 cc/mole.

IX. REPORTS AND PUBLICATIONS ISSUED DURING THE QUARTER

1. D. R. Evans, Pilot Plant Studies with a Six-inch Diameter Fluidized Bed Calciner, IDO-14539.
2. E. S. Grimmer and P. R. Brown, Physical and Operational Features of a Pulsed Continuous Countercurrent Liquid-solids Contactor, IDO-14541.
3. A. J. Moffat and R. D. Thompson, Basic Studies of Chemical Stability and Extraction Systems I. The Effect of Zirconium Nitrate and Nitric Acid upon the Chemical Stability of Tributyl Phosphate, IDO-14543.
4. M. W. Wilding, Cesium Removal from Acidic Radioactive Waste Solutions, IDO-14544.
5. L. T. Lakey, Plant Tests on the Decomposition of Nitrous Oxide over a Heated Rhodium Catalyst, IDO-14545.
6. C. R. Ford and H. V. Chamberlain, Steam Stripping TBP-Amsco Solutions from Non-volatile Contaminants, IDO-14546.
7. B. M. Legler and J. I. Stevens, Pneumatic Atomizing Nozzles in Fluidized Bed Calcining I. Calibration Tests, IDO-14548.
8. N. D. Stolica, G. S. Adams, and M. R. Bomar, Corrosion Tests in Molten Lead-lead Chloride, IDO-14554.

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