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CHEMICAL TECHNOLOGY DIVISION
CHEMICAL DEVELOPMENT SECTION B
MONTHLY PROGRESS REPORT
APRIL 1960

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CHEMICAL TECHNOLOGY DIVISION
CHEMICAL DEVELOPMENT SECTION B

MONTHLY PROGRESS REPORT FOR CHEMICAL DEVELOPMENT SECTION B

APRIL, 1960

R. E. Blanco

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ABSTRACT

Dissolution of Uranium-Molybdenum Alloy Fuel

Three to four moles of nitric acid were consumed for each mole of U-8.4% Mo alloy dissolved in HNO_3 or $\text{HNO}_3\text{-Fe}(\text{NO}_3)_3$ solution. The solutions produced contained 0.25 to 1 M iron and 0.3 to 2 M uranium. These results are valid only for the experimental conditions employed since the amount of acid apparently consumed is partially governed by the efficiency of the off-gas condensing system.

Dissolution of Consolidated Edison Fuel

The insoluble residue obtained from the dissolution in boiling 13 M HNO_3 -0.04 M NaF-0.1 M $\text{Al}(\text{NO}_3)_3$ of NUMEC pellets used in 3-min irradiation tests was identified as $6 \text{ Al}_2\text{O}_3 \cdot \text{CaO}$. The pellets contained about 0.4% Al. In other experiments with $\text{ThO}_2\text{-UO}_2$ pellets having densities which were 93% of theoretical, the initial 10-min rate of dissolution was 2.1, 3.0, and 2.4 $\text{mg min}^{-1}\text{cm}^{-2}$ when the UO_2 content was 2.95, 5.98, and 9.12%, respectively. Fused ThO_2 dissolved much more slowly than 95.8% $\text{ThO}_2\text{-UO}_2$ which was 93% of theoretical density; e.g., in 5 hr only about 30% of the fused ThO_2 (-4+8 mesh) dissolved compared to about 88% of the other material of the same mesh size.

Darex Off-Gas Studies

The maximum nitrous oxide content of the off-gas from Darex-type dissolutions of stainless steel (total $\text{HNO}_3 + \text{HCl}$ molarity = 7) increased from 0.7 to 10 vol % as the hydrochloric acid content of the dissolvent was increased from 2 to 4 M.

Zircex Process for Dissolution of Zirconium-bearing Fuels

The initial chlorination rate of high zirconium (STR) Zircex hydrochlorination residues with carbon tetrachloride in an inert carrier gas is one-third as rapid at 350°C as at 600°C. No reaction occurs with high uranium (EBWR) residues below approximately 500°C. An attempt to chlorinate completely a high zirconium residue at 375°C resulted in incomplete conversion. At 500°C, chlorination was rapid but a small amount of material thought to be copper chloride remained behind. At 600°C, the conversion to volatile chlorides occurred rapidly and completely.

Dissolution of Niobium in Concentrated Sulfuric Acid

The dissolution rate of niobium in refluxing sulfuric acid increased from 0.75 to 6 $\text{mg/cm}^2\text{-min}$ as the sulfuric acid concentration increased from 14 to 18.3 M.

Recovery of Uranium and Thorium from Graphite Fuels

Simultaneous disintegration and leaching with two portions of 90% nitric acid (0.2% maximum dissolved oxides) at 25°C of graphite fuels containing at least 2% uranium recovered 99.5% or more of the metal. This recovery was only 0.3% lower than that obtained by leaching with boiling acid. Operation at 25°C should minimize both corrosion and the formation of colored, nitric acid soluble, graphite degradation products. When boiling 15.8 M nitric acid was used in the second leach, the uranium recovery from all fuels studied was independent of the temperature of the first leach with 90% acid between 25°C and the boiling point (~103°C). Since 25-30% of the total uranium recovered was found in the wash solutions, high recoveries can be achieved only after thorough washing of the graphite matrix.

Flowsheet Demonstration on Irradiated Fuel

A test of the Nuclear Ship Savannah first cycle solvent extraction flowsheet using unirradiated fuel in the Immi mixer-settlers showed uranium losses to the raffinate and stripped solvent to be less than 0.01%, but stage samples indicated that excessive uranium reflux took place in the extraction-scrub bank.

Solvent Extraction Studies

The volume of 0.008 M $\text{Al}(\text{NO}_3)_3$ required to strip thorium and uranium from 30% TBP-Amsco in 6 stages is sensitive to the acidity of the organic phase. One and 1.2 volumes of aqueous phase are required to strip the uranium and thorium from organic phases containing 0.01 and 0.2 M HNO_3 , respectively. In 5 stages, 1.5 aqueous volumes are required to strip an organic phase containing 0.2 M HNO_3 .

A final U-233 purification system using 2.5% TBP-Amsco and acid salting showed decontamination factors from ruthenium, zirconium-niobium, protactinium, and thorium of 2,000, 200, 10, and 40, and a uranium loss of less than 0.1%.

Equilibrium data in the system 30% TBP-Amsco, water, thorium nitrate, uranyl nitrate, nitric acid, showed that for systems containing less than one mole of total nitrate, the uranium extraction is approximately proportional to the total nitrate concentration and is independent of cations present.

Corrosion Studies

Under complete reflux conditions, titanium continued to show local weld-metal attack in the condenser above boiling Thorex feed-adjustment solutions after 840 hr. After about 100 hr in successive boil-downs, no localized attack was noted. In 0.05 M fluoride solutions the corrosion rate of titanium decreased almost logarithmically with increase in HNO_3 between 6 and 15 M HNO_3 . In 13 M HNO_3 the rate increased almost logarithmically between 0.005 and 0.05 M F^- .

In Zirflex (6.0 M NH_4F ·1.0 M NH_4NO_3) dissolver solution containing dissolved Zircaloy, Ni-o-nel corroded at rates of 28-32 mils/mo until the concentration of zirconium reached about 0.4 M. Between 0.4 and 0.6 M Zr^{+4} the corrosion rate decreased to about a mil/mo. In flowing 6 M NH_4F -1.0 M NH_4NO_3 -0.003 M H_2O_2 , Ni-o-nel corroded at maximum rates of 0.6, 5.5, and 1.4 mils/mo in vapor, interface and solution phases, respectively.

In Darex-Purex waste storage tests (dissolved stainless steel - 5 M HNO_3 -100 ppm Cl^-) Type 347 stainless steel exposed at 80°C for 672 hr showed the start of intergranular attack. In similar solutions only 2 M in HNO_3 , neither Type 347 or 304L showed signs of attack after 336 hr.

In Zircex cyclic tests (Chlorimet-2 and Type 316 stainless steel showed rates of 5-18 and 19-21 mils/mo, respectively. The addition of CO to the CCl_4 part of the cycle did not appear to improve the corrosion resistance of most alloys appreciably. In boiling 10 M LiCl -0.1 M HCl solution Hastelloy A gave rates of less than 1 mil/mo.

Radiation Damage to Solvents and Diluents

During the use over a 3-year period starting January 1, 1957, of three lots of Amsco 125-82 as a diluent for tributyl phosphate (TBP) in radiation damage studies, significant variations in results were obtained. These include variations in density, gas chromatography retention times, initial degree of carbon-carbon bond unsaturation from 0.1 to 0.5%, yields (G-total gas) of total gas from diluent of 1.7 to 4.6, and yields (G-acid) of acid radiolysis products from 1 M TBP in diluent of 0.98 to 1.33. The differences are large enough to warrant designating the different lots as significantly different materials.

Evaporation and Calcination of Purex Waste

Synthetic Purex LWV waste concentrate containing sodium and calcium as additives to reduce sulfate volatility was calcined to 900°C in the semi-continuous manner which probably would be used in a production plant, in a 4" x 18" pot. An over-all volume reduction factor of 8 was obtained, equivalent to 5 gal of solid waste per ton of uranium processed. The solid residue had a density of 1.56, equivalent to a porosity of about 48%. The condensate contained 98% of the feed nitrate and 0.71% of the feed sulfate. The water in the off-gas scrubber contained 2% of the feed nitrate and 0.02% of the feed sulfate. The thermal conductivity of the as-formed solid waste was found to increase linearly with temperature, from 0.210 Btu/hr/ft-°C at 230°F to 0.311 to 1330°F.

In batch evaporation and calcination of synthetic Purex LWV containing stable ruthenium and Ru-106 tracer, only 0.9% of the Ru-106 reported to the condensate when NO was used as a sweep gas, compared with 72% in the absence of NO.

Intermediate Level Waste Treatment

Synthetic Zirflex decladding waste was heated with $\text{Ca}(\text{OH})_2$ to volatilize ammonia and reduce the volume before adding sand and cement. The final cake had 23% less volume than the original waste and a compression test strength of 4200 psi. Heating similar briquettes made from synthetic Sulfex decladding waste reduced their compression test strength from 2500 psi at 25°C to 1150 psi at 500°C .

Low Level Waste Treatment

Fifty liters of effluent from the lime-soda process water waste treatment plant (pH 10.9) was spiked with 1 millicurie each of Cs-137, Sr-85 and Ce-144-Pr-144, filtered and passed through a 22.5 ml bed of Duolite C-3 (sulfonated phenolic resin). Filtration removed 31% of the gross gamma and filtration and ion exchange combined removed 95%. The activity coming through the resin bed was primarily Ce-144-Pr-144. The presence of a large amount of calcium in the waste treatment plant effluent and the lower pH (10.9) reduced the efficiency of the phenolic resin. Direct treatment of process water, which had been adjusted to 0.01 M NaOH (pH 11.8) and filtered, showed a decontamination factor of 10^4 for cesium.

Fission Product Recovery by Ion Exchange

After 67 resin volumes of 10X diluted LWW Purex waste concentrate, made 0.124 M in oxalic acid to complex iron, had passed through one volume of Dowex 50W X-8 resin, no rare earth breakthrough was detectable. This indicates at least a 4-fold increase in resin capacity for rare earths over a similar run in which the feed contained no oxalic acid.

Radiation Damage to Ion Exchange Resin

An extended analysis of new and irradiated Dowex 50W X-12 (100-200 mesh) resin was made in an attempt to resolve discrepancies reported previously. Two columns of each type of resin was used. The new resin was treated as follows: 1 column $\text{HCl}-\text{H}_2\text{O}$; 1 column $\text{HCl}-\text{H}_2\text{O}-\text{NaOH}-\text{H}_2\text{O}$. The irradiated resin was treated as follows: 1 column, diammonium citrate $-\text{HNO}_3-\text{H}_2\text{O}$; 1 column diammonium citrate $-\text{HNO}_3-\text{H}_2\text{O}-2\text{X}$ ($\text{NaCl}-\text{NaOH}-\text{HNO}_3$).

Moisture content determinations on both new and irradiated resin indicated that the present analytical procedure does not give reproducible results. The wet resin bulk density data of runs done in triplicate were not reproducible while the corresponding oven-dried bulk density data were more consistent.

Using the dry density data of both the new and irradiated resin, a material balance of better than 90% was obtained on the 500 ml of new resin employed by Isotopes Division to recover Pm-147. Assuming no resin weight loss due to irradiation and a total energy dose to the bed of 2780 watt-hr, it was calculated that the unit radiation dose to the resin was almost 13 watt-hr/dry g resin.

Chemical Applications of Nuclear Explosions (CANE)

Preliminary results from a single determination indicate that about 12% exchange of tritium may have occurred when tritiated water vapor and hydrogen were passed over calcium sulfate at 600°C at flow rates of 0.50×10^{-3} and 9.0×10^{-3} moles/min, respectively. Only 0.73% exchange occurred in a blank determination with a hot quartz vessel alone. At 380°C, however, about 5% exchange occurred in both the CaSO_4 and blank determinations. The determinations must be repeated before firm conclusions can be made. Further runs, in which no blanks have been made as yet, show that the combined effect of quartz and CaSO_4 increases the exchange by a factor of 100 when temperature is increased from 380°C to 700°C.

