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CHEMICAL TECHNOLOGY DIVISION
MONTHLY PROGRESS REPORT
FOR CHEMICAL DEVELOPMENT SECTION B
JUNE 1959

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CHEMICAL TECHNOLOGY DIVISION

MONTHLY PROGRESS REPORT FOR CHEMICAL DEVELOPMENT SECTION B

JUNE, 1959

Date Issued

AUG 25 1959

OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE NUCLEAR COMPANY
P. O. Box X
Oak Ridge, Tennessee

ABSTRACT

Dissolution of Consolidated Edison Fuel

The effect of sulfate concentration on the rate of dissolution of sintered 95.5% $\text{ThO}_2\text{-U}_3\text{O}_8$ pellets in a 200% excess of boiling 13 M HNO_3 -0.04 M NaF -0.1 M $\text{Al}(\text{NO}_3)_3$ was investigated. As the sulfate concentration increased, the rate of pellet dissolution decreased. For example, 50% of the thorium dissolved in 1 hr with no sulfate present, but only 1% dissolved when the sulfate concentration was 0.3 M.

Feed Adjustment for Consolidated Edison Fuel

The solubility of boric acid in Thorex dissolver solution, 13 M HNO_3 , 0.1 M Al , 0.04 M F , increases from 0.26 M at 23°C to 1.18 M at 85°C. The presence of the boric acid did not increase the dissolution time of $\text{ThO}_2\text{-UO}_2$ pellets. Thorex dissolver solutions may be steam stripped to an acid deficient condition at 120°C. Alternatively, the solutions must be heated to greater than 150°C to remove the free acid.

Radiation-Induced Uranium Losses to Consolidated Edison Decladding Reagents

Radiation-induced uranium losses from Consolidated Edison type pellets were measured with 6 M H_2SO_4 and 5 M HNO_3 -2 M HCl , the Sulfex and Darex decladding reagents, respectively. Losses in 3 hr were less than 0.3% in all runs. The percentage increase in losses caused by Co^{60} radiations was inversely dependent on temperature. A 40% increase in loss occurred in 3 hr with 5 M HNO_3 -2 M HCl at 35°C, but at 75°C no increase was observed. Similarly, in 6 M H_2SO_4 a 70% increase in loss occurred at 35°C, but only a 40% loss increase was found at 75°C. In a single run in boiling 6 M H_2SO_4 with a crushed reactor-irradiated pellet, the uranium losses were about 3% after 3 hr. Much acid-insoluble thorium sulfate formed during this run.

Yankee Atomic Fuel

Continued Sulfex flowsheet studies of depassivation techniques applied to irradiated, prototype Yankee Atomic fuel specimens, i.e., UO_2 pellets clad in 304L stainless steel, showed that iron wire in contact with the passive steel surface consistently initiates complete dissolution of the clad in boiling 6 M H_2SO_4 . Also, depassivation was accomplished by a 15 min exposure to 0.8 M CrSO_4 -0.5 M H_2SO_4 chromous sulfate at 85°C, after which clad dissolution proceeded at a reduced rate in boiling 6 M H_2SO_4 .

Studies of soluble uranium and plutonium losses during the Sulfex decladding operation with irradiated fuel specimens showed that loss of fissile material during clad dissolution is reasonably small, 0.05% maximum at the 1440 Mwd/Ton U irradiation level if contact is limited to <2 hrs. However, the loss increases to 1.4% after an additional 4 hr contact of the core material with boiling decladding solution.

Loss rates of 0.05 to 0.8%/hr were obtained under a variety of conditions simulating maloperation in the plant.

Hot caustic or cold sodium versenate-caustic mixture appear promising for decontamination of highly radioactive solids before disposal as waste. About 90% of the gamma activity was removed.

APPR - Darex Feed Clarification

Approximately 40% of the silica at the end of Darex dissolution of APPR fuel has a particle size of $>13\mu$. It is removed by medium fritted glass but not by 30 mesh sand. The remainder of the silica passes through fine fritted glass and is therefore in true solution or possesses a particle size of $<5\mu$.

By addition of 0.4 g/l gelatin after dissolution and cooling to 60°C , 50% of the silica was removed by medium fritted glass immediately and an additional 10% after 24 hr. By addition of .005 M HF during dissolution, 60% of the silica was removed immediately and 100% after 2 days by medium fritted glass.