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1.0 POWER REACTOR FUEL PROCESSING

1.1 Dissolution Studies (L. M. Ferris)

1.1.1 Dissolution of Consolidated Edison Fuel (A. H. Kibbey)

The study of the dissolution of various types of high density $\text{ThO}_2\text{-UO}_2$ fuel pellets in boiling 13 M HNO_3 -0.04 M NaF -0.1 M $\text{Al}(\text{NO}_3)_3$ was continued during the last month with particular attention being given to the formation of insoluble residues. It was reported previously¹ that less than 50% of one type of pellet (4% UO_2 , 93% of theoretical density) was dissolved in 136 hr in glass apparatus. These experiments are being repeated in Teflon equipment since, in the first 60 hr of dissolution, the fluoride concentration was reduced from 0.04 to about 0.002 M.

In experiments with another type of pellet, residues were found after four, 5-hr digestions with fresh reagent.² These pellets, manufactured by NUMEC and used in 3-min irradiation tests to determine the effect of power density on pellet stability, were about 93% of theoretical density and contained about 4% UO_2 and 0.4% Al. X-ray and chemical analyses of the insoluble residue showed it to be mainly $6 \text{ Al}_2\text{O}_3 \cdot \text{CaO}$ containing less than 0.05% of the original thorium.

With pellets manufactured by the Babcock and Wilcox Co. which are representative of those to be used as Consolidated Edison fuel (~92% of theoretical density, $\text{O/U} \leq 2.01$), the initial 10-min rate of dissolution in 200% excess of boiling 13 M HNO_3 -0.04 M NaF -0.1 M $\text{Al}(\text{NO}_3)_3$ was independent of UO_2 content up to 9%. For pellets containing 2.9%, 5.98, and 9.12% UO_2 the initial 10-min rates were 2.1, 3.0 and 2.4 $\text{mg min}^{-1}\text{cm}^{-2}$, respectively.

The amount of fused ThO_2 dissolved in 200% excess of boiling 13 M HNO_3 -0.04 M NaF -0.1 M $\text{Al}(\text{NO}_3)_3$ was determined as a function of time and mesh size and the results compared to those obtained under similar conditions with 95.8% $\text{ThO}_2\text{-UO}_2$ which was 93% of theoretical density. As expected, the fused ThO_2 dissolved much more slowly; e.g. after 5 hr, only about 30% of the -4+8 mesh fused ThO_2 dissolved compared to about 88% of the other material (Fig. 1). Since the presence of up to 9% UO_2 apparently has no effect on the rate of dissolution, the results obtained with fused ThO_2 are attributed mainly to its higher density, which should be close to theoretical.

1.1.2 Dissolution of Uranium-Molybdenum Alloy Fuel (L. M. Ferris)

Data on the solubility of molybdenum in solutions produced by the dissolution of U-Mo alloy fuels in $\text{HNO}_3\text{-Fe}(\text{NO}_3)_3$ mixtures have been reported elsewhere.^{3,4,5} In using these data to determine optimum processing conditions, some knowledge of the stoichiometry of the reaction is essential.

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Fig. 1. Comparison of the rates of dissolution of fused ThO_2 and 95.8% $\text{ThO}_2\text{-UO}_{2.36}$ (93% of theoretical density) in 200% excess of boiling 13 M HNO_3 - 0.04 M NaF - 0.1 M $\text{Al}(\text{NO}_3)_3$.

In this connection, the amount of HNO_3 consumed in the dissolution of U-8.4% Mo alloy in HNO_3 and $\text{HNO}_3\text{-Fe}(\text{NO}_3)_3$ mixtures was determined. Under the experimental conditions employed roughly 3 to 4 moles of acid were consumed per mole of alloy dissolved.

Five- to 15-gram specimens of U-8.4% Mo alloy were completely dissolved in boiling HNO_3 and $\text{HNO}_3\text{-Fe}(\text{NO}_3)_3$ mixtures in 500 ml flasks each fitted with two 21-in.-long condensers. In one series of experiments, the initial HNO_3 concentration was varied from 3 to 11 M and no iron was present. In another series, the initial HNO_3 concentration was 5 M and the iron concentration was varied from 0.25 to 1 M. The uranium concentration in the solutions produced varied from 0.3 to 2 M. In HNO_3 alone 3 to 4 moles of acid were consumed for each mole of alloy dissolved (Table 1). This result appeared to be independent of initial HNO_3 concentration. With no iron present most of the molybdenum precipitated as MoO_3 .

Table 1. Consumption of HNO_3 in the Dissolution of U-8.4% Mo Alloy

Run No.	Initial HNO_3 Conc., M	U Conc. in Resulting Solution, M	moles HNO_3 Consumed / mole metal dissolved
1	3.0	0.39	3.4
2	8.0	1.60	3.6
3	11.0	1.08	4.6
4	11.0	1.98	3.9

The consumption of acid was not affected by the presence of 0.25 to 1 M $\text{Fe}(\text{NO}_3)_3$ (Table 2). In each of these experiments the molybdenum remained in solution through the complexing action of the iron. The acid consumption also appeared to be independent of terminal uranium concentration. It must be recognized that these results do not allow determination of the stoichiometry of the reaction, since the type of condenser used affects the reflux of water, HNO_3 , and nitrogen oxides. It seems reasonable, however, to assume that close to 3 moles of acid will be consumed per mole of 8.4% Mo alloy dissolved if a very efficient condenser were used.

Scouting experiments revealed that neither $\text{Co}(\text{II})$, $\text{Cr}(\text{III})$, nor $\text{Ni}(\text{II})$ in 5 M HNO_3 was as efficient as $\text{Fe}(\text{III})$ for complexing molybdenum.

Table 2. Consumption of HNO_3 in the Dissolution of U-8.4% Mo Alloy in 5 M HNO_3 Containing $\text{Fe}(\text{NO}_3)_3$

Run No.	Initial Fe Conc., M	U Conc. in Resulting Solutions, M	$\frac{\text{moles } \text{HNO}_3 \text{ Consumed}}{\text{mole metal dissolved}}$
5	0.25	0.60	2.7
6	0.50	0.53	2.7
7	0.75	0.65	3.2
8	1.0	0.76	3.3
9	1.0	0.68	3.1
10	1.0	0.88	3.3
11	1.0	0.77	3.5
12	1.0	0.60	3.8
13	1.0	0.53	3.5
14	1.0	0.37	4.3
15	1.0	0.32	4.5

1.1.3 Darex Off-Gas Studies (T. A. Gens)

Evolution of nitrous oxide during Darex dissolution of stainless steel is a problem of major concern because of the explosive potential of nitrous oxide in certain gas mixtures and the difficulty in removing nitrous oxide from the off-gas.⁶

Experiments were made to determine the volume percent nitrous oxide (N_2O) in the off-gas from Darex-type dissolutions of 304 SS as a function of the fraction of total dissolving time (Fig. 2). The off-gas passed through a 6-in-water-cooled condenser before samples were taken. The nitrous oxide composition of the off-gas increased from a maximum of 0.7 vol % in 5 M HNO_3 -2 M HCl to a maximum of about 10 vol % in 3 M HNO_3 -4 M HCl , 2 M HNO_3 -5 M HCl , and 1 M HNO_3 -6 M HCl . In dissolving 304 stainless steel in 4 M HNO_3 -3 M HCl , the maximum nitrous oxide content was about 6 vol %. The maximum volume percent nitrous oxide in all runs was observed when about 30% of the total dissolving time had elapsed.

1.1.4 Zircex Process For Dissolution of Zirconium-bearing Fuels (T. A. Gens)

In the Zircex process, the nonvolatile product from hydrochlorination of U-Zr alloy, consisting mostly of mixed oxides and chlorides of uranium and zirconium, is converted to volatile chlorides by chlorination with

Fig. 2. Nitrous oxide in batch Darex off-gas as a function of stainless steel dissolving time.

carbon tetrachloride vapor in an inert carrier gas.⁷ Because carbon tetrachloride vapor at 600°C proved highly corrosive to most materials of construction,⁸ experiments were made to determine if a lower temperature might be used during chlorination. Samples of residues from engineering-scale STR and EBWR (nonirradiated) hydrochlorinations⁹ were placed in porcelain boats in a heated quartz tube, chlorinated 0.25-1.0 hr at various temperatures, and weight losses were compared.

The initial weight loss with high zirconium (STR) residues at 350°C was found to be approximately one-third that at 600°C (Fig. 3) indicating that a lower chlorination temperature might be feasible. However, with high uranium (EBWR) residue, no reaction was observed at 400°C and a rapid increase in reaction rate occurred when the temperature was increased to 500°C or higher (Fig. 3). Since it will probably be possible to reduce the amount of nonvolatile zirconium compounds produced during Zircex hydrochlorination by carefully purifying the hydrogen chloride before use,⁹ the residues should be high in uranium content and a chlorination temperature of 500°C or higher will probably be required.

An unsuccessful attempt was made to quantitatively recover the uranium from a sample of the high zirconium-STR hydrochlorination product at 375°C. Chlorination with carbon tetrachloride in hydrogen chloride carrier gas was continued for 5 hr, after which 79 wt % of the sample had volatilized. Passage of hydrogen chloride over the remainder of the sample for 1 hr at 600°C removed all but 1.8 wt %, based on the original residue weight. By careful leaching of the remaining material in boiling 5 M HNO₃, a quantity of uranium was dissolved corresponding to 5.4% of the uranium in the hydrochlorination product. The nitric acid-insoluble material remaining contained 0.3% of the uranium in the hydrochlorination product.

An attempt to quantitatively recover the uranium from a sample of the high zirconium-STR hydrochlorination residue by chlorination at 500°C for 1.5 hr was not completely successful. After admitting air for 5 min at 500°C to burn off carbon, the temperature had to be raised to 600°C for 0.1 hr to remove a very small amount of less volatile material, thought to be copper chloride.

The vapor from boiling carbon tetrachloride was used satisfactorily without any carrier gas in one 0.5-hr run to chlorinate high zirconium-STR residue at 565°C. No decomposition products from the carbon tetrachloride were observed.

1.1.5 Dissolution of Niobium in Concentrated Sulfuric Acid (T. A. Gens)

Niobium can be dissolved in refluxing sulfuric acid more concentrated than 14 M (Fig. 4). The dissolution rate increased rapidly with sulfuric acid concentration to 6 mg/cm²-min at 18.3 M H₂SO₄, the point at which the reflux temperature is the maximum. The dissolution rate increased less rapidly as the sulfuric acid (i.e. sulfur trioxide) concentration increased above 18.3 M, probably because the reflux temperature decreases.

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Fig. 3. Chlorination of Zircex hydrochlorination residues with CCl_4 in HCl carrier gas.

Fig. 4. Dissolution of niobium in refluxing sulfuric acid.

1.1.6 Recovery of Uranium and Thorium from Graphite Fuels (M. J. Bradley)

Fifteen-gram (1.2 x 1.4 x 4.5 cm) samples of graphitized uranium-graphite fuel were simultaneously disintegrated and leached with 50 ml of 90% HNO_3 in 4 hr at 25°C. The mixture was filtered, the residue washed with three 25-ml portions of cold water, and the residue divided into two portions. Half was leached again at 25°C with 25 ml of 90% acid; the other half with 25 ml of boiling 70% HNO_3 . Finally the residues were washed once more with 25 ml of cold water. Washing was achieved by contacting the residue on the filter with each portion of water for 15 min. Vacuum filtration was used throughout. The final graphite residue was a -20 mesh powder.