Recovery of Uranium and Thorium from Graphite Fuels

Using a grind-leach process, 99.9% or more of the uranium was recovered from 5.5, 9.7, and 14.0 wt % uranium in graphite fuel specimens when the samples were ground to -200 mesh, leached twice for 4 hr with boiling 15.8 M HNO_3 and the residue washed with cold water after each leach. The iron content in these specimens varied from 0.07 to 0.4%. Under the same conditions only 99.7% of the uranium was recovered from 11.2 wt % uranium fuel; however, the iron concentration in this fuel was about 0.8%. In general, the uranium recovery decreases with increasing iron content, possibly because of solid solution formation. Soxhlet extraction with azeotropic nitric acid of General Atomics 1.5% uranium- 7.1% thorium-graphite fuel plates offered no advantages over a single leach with boiling 15.8 M HNO_3 .

Dissolution of Borax-IV Fuel

Alternative decladding methods for the Borax-IV fuel are being investigated. The preferred method at present is removal of the aluminum cladding with boiling 2 M NaOH-1.78 M NaNO_3 and separate dissolution of the lead bond in 1-2 M HNO_3 before the sintered $\text{ThO}_2\text{-U}_3\text{O}_8$ core is dissolved in boiling 13 M HNO_3 -0.04 M NaF-0.1 M $\text{Al}(\text{NO}_3)_3$. The initial rate of dissolution of lead foil increased from 3.3 to 15.9 mg/min/cm² as the nitric acid concentration increased from 0.5 to 2.0 M. To dissolve both the aluminum and lead with mercury-catalyzed nitric acid, a mercury concentration of 0.5 M is required to assure an adequate rate of dissolution.

In tests of the Sulfex process in new "Hot Cell Equipment" on unirradiated Consolidated Edison fuel, the core pellet dissolution in 13 M HNO_3 -0.04 M HF -0.1 M $\text{Al}(\text{NO}_3)_3$ was not seriously inhibited if the residual sulfate concentration was reduced to 0.03 M or less.

Radiation Damage to Solvents and Diluents

Di-sec-butyl phenylphosphonate, irradiated to 200 watt-hr/liter as pure extractant or as a 1 M solution in 20 vol % o-xylene in Amsco 125-82, is about four times as resistant to radiation damage as is tributyl phosphate.

Corrosion Studies

Type 347 stainless steel showed no sign of attack after immersion in Darex-Purex solutions for 2 years. At the end of 25 cyclic Darex-Thorex dissolutions titanium showed an over-all rate of 0.2 mils/mo vs 2.3 mils/mo for Ni-o-nel after 15 Sulfex-Thorex cyclic dissolutions. Over 669 hours exposure to Thorex solution contaminated with 100 ppm Cl^- , titanium corroded at a maximum rate of 0.3 mils/mo. In 8 M HNO_3 -0.05 M $\text{Hg}(\text{NO}_3)_2$, titanium corroded at a maximum rate of 0.8 mils/mo over a 456 hour exposure. In 1 M HF -0.06 M H_2O_2 , monel corroded at a maximum rate of 157 mils/mo over a 4 hour exposure. This was decreased to 57 mils/mo by contact with dissolving Zr and blanketing with N_2 . In 1 M HF -0.06 M H_2O_2 , INOR-8 corroded at a maximum rate of 47 mils/mo over a 24 hour exposure.

Characterization of High Level Wastes

In the evaporation and calcination of synthetic TBP-25 waste to 350°C, approximately 17% of the nitrate remained in the residual solids, 79% reported to the condensate and 4% remained in the off-gases from the condenser. In the evaporation and calcination of synthetic Darex waste to 400°C the corresponding nitrate percentages were approximately 1%, 95%, and 4%, respectively. In both cases the nitrogen oxides in the condenser off-gases were essentially completely absorbed in water scrubbers, so that the net off gas volume was negligible.

The measured values of thermal conductivity of calcined TBP-25 waste were fitted empirically to a theoretical equation but no good means has been found for predicting the measured values without empirical fitting.

In the batch evaporation to dryness of synthetic Darex and Purex wastes, ruthenium retention in the residual solids varied from 28% to 54%. In these same runs 23-41% of the ruthenium reported to the condensate. Since little or no ruthenium appeared in the condenser off-gases, the unaccounted-for balance of the ruthenium is assumed to have plated out on the walls of the equipment.

Maritime Reactor Waste Disposal Studies

The pressurized water loop for studying decontamination of maritime reactor primary coolant water has been operated for about two weeks. Performance of the mixed-bed demineralizers is being studied both by conductivity measurements and by visual observation of the resin, which changes color upon exhaustion. Chemical analyses will be made after bed exhaustion is complete. Radioisotope tracers for interim analyses will be added after "cold" operation is felt to be satisfactory.

Conversion of Darex wastes to solid oxalates followed by pyrolysis in the presence of carbon monoxide at 500°C converts nickel to metal and iron and chromium to oxides.