Specimens containing more than 2% uranium were disintegrated and leached almost as efficiently at 25°C as at the boiling point (~103°C). The amount of uranium recovered after the first leach and three washes was only 2 to 3% lower at 25°C than at ~103°C, and, after the second leach, only about 0.3% lower (Table 3). Less than 90% of the uranium was recovered from fuel containing 0.7% uranium after two leaches at 25°C, with 90% acid (Table 3). When boiling 15.8 molar nitric acid was used in the second leach, the uranium recovery from all the fuels studied was independent of the temperature of the first leach with 90% acid between 25°C and the boiling point (~103°C). Disintegration and leaching at 25°C should reduce corrosion and will yield solutions which are light yellow in color. When graphite was digested with 18 M (or greater) nitric acid, wine-red colored solutions were always obtained. The colored material has not been isolated, but presumably is a graphite degradation product.

Large quantities of fuming nitric acid were absorbed by the graphite, in part presumably through formation of the graphite-nitric acid lamellar compound. Since 25 to 30% of the uranium was recovered in the washing steps, high recoveries can be achieved only after thorough washing of the graphite matrix. When vacuum filtration was used for the solid-liquid separation, the amount of uranium recovered in the first water wash was about 1/2 that found in the first leach solution; the second wash contained about one-tenth as much as the first wash, and the third wash about one-tenth that of the second (Table 4, Runs 1, 2, 3, and 5). If the uranium solution recovered in the washing procedure is merely sorbed in the graphite matrix, this would correspond to an approximate sorption of 1 ml of 90% nitric acid solution per gram of graphite and 0.2 ml of water solution per gram. When graphite fuel and 90% nitric acid were placed in a beaker, no liquid was visible after disintegration occurred unless 3 ml of acid had been added for each gram of graphite. Water is a more efficient washing agent than nitric acid (Table 4, Runs 3 and 4). It instantly destroys the graphite-nitric acid lamellar compound¹⁰ which may be present. There is some advantage in washing with nitric acid in that the acid used in the second leach would not be diluted with the water sorbed by the graphite.

Table 3. Effect of Temperature

Fuel Composition Temperature	Uranium Found, %							
	0.7% U		2.6% U		5.4% U		10.2% U	
	25°C	Boiling	25°C	Boiling	25°C	Boiling	25°C	Boiling
90% HNO ₃ 1st Leach + 3 Water Washes	76.8	90.4	94.1	97.0	96.6	98.3	96.4	98.5
90% HNO ₃ { 2nd Leach + 1 Wash	11.1	6.2	5.5	2.5	2.9	1.6	3.3	1.4
	Graphite	12.1	3.3	0.5	0.5	0.47	0.15	0.28
70% HNO ₃ { 2nd Leach ^a + 1 Wash	19.0	5.5	4.9	1.9	3.0	1.3	3.3	1.2
	Graphite	4.1	3.7	1.0	1.1	0.45	0.35	0.29

^aAll 70% leaches were at the boiling point.

Table 4. Effect of Washing

Run No.	Fuel Composition, %	Uranium Found, %					
		90% HNO ₃ 1st Leach, 25°C	1st Water Wash	2nd Water Wash	3rd Water Wash	2nd Leach 25°C	Graphite Residue
1	0.72	49.7	23.8	2.7	0.6	11.1	12.1
2	2.65	57.8	32.0	3.9	0.4	5.5	0.5
3	5.48	64.1	29.8	2.4	0.3	2.9	0.47
4	5.30	65.2	22.4 ^a	7.4 ^a	-	4.8 ^b	0.16
5	10.29	70.6	23.6	2.0	0.2	3.3	0.28

^a 25°C, 90% HNO₃.

^b Boiling, 70% HNO₃.

1.2 Flowsheet Demonstration on Irradiated Fuels (J. R. Flanary, J. H. Goode)

1.2.1 Mini-Darex Facility

The all-glass head end equipment of the Mini-Darex facility has been removed from the hot cell and the cell partially decontaminated to permit installation of the new dissolver-FAT tank and filters on the cell exhaust system and tank.

1.2.2 Immi Hot-Cell Facility

A series of runs was begun to evaluate the performance of the Immi mixer-settlers using a 30% TBP system. Previous runs using 6% TBP and the Foreign Research Reactor TBP-25--type flowsheet, indicated relatively poor efficiency for the extraction and stripping of uranium.

The Nuclear Ship Savannah 1st cycle flowsheet, a modified Purex system, was used for the first test. The relative flow rates and actual stream composition were as follows:

Feed (100 vol): 136 g U/l, 1.36 M HNO_3 , 41 g SS/l, trace Cl^-
Scrub (40 vol): 3.02 M HNO_3
Solvent (150 vol): 30% TBP³
Strip (300 vol): 0.01 M HNO_3

Initial operating conditions chosen for the run were flow rates of 25, 37.5, 10, and 75 ml/min for the feed, solvent, scrub, and strip, respectively; 11 extraction and 6 scrub stages in the A bank operating at 800 rpm impeller speed; and 11 strip stages in the C bank operating at 660 rpm. Actual rates for the first 12 hr of operation were as follows:

	<u>0-5.7 hr</u>	<u>5.7-12 hr</u>
AF	26.2 ml/min	22.2 ml/min
AX	40.0	36.7
AS	7.6	9.5
CX	79.9	77.5

Flowing stream analyses indicate that equilibrium had been established after 12 hr of operation (Table 5).

After sampling the stages, all flow rates were doubled to nominal values of 50, 75, 20, and 150 ml/min for AF, AX, AS, and CX, respectively. Operation of the A bank was satisfactory, but the C bank flooded at the increased flow rates. Reduction of impeller speed in the C bank at 500 rpm temporarily improved operation, but flooding soon reoccurred. A 10% reduction in flow rates permitted operation of the strip bank at a point just under flooding. This indicated the maximum throughput of the C bank was about 225 ml/min under Purex conditions and would thus fix the flow rates for the other 2 banks.

Actual rates for a 6-hr period of operation at the increased flows were 41.4, 68.4, and 156 ml/min for AF, AX, AS, and CX, respectively. Flowing stream samples taken after 3 and 6 hr of operation showed average uranium contents of 0.011, 86.1, 45.4, and 0.008 mg U/ml for the AW, AP, CU, and CW, respectively, and indicated an increase in uranium losses to the raffinate and stripped solvent at the faster flow rates.

Table 6 and Fig. 5 summarize results of stage sampling at the original and increased flow rates. A tremendous buildup of uranium occurred above and below the feed point of the A bank mixer-settler which did not occur in the batch countercurrent experiment. Fig. 6, a McCabe-Thiel diagram plotting the extraction stage data of the Immi mixer-settler run against the batch countercurrent data shows that the first 3 stages were not functioning as extraction stages and that the next 4 stages (i.e. 4-7) were required to do the work of 2 theoretical stages, giving a 50% stage efficiency. Stages 8-11 apparently operated efficiently. Less efficient stripping of uranium also occurred in the stripping bank with the increased flow rates (Table 6).

Table 5. Uranium Content of Flowing Stream Samples NS Savannah Flowsheet - Immi Mixer-Settlers

Running Time, hr	Volume Changes of Solvent		Stream Sampled			
	A Bank	C Bank	AW, mg U/ml	AP, mg U/ml	CU, mg U/ml	CW, mg U/ml
2.6	3.1	0.1	0.016	84.2	46.4	0.017
5.6	6.1	1.8	0.001	82.2	29.7(?)	0.006
8.4	9.2	3.5	0.002	73.7	29.7(?)	0.001
11.4	12.5	5.4	0.006	83.2	42.6	0.002

Table 6. Stage Data-Immi Mixer-Settler NS Savannah 1st Cycle Flowsheet^a

Slow Rate - 72.5 ml/min total flow in A bank, 147.5 ml/min total flow in C bank.
Fast Rate - 130.5 ml/min total flow in A bank, 224 ml/min total flow in C bank.

Stage No.	Slow Rate, Uranium-mg/ml		Fast Rate, Uranium-mg/ml	
	o	a	o	a
6S	-	19.3	84.2	18.6
4S	106	36.9	-	-
2S	108	61.3	95.8	51.6
1E	117	135	104	105
3E	106	109	92.1	104
5E	72.4	33.0	-	-
7E	4.03	0.178	5.26	0.105
9E	0.014	0.001	-	-
11E	0.003	0.002	0.190	0.001
1ST	46.6	40.7	55.3	37.9
3ST	1.22	5.13	-	-
5ST	0.045	0.042	0.165	0.689
7ST	0.017	0.007	-	-
9ST	0.062	0.002	-	-
11ST	0.406(?)	0.005	0.205(?)	0.046

^a Questioned values doubtful; don't agree with flowing stream samples in Table 5.

Fig. 5. Uranium concentration profile NS Savannah flowsheet - Immi mixer-settler.

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Fig. 6. McCabe-Thiel Diagram. 1st cycle extraction - NS Savannah flowsheet, Immi mixer-settlers.

Causes of the buildup of uranium around the feed points of the A and C banks were apparently mechanical, since the chemistry of the flowsheet has been demonstrated to be satisfactory in batch countercurrent experiments and since the composition of all streams were of correct flowsheet value. Possible mechanical causes of maloperation may have been:

- (a) high interface allowing flow of nonequilibrium aqueous into settling sections,
- (b) inadequate contact time in mixing sections,
- (c) impeller design such that there is poor mixing coupled with high pumping rates.

Purex runs¹¹ will be made to afford a comparison with a standard system after a thorough mechanical examination of the initial extraction and scrub stages.

1.2.3 20% Enriched Research Reactor - Second Solvent Extraction Cycle

Batch countercurrent experiments were used to establish equilibrium data for uranium extraction scrubbing, and stripping in the Foreign Research Reactor processing flowsheet. The uranium product from the 1st cycle is continuously adjusted to 2nd cycle feed composition by the addition of 2 M $\text{Al}(\text{NO}_3)_3$ and nitric acid, and fed to the center of the 2A column, in which the uranium is re-extracted by 6% TBP. The organic phase is scrubbed free of fission products and plutonium with a neutral 1.8 M $\text{Al}(\text{NO}_3)_3$ -0.03 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ scrub solution, and cascades to a 2C column, where the uranium is stripped with dilute nitric acid. Table 7 presents the equilibrium data obtained in the experiments, and indicates that about 4.5 extraction and 3 strip stages are required to hold uranium losses to less than 0.01%.

Table 7. Foreign Research Reactor Fuel Processing - Second Solvent Extraction Cycle

Feed (145 vols): 6.59 g U/l, 0.96 M HNO_3 , 1 M $\text{Al}(\text{NO}_3)_3$
 Scrub (29 vols): 1.8 M $\text{Al}(\text{NO}_3)_3$, 0.03 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$
 Solvent (92 vols): 6% TBP
 Strip (58 vols): 0.01 M HNO_3

Extraction Scrub				Stripping			
Stage	Uranium-mg/ml		E_a^o	Stage	Uranium-mg/ml		E_a^o
No.	o	a		No.	o	a	
4S	9.65	0.012	804	1ST	0.49	15.6	0.032
3S	9.92	0.014	719	2ST	0.024	0.77	0.03
2S	9.84	0.022	447	3ST	0.0003	0.03	0.01
1S	9.95	0.026	383	4ST	0.0001	0.0009	0.1
1E	9.84	0.558	17.6				
2E	0.964	0.032	30.5				
3E	0.062	0.001	62.0				
4E	0.003	0.0001	30.0				
5E	0.0001	0.00004	2.5				

1.3 Solvent Extraction Studies (R. H. Rainey, J. G. Moore)

1.3.1 Stripping of Uranium and Thorium from 30% TBP-Amsco

The difficulty in costripping uranium and thorium from 30% TBP Amsco increases with increasing acid in the solvent. The acidity in the solvent following an Acid Thorex first cycle will vary from 0.02 to about 0.2 N. As previously reported,¹² organic feed solutions containing about 45 g/l Th, 2.5 g/l U, and less than 0.01 M HNO_3 can be stripped to less than 0.08% of the uranium in 6 stages by using an equal volume of 0.008 M $\text{Al}(\text{NO}_3)_3$. Similar solutions containing 0.1 and 0.2 M HNO_3 required 7 stages to strip to less than 0.1% of the uranium by contacting with an equal volume of aqueous (Table 8). By increasing the volume of aqueous strip to 1.2 volumes the number of stages required was reduced to 6. Only 4 stages were required if the volume of strip was further increased to 1.5 volumes.

1.3.2 Uranium and Thorium Distribution Coefficient in the TBP- HNO_3 System

Equilibrium data have been determined in order to evaluate flowsheets which have been suggested for processing spent Consolidated Edison fuel. Distribution coefficients are reported for the following three systems: 30% TBP-Amsco, 0.1 to 20 g/l uranium, 5 to 20 g/l thorium, and 0.1 to 0.2 M HNO_3 ; 30% TBP-Amsco, 0.1 to 20 g/l uranium and 0 to 0.2 M HNO_3 ; 2.5% TBP-Amsco, 0 to 60 g/l uranium, and 0 to 7 M HNO_3 . These values are used in McCabe-Thiel diagrams to determine flowsheet conditions. Laboratory countercurrent batch extraction experiments are then used to measure decontamination factors from fission products.

The extraction of uranium, thorium, and nitric acid by 30% TBP-Amsco (Table 9, Fig. 7) together with the data previously reported¹² for the extraction of uranium and thorium not containing acid are used to determine conditions for uranium-thorium partitioning or costripping. In this low concentration range (less than 1 N total nitrate) the extraction of uranium is a function of the total nitrate concentration and did not vary with the cation present. These results are contrary to data which has shown a strong difference in the effect of various nitrate salts in high nitrate systems. Previous data¹³ also demonstrated that at 4.7 N total nitrate, uranium extraction was much higher from an aluminum nitrate than from a nitric acid solution.

In order to strip uranium to high concentration in a minimum of stages, it is necessary to maintain the acidity in the strip column as low as possible. Distribution of uranium between 30% TBP-Amsco and aqueous solutions containing 0.2 M or less nitric acid (Table 10, Fig. 8) demonstrate the large increase in the extraction of dilute uranium with increasing acidity. At 1 g/l uranium in the aqueous phase the uranium in the organic phase increased from 0.01 g/l at no acid to 0.2 at 0.05 M HNO_3 and 1 g/l at 0.2 N HNO_3 . When the solvent is less than 10% saturated with uranium, a log-log plot of the uranium concentration in the organic vs the aqueous gives a straight

Fig. 7. Distribution of uranium between thorium- HNO_3 solutions and 30% TBP-Amsco.

Fig. 8. Distribution of uranium between 30% TBP-Amsco and HNO_3 at low acidities.

Table 8. Effect of Acidity on Costripping Uranium and ThoriumA. Thorium concentration g/liter organic-30% TBP in Amsco; aqueous = 0.008 M $\text{Al}(\text{NO}_3)_3$

Flow Ratio Feed Thorium H^+ M Stage	1 aqueous; 1 organic						1.2 aqueous; 1 organic						1.5 aqueous; 1 organic					
	40.2		42.7		43.1		46.2		45.5		48.0		46.1		43.0			
	0.005		0.11		0.22		0.003		0.13		0.200		0.001		0.21 N			
	aq.	org.	aq.	org.	aq.	org.	aq.	org.	aq.	org.	aq.	org.	aq.	org.	aq.	org.	aq.	org.
1	44.2	8.45	40.9	10.7	43.8	13.0	38.6	6.14	35.7	8.04	38.1	23.4	29.9	3.31	27.0	4.89		
2	9.12	0.275	11.5	0.55	12.6	0.725	4.82	0.082	7.19	0.190	8.63	0.107	2.10	0.034	3.31	0.085		
3	0.468	0.016	0.748	0.015	0.918	0.024	0.119	*	0.169	0.007	0.217	0.005	0.023	0.012	0.040	0.037		
4	0.110	*	0.031	0.007	0.110	0.006	0.024	*	0.005	*	0.006	0.006	*	0.009	*	0.014		
5	0.015	*	0.006	*	0.008	*	*	*	*	*	*	*	*	0.005	*	0.014		
6	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*		
7	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*		

* <0.005 g/liter thorium.

B. Uranium Concentration g/liter

Feed g/l	2.4		2.56		2.28		2.23		2.61		2.23		2.74		2.19	
	aq.	org.	aq.	org.	aq.	org.	aq.	org.	aq.	org.	aq.	org.	aq.	org.	aq.	org.
1	2.47	9.96	2.28	10.2	1.98	10.7	2.46	8.49	2.41	9.96	2.36	10.2	1.75	4.32	1.49	5.15
2	10.7	9.29	10.5	12.7	10.4	15.0	7.34	3.94	8.22	6.71	8.38	7.55	2.95	0.430	3.49	1.24
3	9.96	3.33	12.4	5.68	14.5	8.05	3.04	0.333	5.24	0.915	6.24	1.09	0.404	0.031	0.781	0.068
4	3.07	0.25	5.38	0.91	7.46	1.62	0.214	0.082	0.760	0.120	0.917	0.099	0.023	0.004	0.050	0.018
5	0.280	0.055	0.81	0.094	1.64	0.11	0.045	0.040	0.055	0.046	0.081	0.027	0.002	*	0.012	*
6	0.084	0.002	0.094	0.046	0.044	0.115	0.021	0.005	0.023	0.008	0.030	0.005	*	*	*	*
7	0.023	0.001	0.038	0.008	0.040	0.005	0.004	*	0.004	0.001	0.003	*	*	*	*	*

* <0.0005 g/liter uranium.

Table 9. Extraction of Thorium Nitrate Uranium Nitrate and Nitric Acid by 30% TBP-Amsco

Initial aqueous phase = ~5 g/l Th; ~0.1 M HNO₃

U _a	U _{org}	UDC _a ^o	Th _a	Th _{org}	ThDC _a ^o	H ⁺ _a	H ⁺ _{org}	H ⁺ DC _a ^o
0.074	0.030	0.41	4.88	0.085	0.017	0.085	0.015	0.176
0.622	0.305	0.49	5.02	0.085	0.017	0.085	0.013	0.153
1.73	1.23	0.71	5.03	0.090	0.018	0.075	0.015	0.20
2.84	2.52	0.89	5.05	0.107	0.021	0.085	0.017	0.20
5.26	5.04	0.96	5.14	0.144	0.028	0.10	0.032	0.32
9.62	9.77	1.02	5.03	0.200	0.040	0.10	0.055	0.55
~10 g/l Th; ~0.1 M HNO ₃								
0.059	0.040	0.68	9.50	0.270	0.0284	0.085	0.025	0.29
0.510	0.405	0.79	9.50	0.296	0.0312	0.090	0.015	0.17
1.43	1.71	1.20	10.0	0.326	0.0326	0.095	0.025	0.27
2.32	2.93	1.26	9.54	0.318	0.0333	0.087	0.025	0.29
4.58	5.99	1.31	9.48	0.371	0.0391	0.095	0.04	0.42
8.44	12.0	1.42	9.48	0.444	0.0468	0.10	0.07	0.70
~20 g/l Th; ~0.1 M HNO ₃								
0.045	0.053	1.18	18.5	1.30	0.070	0.085	0.025	0.29
0.352	0.753	2.14	18.7	1.32	0.071	0.085	0.02	0.24
1.02	2.04	2.00	18.7	1.33	0.071	0.087	0.025	0.29
1.70	3.52	2.07	18.5	1.36	0.074	0.087	0.03	0.34
3.33	6.90	2.07	17.9	1.32	0.074	0.087	0.05	0.57
6.56	13.30	2.03	18.5	1.40	0.076	0.092	0.07	0.76
~5 gm/l Th; ~0.2 M HNO ₃								
0.037	0.050	1.35	4.94	0.202	0.041	0.18	0.025	0.14
0.510	0.50	0.98	4.93	0.205	0.042	0.18	0.025	0.14
1.24	1.83	1.48	4.96	0.222	0.045	0.18	0.03	0.17
2.08	3.00	1.45	4.97	0.228	0.046	0.18	0.035	0.19
4.15	5.78	1.39	4.97	0.252	0.051	0.19	0.045	0.24
7.86	11.4	1.45	4.94	0.298	0.060	0.20	0.075	0.38

Table 9. (Cont.)

U_a	U_{org}	UDC_a^O	Tha	Thorg	ThDC $_a^O$	H^+_a	H^+_{org}	$H^+DC_a^O$
$\sim 10 \text{ g/l Th; } \sim 0.2 \text{ M HNO}_3$								
0.034	0.053	1.56	9.65	0.559	0.058	0.17	0.04	0.24
0.400	0.500	1.25	9.59	0.574	0.060	0.17	0.04	0.24
1.10	2.10	1.91	9.65	0.689	0.071	0.18	0.04	0.22
1.84	3.26	1.77	9.56	0.618	0.065	0.17	0.04	0.24
3.52	6.26	1.78	9.56	0.669	0.070	0.18	0.06	0.33
6.74	13.2	1.96	9.50	0.698	0.073	0.18	0.09	0.50
$\sim 20 \text{ g/l Th; } \sim 0.2 \text{ M HNO}_3$								
0.037	0.058	1.57	17.2	1.99	0.116	0.17	0.08	0.47
0.306	0.625	2.04	17.7	2.02	0.114	0.17	0.07	0.41
0.820	2.34	2.85	18.2	2.03	0.112	0.17	0.085	0.50
1.36	3.58	2.63	18.1	1.99	0.110	0.17	0.09	0.53
2.94	7.03	2.39	17.3	1.96	0.113	0.17	0.12	0.71
5.44	15.0	2.76	17.0	1.97	0.116	0.17	0.19	1.12

Table 10. Extraction of Uranium from Nitric Acid Solutions
with 30% TBP-Amsco

(Equal Volumes of Feed and Solvent)

U_{Feed}	U_a	U_o	DC_a^O	U_{Feed}	U_a	U_o	DC_a^O
No Acid in Feed				0.1 M HNO_3			
0.1	0.094	<0.0002	<0.002	0.011	0.009	0.003	0.33
0.5	0.508	<0.001	<0.002	0.100	0.085	0.029	0.34
1.0	1.02	0.005	0.005	1.05	0.786	0.325	0.41
5.0	4.87	0.380	0.078	11.2	7.00	4.17	0.60
10.0	8.98	1.52	0.169				
20.0	15.5	5.68	0.366				
0.05 M HNO_3 in Feed				0.2 M HNO_3			
				0.012	0.006	0.006	1.0
0.01	0.0104	0.0016	0.15	0.101	0.062	0.06	0.97
0.10	0.088	0.008	0.09	1.04	0.539	0.517	0.96
1.03	0.911	0.156	0.17	11.3	5.42	5.94	1.10
11.1	8.15	2.68	0.33				

Table 11. Extraction of Uranium from Nitric Acid Solutions with
2.5% TBP-Amsco

(Equal volumes of feed and solvent)

U_{Feed} g/l	U_A g/l	U_O g/l	DC_a^O	U_{Feed} g/l	U_A g/l	U_O g/l	DC_a^O
No acid in feed				3.0 N HNO_3 in feed			
0.980	1.01	<0.001	<0.001	-	0.069	0.088	1.27
2.98	3.01	<0.001	<0.0003	-	0.513	0.508	0.99
4.90	4.90	0.004	0.0008	-	0.811	0.816	1.00
10.1	9.94	0.032	0.0032	-	1.91	1.66	0.87
20.2	20.2	0.190	0.0094	-	4.61	3.06	0.664
29.0	28.1	0.424	0.015	-	8.42	4.16	0.494
38.4	37.3	0.826	0.022	-	13.7	5.26	0.384
49.6	48.5	1.42	0.029	-	20.0	5.84	0.292
57.8	54.6	1.99	0.036				
0.5 N HNO_3 in feed				4.1 N HNO_3 in feed			
0.1	0.103	0.006	0.058	0.1	0.039	0.065	1.67
0.3	0.290	0.019	0.066	0.3	0.123	0.197	1.60
0.5	0.474	0.031	0.065	0.5	0.212	0.326	1.54
1.0	0.974	0.070	0.072	1.0	0.443	0.599	1.35
5.0	4.76	0.337	0.071	5.0	2.70	2.54	0.94
10.0	9.74	0.682	0.070	10.0	6.04	4.09	0.68
20.0	18.4	1.33	0.072	20.0	14.8	5.90	0.40
1.0 N HNO_3 in feed				5.2 N HNO_3 in feed			
0.1	0.085	0.018	0.21	0.1	0.037	0.060	1.62
0.3	0.254	0.056	0.22	0.3	0.125	0.190	1.52
0.5	0.411	0.093	0.23	0.5	0.202	0.300	1.49
1.0	0.822	0.173	0.21	1.0	0.409	0.594	1.45
5.0	4.22	0.764	0.18	5.0	2.62	2.51	0.96
10.0	8.51	1.52	0.18	10.0	6.04	3.98	0.66
20.0	16.9	2.76	0.16	20.0	14.4	5.73	0.40
2.0 N HNO_3 in feed				7.25 N HNO_3 in feed			
-	0.11	0.096	0.856	0.1	0.046	0.055	1.20
-	0.768	0.447	0.583	0.3	0.146	0.165	1.14
-	1.30	0.70	0.546	0.5	0.236	0.265	1.12
-	2.96	1.42	0.480	1.0	0.487	0.523	1.07
-	6.58	2.58	0.392	5.0	2.90	2.17	0.75
-	11.4	3.68	0.323	10.0	6.64	3.57	0.54
-	16.8	4.47	0.266	20.0	15.6	5.02	0.32

line for each concentration of nitric acid. Literature values¹⁴ have demonstrated that at acid concentrations above 0.5 M the slope of this line is about 1. When no acid was present the slope was about 2. The present data show that at 0.2 M HNO_3 the slope is 1 and increases to only 1.2 at 0.05 M HNO_3 .

A cost evaluation of the storage of radioactive waste solutions¹⁵ has pointed out the desirability of using volatile salting agents in solvent extraction processes. All solvent extraction processes in present use which extract with less than 10% TBP-Amsco have aluminum nitrate as a salting agent. The 2.5% TBP flowsheet for the final purification of the U-233 product previously developed¹⁶ resulted in 58 liters of aqueous waste containing 2.0 M $\text{Al}(\text{NO}_3)_3$ per kilogram of U-233 processed. Equilibrium data for the extraction of uranium with 2.5% TBP from solutions containing 0 to 7 M HNO_3 (Table 11, Fig. 9), show that a maximum extraction of uranium is obtained when the aqueous is about 4 M HNO_3 . At 2.5 g/l uranium in the organic phase the distribution coefficient of uranium is nearly 1. These data indicate the feasibility of a nitric acid salted 2.5% TBP flowsheet (Fig. 10).

1.3.3 Final Purification Cycle of U-233

A 2.5% TBP decontamination cycle using nitric acid salting has been developed for U-233 which had been partitioned in an Acid Thorex first solvent extraction cycle. A laboratory countercurrent batch experiment evaluating this flowsheet showed decontamination factors from ruthenium, zirconium-niobium, protactinium, and thorium of 2,000, 200, 10 and 40, respectively (Fig. 10). Uranium loss to the aqueous phase was 0.07%. Flowsheet conditions were:

Feed: 6.1 g/l U, 1.6 g/l Th, 2.14 M HNO_3
Scrub: 2 M HNO_3
Acid: 13 M HNO_3 at 4th extraction stage
Solvent: 2.5% TBP-Amsco
Volume Ratio: feed/acid/scrub/solvent = 1/.5/1.2/6
Stages: 7 extraction, 4 scrub

Elimination of the salting acid and increasing the acid in the feed to 5 M and in the scrub to 3.3 M and decreasing the solvent to 3 volumes increased the decontamination factors from ruthenium, zirconium-niobium, and protactinium to 3,500, 350, and 20, respectively. The uranium loss, however, increased to 0.16%.

Fig. 9. Distribution of uranium between 2.5% TBP-Amsco and HNO_3 .

Fig. 10. Conditions for McCabe-Thiele diagram.

1.4 Corrosion Studies (Work done by members of the Reactor Experimental Division, ORNL) (W. E. Clark)

Work has continued on the corrosion of titanium under Thorex boildown conditions, on Ni-o-nel in Zirflex systems, and on various alloys in Zircox scouting tests. In addition, scouting tests were run on various alloys in boiling 10 M LiCl-0.1 M HCl (for transplutonium element recovery equipment), and titanium and Ti-0.2% Pd alloy were scouted in acid-high fluoride solutions.

1.4.1 Thorex Process

Three Thorex feed adjustment tests are presently in progress. These consist of (1) total reflux of the initial solution, (2) repeated boildowns of the initial solution, and (3) total reflux of the bottoms from the repeated boildowns. The solution used in the first two tests consists of 9.5 M HNO₃, 0.04 M NaF, 0.04 M Al(NO₃)₃, 0.06 M UO₂(NO₃)₂, 0.8 M Th(NO₃)₄, 0.1 M H₂BO₃, 0.0025 M HCl, 0.004 M Fe(NO₃)₃. Boildown tests result in concentration of the nonvolatile constituents by a factor of 3-1/3.

No attack has been observed on Titanium-45A weld specimens or steam tubes immersed in any of the solutions. Condenser specimens in the total reflux tests have significant corrosion rates which appear to be due primarily to attack in the weld and heat-affected zones. The rate of attack on the condenser above the initial FAT solution increased with exposure time as is to be expected from the increasing surface area resulting from aggressive attack (Table 12). The condenser above the final solution shows no indication of an accelerated rate with time. The titanium cover, steam tubes, and condenser suffered a localized attack in welds; however, the penetration does not appear to be as extensive as that observed on the cover used for a solution which did not contain boron as reported last month.¹⁷ This conclusion will be checked by metallographic examination. Specimens exposed during successive boildowns have thus far shown no sign of localized attack.

The total reflux tests probably represent the worst possible case. Conditions during these tests do not change as will be the case during actual reprocessing. The successive boildown tests will more nearly duplicate the latter. At present these tests have run for less than 100 hr of total exposure time.

In order to evaluate the possibility of severe corrosion if fluoride should become concentrated during rectification of vapors from the Thorex boildown, titanium specimens were exposed in and above solutions 0.05 M and 0.005 M in HF and from 3 to 15 M in HNO₃. The results (Table 13) indicate highly corrosive conditions in the presence of 0.05 M fluoride, the degree of corrosion decreasing with increasing concentration of nitric acid. In the presence of 0.005 M fluoride, the attack first increases with increasing acid, reaching a maximum of about 13 mils/mo at about 6 M acid. Further increase in nitric acid concentration results in decreased

Table 12. Corrosion Rates of Titanium-45A Weld Specimens in Thorex Feed Adjustment Tests

Specimen Position	Corrosion Rate (mpm)				
	168 hr	336 hr	504 hr	672 hr	840 hr
A. Total Reflux of Initial FAT Solution ^a					
C ^b	Neg.	0.27	0.40	0.55	0.71
	0.02	1.31	0.41	0.58	0.62
V	g	0.05	0.04	0.07	0.05
	g	0.06	0.07	0.21	0.18
I	g	g	g	g	g
	g	g	g	g	g
S	g	g	g	g	g
	g	g	g	g	g

B. Total Reflux of Bottoms^c from Boildown Tests

Specimen Position	Corrosion Rate (mpm)		
	168 hr	336 hr	504 hr
C ^b	0.44	0.40	0.34
	0.56	0.48	0.40
V	g	0.01	g
	0.01	0.01	0.01
I	g	g	g
	g	g	g
S	g	g	g
	0.01	g	g

^a 9.5 M HNO₃, 0.04 M NaF, 0.04 M Al(NO₃)₃, 0.06 M UO₂(NO₃)₂, 0.8 M Th(NO₃)₄, 0.1 M H₃BO₃, 0.0025 M HCl, 0.004 M Fe(NO₃)₃.

^b Condenser specimens.

^c 1.0 M HNO₃, 0.13 M NaF, 0.13 M Al(NO₃)₃, 0.20 M UO₂(NO₃)₂, 2.6 M Th(NO₃)₄, 0.33 M H₃BO₃, 0.008 M HCl, 0.013 M Fe(NO₃)₃.

Table 13. Corrosion Rates of Titanium-45A in Various Mixtures of Nitric and Hydrofluoric Acid

(Test period: 24 hr)

HNO ₃ Concentration M	Corrosion Rate (mpm)					
	0.05 M HF			0.005 M HF		
	V	I	S	V	I	S
3.0				0.1	4.8	5.0
				0.2	5.2	5.0
6.0	0.6	147	149	0.8	8.3	12.2
	0.4	136	121	0.8	7.9	12.9
9.0	4.6	49.5	56.5	1.3	6.1	9.1
	3.7	42.6	71.3	1.6	6.7	9.1
12.0	4.6	51.8	17.7	1.1	4.6	3.8
	4.2	48.1	17.4	1.3	2.9	3.4
15.0	4.6	23.1	14.8	1.1	3.8	3.7
	5.9	26.2	15.6	1.0	2.7	3.1

corrosion, doubtless due to passivation by the nitric acid. It is not unlikely that minor inhomogeneities in the metal (e.g. welds vs base metal) will result in accelerated localized corrosion, particularly when the titanium is in the near-passive condition.

The average composition of distillate from 6 Thorex FAT boildowns was 7.24 M HNO₃, 0.005 M H₃BO₃, 0.0006 M F⁻ and less than 1 ppm Al. Previous investigations¹⁸ indicate that the first fractions distilled in the course of the boildown are approximately 6 M in HNO₃ and approximately 0.0015 M in F⁻. Whether or not this composition corresponds closely to that of the condensate under total reflux has not yet been established. Small amounts of boron corresponding to the concentration found in the FAT distillate will be added to Thorex rectifier solutions for further study.

The effects on the solution-phase corrosion rate of titanium caused by increasing the fluoride concentration in 13 M HNO₃ and the effect of increasing the nitric acid concentration at 0.05 M HF are shown graphically in Fig. 11.* Rates plotted are for specimens exposed in the solution phase. The abnormally high rates observed on interface specimens (Table 13) appear to be associated with the higher fluoride concentrations.

In Thorex rectifier tests with Type 309 stainless steel welded with Type 308L rod, the welds were preferentially attacked to such an extent that a firm comparison of the corrosive effects of the various solutions could not be made. These experiments will be repeated using unwelded specimens to determine optimum concentrations, and preferred welding techniques can then be ascertained.

* The corrosion rate used for 13 M HNO₃-0.05 M F⁻ was taken from BMI-1375¹⁹.

Fig. 11. Effect of fluoride and nitric acid concentration on the solution phase corrosion of titanium in HNO_3 - HF mixtures.

1.4.2 Zirflex Process

The beneficial effect of H_2O_2 addition on the corrosion of Ni-o-nel in Zirflex dissolver solution¹⁷² was confirmed and the effect measured more precisely by exposing Ni-o-nel specimens in flowing dissolver solution. The results (Table 14) indicate that the rate in fresh, flowing solution is only 1.3-1.4 mil/mo. The reason for the abnormally high rate of 4.6-5.5 observed at the interface is not entirely clear.

A series of 3-hr experiments was run to determine the effect of various amounts of dissolved Zircaloy-2 on the corrosion rate of Ni-o-nel in boiling 6.0 M NH_4F -1.0 M NH_4NO_3 . The required amount of Zircaloy was placed in Zirflex decladding solution and refluxed until it dissolved. The solution was then cooled, the corrosion specimens were inserted, and the solution was refluxed for an additional 3 hr. Specimens were repolished after each test. The results (Table 15, Fig. 12) indicate that the presence of dissolved zirconium has little effect on the corrosion rate until the concentration reaches 0.4 M, after which the rate drops from approximately 32 to about 1 mil/mo. The cause of the initial rise in corrosion rate from about 29 to 31-35 mils/mo as zirconium concentration increases from 0.1 to 0.4 M is not understood but the effect appears to be real.

Table 14. Corrosion of Ni-o-nel in a Boiling 6.0 M NH_4F -1.0 M NH_4NO_3 -0.003 M H_2O_2 Solution

(Test period 24 hr; fresh solution added at a rate of 11.1 ml/min; volume of solution in test vessel approximately 500 ml)

	Vapor	Interface	Solution
Corrosion rate (mpm)	0.5	4.6	1.3
	0.6	5.5	1.4

Table 15. Corrosion Rates of Ni-o-nel in Boiling 6.0 M NH_4F -1.0 M NH_4NO_3 Containing Various Amounts of Dissolved Zircaloy-2

(Test period: 3 hr)

Zr Concentration M	Corrosion Rate (mpm)		
	Vapor	Interface	Solution
0	0.4, g	18.6, 18.0	28.9, 28.9
0.1	0.8, 0.9	16.3, 20.0	29.4, 30.0
0.2	0.2, 0.5	18.5, 19.9	34.5, 31.2
0.4	0.6, 1.6	22.9, 21.4	34.6, 31.0
0.5	0.3, 0.1	5.2, 5.7	11.1, 11.4
0.6	0.2, 0.1	0.3, 0.1	0.1, 0.1
0.8	0.8, 0.8	1.1, 0.8	1.1, 1.2

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Fig. 12. Corrosion Rate of Ni-o-nel
in Boiling 6.0M NH_4F -1.0M NH_4NO_3
Containing Various Amounts of Dissolved
Zirconium.

Table 16. Corrosion Rates of Ni-o-nel in Boiling
2.4 M NH_4F -0.7 M NH_4NO_3

Time (hr)	Corrosion Rate (mpm)		
	Vapor	Interface	Solution
3	1.0, 0.9	2.4, 2.7	2.4, 2.5

In an attempt to determine whether the large decrease in corrosion rate observed is due to inhibition of the reaction by fluozirconate or by simple diminution of free fluoride by complexing, Ni-o-nel specimens were exposed to boiling 2.4 M NH_4F -0.7 M NH_4NO_3 solution.* The results (Table 16) indicate maximum rates of 2.4 to 2.7 mils/mo, intermediate between those obtained in solutions containing 0.5 M and 0.6 M zirconium. Since this region corresponds to the very steep portion of the curve (Fig. 12), it appears likely that the reduction of rate is due entirely to the complexing action of the zirconium.

1.4.3 Darex-Purex Waste Solutions

The exposure of welded Type 347 stainless steel specimens to a simulated Darex-Purex waste solution is being conducted at 80 and 65°C to determine whether a stabilized steel will resist the intergranular effects previously observed on Type 304L stainless steel. After 672 hr in the test solution containing 5.0 M HNO_3 , 1.82 M stainless steel and 100 ppm Cl^- , there was intergranular cracking at both temperatures. No intergranular corrosion has been observed at any temperature in the low-acid solution which contains only 2.0 M HNO_3 instead of 5.0 M. The Type 304L specimens in the low-acid solution appear to be in excellent condition at all three temperatures (Table 17 and 18).

1.4.4 Zircex Process

Scouting tests were run in the Zircex hydrochlorinator using the following modified procedures in the carbon tetrachloride portion of the hot cycle. First, air was bubbled through carbon tetrachloride at room temperature and then passed over the specimens in a quartz tube held at 600°C. In another test, carbon monoxide (a product of the chlorination process) was added to nitrogen saturated with carbon tetrachloride in an equimolar quantity to the carbon tetrachloride and passed over the specimens in a quartz tube at 600°C. Prior to saturation the nitrogen was purified by passing it through copper turnings at 400°C. The results (Table 19) indicate relatively little improvement in rates due to the presence of the carbon monoxide. For example, rates for Nichrome V were 56-48 and 25-21 mils/mo for the two CO cycles vs 56-63 and 41-46 mils/mo for cycles without CO.¹⁷ Due to the scatter normally obtained

* This solution contains the concentrations of nitrate and free fluoride expected after the concentration of zirconium has reached 0.6 M, assuming the dissolution reaction to be:

Table 17. Corrosion Rates of Welded Type 347 Stainless Steel Specimens in Simulated High-Acid Darex-Purex Waste Solutions^a

Specimen Position	Corrosion Rate (mpm)							
	168 hr		336 hr		504 hr		672 hr	
	65°C	80°C	65°C	80°C	65°C	80°C	65°C	80°C
V	0.04	0.06	0.02	0.04	0.02	0.04	0.02	0.03
	0.04	0.05	0.02	0.04	0.02	0.03	0.01	0.03
I	0.08	0.31	0.08	0.31	0.08	0.30	0.08	0.31
	0.08	0.30	0.08	0.31	0.08	0.31	0.08	0.32
S	0.10	0.40	0.11	0.43	0.11	0.46	0.11	0.52
	0.10	0.39	0.10	0.42	0.11	0.45	0.11	0.50

^a5.0 M HNO₃, 1.82 M stainless steel, 100 ppm Cl⁻

Table 18. Corrosion Rates of Welded Types 347 and 304L Stainless Steel in Simulated Low-Acid Darex-Purex Waste Solutions^a

Specimen Position	Alloy	Corrosion Rate (mpm)					
		168 hr			336 hr		
		50°C	65°C	80°C	50°C	65°C	80°C
V	347	0.02	0.02	0.04	0.01	0.02	0.03
	347	0.02	0.03	0.04	0.01	0.02	0.03
	304L	0.01	0.01	0.03	0.01	0.02	0.02
	304L	Neg.	0.02	0.02	0.01	0.01	0.02
I	347	0.02	0.05	0.14	0.02	0.05	0.16
	347	0.02	0.05	0.17	0.01	0.05	0.16
	304L	0.01	0.03	0.12	0.01	0.03	0.12
	304L	0.01	0.04	0.11	0.01	0.03	0.12
S	347	0.02	0.07	0.26	0.02	0.06	0.25
	347	0.03	0.07	0.24	0.02	0.06	0.24
	304L	0.02	0.04	0.17	0.02	0.04	0.19
	304L	0.02	0.05	0.17	0.01	0.04	0.19

^a2.0 M HNO₃, 1.82 M stainless steel, 100 ppm Cl⁻.

Table 19. Corrosion of Various Alloys in Modified Carbon Tetrachloride Zircex Cycles at 600°C (2-hr tests)

Alloy	Corrosion Rate (mpm)			
	Air as Carrier	N ₂ + CCl ₄ + CO		
		1st Cycle	2nd Cycle	
Illium-R	44.0, 30.0	71.0, 66.0	57.0, 43.0	
Hastelloy-C	43.0, 66.0	48.0, 18.0	43.0, 35.0	
Nichrome-V	10.0, 11.0	56.0, 48.0	25.0, 21.0	
Inconel	29.0, 41.0	61.0, 13.0	17.0, 48.0	
Inor-8	27.0, 58.0	49.0, 36.0	10.0, 46.0	
Durimet-20			221.0 260.0	

in the data there is some question as to the validity of the improvement shown with CO. The results obtained with air indicate lower corrosion rates on Nichrome V, but the use of air in the process is not feasible since its use would materially retard the chlorination of zirconium.

Scouting tests were run on several other alloys using the complete Zircex cycle (Table 20). The lowest rates observed were on Chlorimet-2 (5-18 mils/mo) and Type 316 stainless steel (19-21 mils/mo).

Table 20. Corrosion of Various Alloys in a Zircex Cycle^a at 600°C

Alloy	Corrosion Rate (mpm)
S-816	38.0, 20.0
Chlorimet-2	18.0, 5.0
Hastelloy-B	46.0, 47.0
Silicon carbide ^b	2640
316 stainless steel	19.0, 21.0
329 stainless steel ^c	210, 216

^aHCl for 11 hr followed by nitrogen-containing carbon tetrachloride vapor for 1 hr, oxygen 5 min., nitrogen plus carbon tetrachloride for 1 hr. Total cycle time, 13 hr.

^b"KT self-bonded silicon carbide."

^cHeated 12 hr at 1350°F; cooled in furnace.

1.4.5 Transuranium Separation Process

Screening tests have been completed with 12 materials which might be used in the construction of an evaporator in the recovery process for americium and curium. The test environment was one simulating the final conditions in an evaporator where a lithium chloride solution containing

americium, curium, rare earths, and possibly some free hydrochloric acid would be evaporated to a concentration of 10 M LiCl and 2 g/liter of americium-curium.

Single specimens of the 12 alloys were exposed in boiling 10 M LiCl solution containing 0.1 M HCl for a period of 24 hr. The boiling point of the solution was approximately 128°C. Though in actual practice some peroxide would be present in the process solution, the preliminary tests were made without peroxide but with oxygen bubbling through the solution. Penetration rates (Table 21) indicate that of the alloys tested in the first 24-hr period, Chlorimet-2 (a cast alloy), Hastelloy-A, Hastelloy-B, and Zircaloy-2 showed rates of 11 mils/mo or less. Two additional 24-hr tests were run on these four alloys in the oxygenated, boiling lithium chloride-hydrochloric acid solution. Hastelloy A continued to give the best performance of any material tested, with rates less than 1 mil/mo, followed by Chlorimet-2 (0.9-1.2 mils/mo) and Hastelloy B (4.5-10.4 mils/mo) (Table 22). Tests will be continued on these three alloys. Zircaloy-2 will be dropped from consideration because of the increase in corrosion rate with number of cycles (from 7.8 to 19.0 mils/mo over 1-3 cycles).

Table 21. Corrosion of Prospective Evaporator Materials
During a 24-hr Period at 128°C in Oxygenated
10 M LiCl-0.1 M HCl Solution

Material	Penetration Rate (mpm)
Chlorimet-2	0.9
Chlorimet-3	35.4
Durichlor	11.7
Durimet-20	178.0
Hastelloy-A	0.4
Hastelloy-B	10.4
Haynes-25	349.0
Inconel	388.0
Monel	554.0
Multimet	444.0
Worthite	222.0
Zircaloy-2	7.8

Table 22. Corrosion of Promising Evaporator
Materials by Oxygenated 10 M LiCl-0.1 M HCl Solution
at 128°C

Material	Cumulative 24-hr Cycles	Cumulative Penetration Rate (mpm)
Chlorimet-2	1	0.9
	2	1.2
	3	1.1
Hastelloy-A	1	0.4
	2	0.8
	3	0.8
Hastelloy-B	1	10.4
	2	6.1
	3	4.5
Zircaloy-2	1	7.8
	2	14.9
	3	19.0

1.5 Radiation Damage to Solvents and Diluents (Work performed at Stanford Research Institute on Subcontract 1081) (W. Davis, Jr.)

Since the initiation of this subcontract on January 1, 1957, many studies have been made of the effects of nominal 1 Mev electron radiation on solutions of TBP in Amsco 125-82 because such solutions are used as extractants in the ORNL pilot plant. Since January 1, 1957, three different batches of Amsco 125-82 were used, two from ORNL and one purchased directly from the Oakland, California, office of the American Mineral Spirits Company. Discrepancies in results of irradiation experiments during this time initiated a detailed examination of the uniformity of the three batches of diluent. From this examination several significant differences from batch to batch were found (Table 23): (1) the degree of carbon-carbon bond unsaturation is 0.1% for batch 2 vs 0.5% for batch 3; (2) the radiolysis yield, G, for unsaturation and gas formation is less with batch 3 than with batches 1 or 2; (3) the yields of gas and acid from 1 M TBP solutions in the various batches are lower with batch 3 than with batches 1 or 2. These and other differences summarized in Table 23 show that the three different batches of Amsco 125-82 behaved differently enough to warrant designating them as significantly different diluents.

Table 23. Comparison of Three Lots of Amsco 125-82 Used at Stanford Research Institute

	Lot Number		
	1	2	3
Origin of Lot	ORNL	ORNL	American ^a Mineral Spirits Company
Quantity of Lot, gal	5	5	10
Date Received at SRI	Jan. 1957	July, 1958	May, 1959
Inclusive dates of use at SRI	3/57-8/58	8/58-9/59	9/59-date
PROPERTIES			
Density, g/ml	0.73-0.74	-	0.80
Unsaturation, %	-	0.1	0.5
Gas Chromatography			
Retention Time, min	1.5-4.5	-	3-9
RADIATION YIELDS, G, molecules/100 ev - AS RECEIVED DILUENT			
G _{c=c} , Liquid Phase	-	3.5	2.8
G (Total Gas)	4.6	2.7	1.8
G(CH ₄)/G (H ₂)	0.22	-	0.03
RADIATION YIELDS, G, molecules/100 ev - 1 M TBP IN DILUENT			
G(Gas)	~3.4	2.0	1.7
G(Acid)	1.33	1.18	0.98

^aOakland, California branch.

2.0 WASTE TREATMENT (J. T. Roberts)

2.1 Evaporation and Calcination of Purex Waste (H. W. Godbee, F. R. Clayton, P. S. Lawson)

A synthetic Purex 1WW waste (Table 24) to which had been added sodium and calcium was evaporated and calcined to 900°C. The experimental apparatus (Fig. 13) consisting of a feed system, a calcination vessel and furnace, and an off-gas handling system has been described previously.²⁰

Table 24. Composition of Simulated Purex 1WW Concentrate (Molarity)

H ⁺	NO ₃ ⁻	SO ₄ ⁻²	Na ⁺	Al ⁺³	Fe ⁺³	Cr ⁺³	Ni ⁺²	Ru
5.6	6.1	1.0	0.6	0.1	0.5	0.01	0.01	0.002

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Fig. 13. Apparatus for calcining wastes and scrubbing volatile ruthenium from off-gas.

Sodium was added as 50% NaOH solution (62.6 ml/liter of waste) and calcium as $\text{Ca}(\text{OH})_2$ (14.8 g/liter of waste). The criteria for addition of sodium and calcium are that the equivalents of sodium plus calcium be greater than the equivalents of sulfate, to prevent sulfate volatility, and that the equivalents of sulfate be greater than the equivalents of sodium, to prevent sodium volatility.

A volume reduction factor, volumes of feed/volume of solid residue, equal to 8.4 was obtained. The solid residue had an apparent density of 1.56 g/ml which is equivalent to a porosity of 48%. The condensate, residue, and off-gas contained 87, 11, and 0.5%, respectively, of the initial weight of feed. The condensate and off-gas contained 98 and 2%, respectively, of the initial nitrate in the waste and 0.71 and 0.02%, respectively, of the sulfate originally present in the waste. Analyses of the solid residue are not yet available.

Approximately 5 liters of a noncondensable off-gas were produced per liter of Purex 1WW concentrate. Analysis of this gas by gas chromatography indicated that the gas contained about 35 volume % O_2 , 0.1% N_2O , 0.1% NO_2 , and the balance nitrogen. Presumably, the gas is rich in oxygen because the nitrogen dioxide (NO_2), from the decomposition of nitrate salts, is more readily absorbed in the packed column than the oxygen.

2.2 Thermal Conductivity of Calcined Wastes (H. W. Godbee)

Variation of thermal conductivity, k , with temperature has been determined experimentally for the calcined Purex 1WW waste described above. The measurements showed that k varied from 0.210 Btu/hr/ft. 2 °F at 230°F to 0.311 Btu/hr/ft. 2 °F at 1329°F (Fig. 14).

Thermal conductivity was determined by a steady-state method employing radial heat flow in a hollow cylinder.²¹ The cylinder had an i.d. of 1/2 in., an o.d. of 4 in., and was 18 in. long.

The values of k obtained increase almost linearly with increasing temperature (Fig. 14). This variation of k with temperature is typical of a powder rather than of a cellular material, in which the solid phase is continuous, though the calcined waste has the physical appearance of a cellular material.

2.3 Volatility of Ruthenium during Waste Evaporation and Calcination (H. W. Godbee, F. R. Clayton)

An experiment was performed in glass equipment to study the volatility of ruthenium during the batch evaporation to 425°C of simulated Purex 1WW waste containing 0.184 g/liter of stable ruthenium (Table 24). Chemical analysis (development of a blue color with thiourea) showed that the condensate contained about 28% (Fig. 15), of the original ruthenium and that the ruthenium concentration in the condensate reached a maximum when about 74% (Fig. 16) of the original waste volume had distilled over.

Fig. 14. Variation of thermal conductivity with temperature for a calcined Purex 1WW waste.

Fig. 15. Volatility of ruthenium during evaporation of Purex 1WW concentrate in glass equipment.

Fig. 16. Concentration of ruthenium in condensate during evaporation of Purex 1WW concentrate in glass equipment.

Analysis of solutions containing known amounts of stable ruthenium showed that dissolved oxides of nitrogen, such as obtained in the decomposition of nitrate salts, interfere with the determination of ruthenium by the procedure mentioned above. This point is illustrated by the break in the curve for stable ruthenium in Fig. 15.

A second experiment was performed as above with 2.7×10^5 total γ cpm/ml of Ru-106 tracer added to the waste in addition to the stable ruthenium. Analysis for Ru-106 using counting techniques showed that the condensate contained about 72% (Fig. 15) of the original ruthenium. However, as in the experiment with stable ruthenium only, the concentration of ruthenium reached a maximum when about 74% (Fig. 16) of the original waste had distilled over.

A third experiment was performed as above with 2.7×10^5 total γ cpm/ml of Ru-106 tracer added to the waste in addition to the stable ruthenium. In addition nitric oxide (NO) was swept through the vapor space of the evaporator at a rate of approximately 30 ml/min during the evaporation. Analysis for Ru-106 using counting techniques showed that the condensate contained about 0.86% (Fig. 15) of the original Ru-106. The evaporator, distilling head, and condenser were completely free of any colored deposits at the end of the evaporation. However, the residue obtained from the evaporation was about three times as voluminous (58 ml compared to 18 ml) as the residues from the evaporation of Purex 1W without NO sweep gas.

2.4 Intermediate Level Waste Treatment (W. E. Tomlin)

Based on a compression test, a satisfactory method of solidifying Zirflex decladding waste has been found. The waste solution was heated with $\text{Ca}(\text{OH})_2$ to drive off NH_3 and reduce the volume before adding sand and cement.² The composition of a test briquette made by this method and others are given in Table 25.

Table 25. Composition - Physical Properties

2 in. cube briquettes (Declad wastes)					
Composition Weight Ratio	Density g/cc	Volume Increase %	Compression Test psi	Curing Time Days	
Sulfex declad	1.0	1.32	43	1500	7
Ca(OH) ₂	0.32				
sand	0.53				
cement	0.26				
Sulfex declad	1.0	0.90	21	1000	7
Ca(OH) ₂	0.26				
plaster of Paris	0.20				

Table 25. (Cont.)

Composition Weight Ratio		Density g/cc	Volume Increase %	Compression Test psi	Curing Time Days
Zirflex declad	1.0	1.66	75	10,200	7
Ca(OH) ₂	0.32				
sand	0.32				
cement	2.02				
Zirflex declad	1.0	1.33	54	3,200	7
Ca(OH) ₂	0.25				
plaster of Paris	0.32				
sand	0.32				
cement	0.94				
Zirflex declad	1.00 ^a	1.85	23	4,200	7
Ca(OH) ₂	0.06		(decrease)		
sand	0.26				
cement	0.90				

^aHeated with Ca(OH)₂ to drive off NH₃ and reduce volume.

The strength of uncurved briquettes having the following composition decreased at elevated temperatures: sulfex declad waste 1.0, Ca(OH)₂ 0.26, Ottawa sand 0.26, Portland cement 0.55 parts by weight (Table 26).

Table 26. Temperature - Compression Test

2 in. cube briquettes
(Sulfex declad waste)

Curing Temperature, °C	Compression Test, psi
25	2500
100	1600
300	1100
500	1150

2.5 Thermochemical Studies of Waste Components (W. E. Tomlin)

Thermogravimetric analysis was made of Na₂CO₃. The curve shows the compound to be stable up to 1050°C. A gradual loss of weight then occurred which amounted to 4% at 1175°C. Heating was terminated at 1175°C. New equipment for thermogravimetric analysis and differential thermal analysis is being installed in laboratory B-13.

2.6 Low Level Waste Treatment (R. R. Holcomb)

Several additional experimental laboratory runs have been made in the evaluation of ion-exchange processes for the treatment of low level process water waste.

A 50-liter sample of lime-soda waste treatment plant effluent, pH = 10.9 was spiked with 1 mc Cs^{137} , 1 mc Sr^{85} and 1 mc Ce^{144} , filtered and passed through 22.5 ml (1/2" i.d. x 7" column) of Na^+ form Duolite C-3 (sulphonated phenolic, cation resin) at 60 ml/min. The gross gamma activity was reduced 31.4% in the filtration step and 94.8% after both filtration and ion-exchange. The relatively low decontamination, by comparison with a similar run on plant influent, is probably due to the greater amounts of sodium and calcium in the treated waste.

A 50-liter sample of equilization basin water was spiked with 4 mc Co^{60} tracer, made 0.01 M in NaOH (pH = 11.7), filtered, and passed through 16.1 ml (1/2" i.d. x 5" column) of Na^+ form Duolite C-3 at 60 ml/min. The gross gamma activity was reduced 95.6% by filtration. The tracer was not sorbed on the resin under the conditions used in this experiment, however, the decontamination resulting from precipitation and filtration is sufficient.

A 100-liter sample of equilization basin water was spiked with 40 mc Cs^{137} tracer, made 0.01 M in NaOH (pH = 11.8), filtered and passed through 16.1 ml (1/2" i.d. x 5" column) of Na^+ form Duolite C-3 at 8.8 ml/min. Only 1.1% of the gross gamma activity was removed by filtration. The breakthrough curve in Fig. 17 indicates a decontamination factor of 10^4 for Cs^{137} (99.99% removal) for the passage of 24 liters, 1490 column volumes, of waste.

A sample of Duolite C-3 was treated with Cs^{137} , Ce^{144} , Sr^{85} and mixed fission product tracer to be used in several elution studies. In the first run (Fig. 18), an activity reduction of $\sim 10^3$ was obtained with about 9.4 column volumes of 4 M HCl elutrient.

3.0 ION EXCHANGE (J. T. Roberts)

3.1 Fission Product Recovery by Ion-Exchange (W. C. Yee)

An attempt was made to determine the capacity of Dowex 50W X-8 resin for rare earths from a 10X diluted LWX Purex waste concentrate made 0.124 M in oxalic acid to complex iron. Approximately 0.5 mc/l Sr^{85} and 0.1 mc/l Ce^{144} - Pr^{144} was included in the feed as tracer material. The 50% breakthrough for Sr^{85} occurred, as in the previous run,²² at about 22 resin volumes. No significant Ce^{144} - Pr^{144} activity was detectable in the effluent after 67 resin volumes of feed had passed through at which point the run was terminated. This indicates at least a 4-fold increase in the resin capacity for rare earth over a similar run

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Fig. 17. Breakthrough of low level (Cs-137) waste on Duolite C-3.

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Fig. 18. Elution of mixed fission product activity from Duolite C-3 with 4.0 M HCl. Run #21.

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in which the feed contained no oxalic acid. In order to conserve the synthetic waste solution,²² future runs will be made on smaller resin columns.

3.2 Radiation Damage to Ion-Exchange Resin (W. C. Yee)

An extended analysis on the new and irradiated Dowex 50W X-12 (100-200 mesh) resin was carried out in an attempt to clear up discrepancies in previous determinations. The intent was to employ careful handling techniques in order to try to obtain reproducible results on such properties as percent moisture and capacity both by titration and sulfur analysis on each of the resins. Previous analyses of the new resin have not reproduced, exactly, the specifications of the manufacturer. No loss in total capacity of the irradiated resin has been indicated by the titration method of analysis; but sulfur content analysis has indicated an apparent reduction in the sulfonic acid capacity of the resin.²³

Two 50-ml columns each of the new and irradiated resin were employed. The new resin was treated in the standard way prescribed by the manufacturer²³ with 1 liter of 5% HCl (equivalent to 27.2 mols HCl per liter of resin) and rinsing with water until the effluent was neutral. The second column of new resin was treated in the same way except that the water rinse was followed by 500 ml of 1 M NaOH, another water rinse, 1 liter of 5% HCl and a third water rinse. In this case, the purpose was to see if any difference in resin capacity or moisture content would be obtained after the additional treatment.

One column of irradiated resin was treated with 0.2 M diammonium citrate to elute the remaining activity on the resin, rinsed with water, acidified with 4 M HNO₃ and rinsed with water. The second column was treated in this manner and then followed by 500 ml of 1 M NaCl, water rinsed, 500 ml of 1 M NaOH, water rinsed, 350 ml of 4 M HNO₃, and water rinsed. The effluent from the NaCl and NaOH treatments together with their respective water washes were collected in separate containers. The NaCl effluent was titrated to determine salt splitting capacity and the NaOH effluent titrated to determine any additional weak-acid capacity which might be present. The NaCl-H₂O-NaOH-H₂O-HNO₃ treatment cycle was again repeated and the effluents again collected and titrated. The purpose in repeating the cycle was to see if the first treatment had eluted or dissolved something from the resin, thereby changing the resin capacity and/or moisture content from that of the irradiated resin which had been treated with citrate and nitric acid only.

In the water washed Na⁺ form, the color of the bulk irradiated resin in the column was black after the first NaCl-NaOH treatment; after the second, the color of the bulk resin was a deep red. The water-washed H⁺ form of the resin was red in all cases.

After their respective treatments, both columns of new resin measured 50 ml-unchanged from the initial starting volume. The original 50 ml of irradiated resin, after treatment with citrate and nitric acid, increased to 52.1 ml; after the first NaCl-NaOH-HNO₃ treatment, increased to 57.0 ml; and after the second NaCl-NaOH-HNO₃ treatment, increased to 58.8 ml.

Caustic titration of the first NaCl effluent gave a calculated irradiated-resin salt splitting capacity of 0.59 meq/ml H⁺ resin; the second NaCl effluent gave 0.55 meq/ml H⁺ resin. Acid titration of the first NaOH effluent gave a weak-acid capacity of 0.31 meq/ml H⁺ resin; the second NaOH effluent gave 0.23 meq/ml H⁺ resin. Summing the respective results of NaCl and NaOH treatments, the first cycle gave a total capacity of 0.90 meq/ml H⁺ resin while the second cycle gave 0.78 meq/ml H⁺ resin. These numbers are based on a resin volume of 57 ml of H⁺ resin for the first cycle and 58.8 ml H⁺ resin for the second cycle.

The average moisture content for the new resin was 32.4% while for the irradiated resin it was 71.0% (Table 27). The new resin moisture content is lower than the 43-49% range given by the manufacturer. Moisture content results for the irradiated resin ranged from 66% to 76%. The differences found in both the new and irradiated resin are probably due to the analytical method used. The standard procedure²⁴ involves transferring a measured volume of wet resin to a fritted disk glass funnel and applying a vacuum for ten min before transferring to a bottle for weighing and drying. Apparently, the vacuum applied not only removes interstitial water but also removes some water from the interior of the bead in varying amounts.²⁵ As indicated in Table 27, this is probably the cause of the variance in the wet density data of each group. The corresponding dry density data is more consistent. A better technique for moisture content determination is to dry the resin sample first and then put it into a closed container at 100% humidity. When the resin no longer sorbs water, the weight of the sample should be constant.

With the volumes and dry densities of the new and irradiated resin, it is possible to make a material balance on the resin which was used by Isotopes Division to recover Pm 147. Using the average dry density obtained for the caustic-and acid-treated new resin of 0.456 dry g/ml H⁺ resin, the original 500 ml of new resin corresponds to a weight of 227 g of dry resin. The settled volume of irradiated resin in the "as received" state was about 1350 ml. Correcting for volume changes when the resin was treated with citrate and HNO₃, the equivalent volume of H⁺ resin would be 1406 ml. The average dry density of resin treated in this manner was 0.160 g/ml H⁺ resin so that the weight after irradiation is calculated to be 225 g of dry resin. The equivalent volume of H⁺ form irradiated resin, treated with NaCl and NaOH in addition to citrate and acid, would be 1588 ml. The average dry density of resin treated in this manner was 0.133 g/ml H⁺ resin and the weight after irradiation 211 g of dry resin. These numbers give a 99% material balance for the resin in the former case and about 93% in the latter case and indicate little weight loss due to irradiation.

Table 27. Summary of Moisture Content Results on New and Irradiated Dowex 50W X-12 (100-200 Mesh) Resin

Resin	Treatment	Sample	Moisture Content, %	Wet Density of Resin (wet g/ml H ⁺ resin)	Dry Bulk Density of Resin (dry g/ml H ⁺ resin)
New	HCl	1	32.09	0.6830	0.4640
		2	29.27	0.6604	0.4671
		3	33.34	0.7008	0.4671
		Avg.	31.6	-	0.466
New	HCl-NaOH-HCl	1	33.88	0.7047	0.4659
		2	40.53	0.7638	0.4542
		3	25.02	0.5991	0.4491
		Avg.	33.1	-	0.456
Irradiated	Citrate-HNO ₃	1	71.09	0.5506	0.1592
		2	65.94	0.4693	0.1598
		3	68.28	0.5115	0.1622
		Avg.	68.4	-	0.160
Irradiated	Citrate-HNO ₃ -2X (NaCl-NaOH-HNO ₃)	1	76.16	0.5357	0.1277
		2	73.63	0.4767	0.1258
		3	70.73	0.4927	0.1442
		Avg.	73.5	-	0.133

Based on 500 ml of new resin and a total energy dose to the resin bed of 2780 watt-hr,²⁶ the calculated radiation dosage per unit mass of resin was 12.4 watt-hr/dry g resin from 225 dry grams of irradiated resin and 13.1 watt-hr/dry g resin for 211 dry grams of irradiated resin.

It is also evident that the irradiated resin was affected by the NaCl-NaOH treatment. This treatment could have eluted some contaminating element remaining on the resin bed after the citrate elution and/or dissolved some organic matter that was originally part of the resin itself. A spectrographic analysis of each of the treated resins may be able to resolve this problem.

Yet to be reported are the determinations of salt-splitting, total capacity by titration, and sulfur content of the resins.

4.0 CHEMICAL APPLICATIONS OF NUCLEAR EXPLOSIONS (CANE) (W. D. Bond, W. E. Clark)

About 12% tritium exchange occurred from the water form to the molecular form over CaSO_4 at 600°C where, as at 380°C , no measurable exchange occurred in a blank run (Table 28). The exchange was carried out over hot calcium sulfate contained in a quartz furnace tube. Blank determinations were made using the quartz tube and were subtracted from the total exchange to give the exchange due to CaSO_4 alone. One would conclude from these data alone that the exchange on calcium sulfate increased with temperature, whereas on the hot quartz reaction vessel alone it decreased. However, the experiments must be repeated before a firm conclusion can be made. Additional experiments using a smaller quartz furnace tube also show that total exchange increases with temperature (Fig. 19). To date, analysis of the blank determination has not been made so that the independent effects of quartz and CaSO_4 are unknown.

A mole ratio of $\text{H}_2/\text{H}_2\text{O}$ of 14 was used in these experiments. The maximum net exchange (i.e. number of moles) will occur when the ratio is unity, since maximum exchange occurs at mole ratios corresponding to the stoichiometry of the reaction.

The experimental equipment is shown schematically in Fig. 20. Ordinary hydrogen and helium were mixed in a Y tube at flow rates of 200 cc/min each to give a total flow rate of 400 cc/min. The gas stream was saturated with tritiated water (specific activity = 1.52 mc/ml) in a constant temperature bath controlled to $\pm 0.01^\circ\text{C}$. The gas stream was then allowed to flow over a weighed amount of CaSO_4 heated to the desired temperature, the water was removed by the CaSO_4 drying tube and liquid nitrogen trap. The hydrogen was converted to water by a bed of CuO at 380°C which was 12 in. in length and 1 in. dia and the resulting water was analyzed for tritium by conventional radiochemical techniques. The percentage exchange was determined from the quantity and specific activity of tritiated water passed and from the volume and specific activity of water collected. Sampling was accomplished by a syringe and rubber stopper arrangement. Samples of 0.6-1.0 ml were taken at 10 min intervals over a 40-min run. At the termination of the run the volume of residual water and the tritium content were measured.

Two furnace tubes were employed for the calcium sulfate, one of 10-15 g capacity and another of 1-3 g capacity (Fig. 21). The furnace temperature was measured and controlled by a Simplytrol unit equipped with a Chromel-alumel thermocouple.

The calcium sulfate used was prepared from reagent grade $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by dehydrating for 4 hr at 350°C and then presintering for 16 hr at 900°C .

Fig. 19. Exchange of tritium from water vapor to hydrogen over $CaSO_4$.

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Fig. 20. Schematic diagram of exchange apparatus.

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Fig. 21. Typical design of glass furnace tube.

Table 28. Exchange of Tritium from Water Vapor to Hydrogen
over CaSO_4

Flow rates, moles, min: $\text{H}_2 = 9 \times 10^{-3}$, $\text{He} = 9 \times 10^{-3}$, $\text{H}_2\text{O} = 0.5 \times 10^{-3}$
1.5 in. dia quartz vessel

Run No.	Wt of CaSO_4 , g	Temp., °C	Sampling		Tritium Activity, $\mu\text{c/ml} \times 10^{-2}$	Tritium Exchange Based on Total Water, ^a %
			Time, min	Sample Vol, ml		
1	Blank	380	10	0.8	0.61	5.0
			20	0.8	0.59	
			30	0.6	1.08	
			40	0.6	0.61	
2	12.45	380	10	1.0	0.41	5.2
			20	1.1	0.63	
			30	0.4	1.24	
			40	0.8	0.62	
3	Blank	600	10	0.7	0.18	0.73
			20	0.6	0.12	
			30	0.8	0.09	
			40	0.8	0.08	
4	12.45	600	10	0.6	0.41	12.65
			20	0.6	1.26	
			30	0.6	1.79	
			40	0.8	2.09	

^a 1.1 to 1.7 ml of water held up in condenser in each run. This was removed at end of the run and analyzed to obtain total activity in the water.

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