Feed Materials Processing

Sixty four per cent of finely divided uranium was consolidated into a single mass when melted in sodium fluoride under vacuum. The remainder reacted with the NaF to produce sodium and UF_4 , part of which vaporized, and part reacted with the MgO crucible wall to form UO_2 and MgF_2 . The adsorption of methylene blue from a solution buffered with phosphate and NaOH at a pH of 8 by UO_2 powders correlated well with sintered density and fairly well with specific surface area. Thorium perfluorobutyrate was prepared, which is to be used in coating UO_2 powder with ThO_2 . The percentage of UO_2 particles less than 1 micron in size was shown to be significant in evaluating the sinterability of UO_2 powders.

CONTENTS

	<u>Page</u>
1.0 POWER REACTOR FUEL REPROCESSING	7
1.1 Consolidated Edison Fuel	7
1.11 Sulfex-Thorex and Darex-Thorex Dissolution	7
1.12 Feed Adjustment	7
1.13 Radiation Induced Uranium Losses to Decladding Reagents	11
1.14 Demonstration of Sulfex Process on Irradiated Fuel	15
1.2 Yankee Atomic Fuel	16
1.21 Depassivation of Stainless Steel with Chromous Sulfate	16
1.22 Demonstration of Sulfex Process on Irradiated Fuel	18
1.23 Decontamination of Sand Filter Residues	21
1.3 APPR-Darex Feed Clarification	22
1.4 Recovery of Uranium and Thorium from Graphite Fuels	23
1.41 Dissolution of Borax-IV Fuel	25
1.5 Radiation Damage to Solvents and Diluents	30
1.6 Corrosion Studies	31
1.61 Darex-Purex	31
1.62 Darex-Thorex and Sulfex-Thorex	31
1.63 Nitric Acid-Mercuric Nitrate (for dissolution of Al-Clad Fuels in Darex dissolver)	35
1.64 Hydrofluoric Acid-Hydrogen Peroxide System (Perflex Process)	37
2.0 WASTE TREATMENT AND ION EXCHANGE	39
2.1 Characterization of High Level Wastes	39
2.11 Evaporation and Calcination of Acidic Wastes	39
2.12 Thermal Conductivity of Calcined Waste	44
2.13 Volatility of Ruthenium During Evaporation of Radioactive Wastes	50
2.14 Pyrolysis of Waste Solids	51
2.2 Maritime Reactor Waste Disposal Studies	52
3.0 FEED MATERIALS PROCESSING	52
3.1 Reduction of Uranium Fluorides with Sodium	52
3.2 Reactivity, Surface Area and Sinterability of UO_2 Powders	53
3.3 Thoria Coatings for UO_2 Powders	55
3.4 Relationship of Particle Size and Sinterability of UO_2	55
4.0 REFERENCES	57

1.0. POWER REACTOR FUEL REPROCESSING

1.1 Consolidated Edison Fuel

1.11 Sulfex-Thorex Dissolution (L. M. Ferris, A. H. Kibbey)

Use of sulfuric acid as the decladding reagent for Consolidated Edison fuel could lead to problems through cross-contamination of the process solutions. A trace (~ 0.01 M) of nitric acid in 6 M H_2SO_4 is sufficient to produce passivation of stainless steel,¹ and the presence of sulfate in the core dissolvent retards the rate of core dissolution. Results obtained to date show that the presence of 0.1 M sulfate in a 200% excess of boiling 13 M HNO_3 - 0.04 M NaF - 0.1 M $\text{Al}(\text{NO}_3)_3$ seriously retards the rate of dissolution of sintered 95.5% ThO_2 - U_3O_8 pellets (Fig. 1). At sulfate concentrations above 0.3 M, the rate of dissolution is almost negligible. The amount of thorium dissolved in 1 hr decreases from about 50% with no sulfate present to about 0.02% at 1 M sulfate (Fig. 2). Sulfate introduced with the core dissolvent apparently reacts on the surface of the pellets to form insoluble² thorium sulfate. Once the surface film of thorium sulfate has formed, dissolution essentially ceases. The same effect is obtained by soaking pellets for 10-20 hr in boiling 6 M H_2SO_4 .

1.12 Feed Adjustment (R. H. Rainey, J. G. Moore)

Solubility of Boron in Thorex Dissolver Solution. The solubility of boric acid in 13 M HNO_3 , 0.04 M F , 0.1 M Al increases from 0.26 M B at 23°C to 1.18 M B at 85°C . The presence of the boron in the dissolver solution does not effect the time required for the dissolution of ThO_2 - UO_2 pellets.

The value of boric acid as a homogeneous criticality control depends upon the certainty that the boron will not be lost from the solution either by precipitation or volatilization under process conditions. Previous experiments³ have demonstrated that the boron will not be lost by volatilization. Additional experiments have demonstrated that the solubility of boric acid in the Thorex dissolver solution, 13 M HNO_3 , 0.04 M F , 0.1 M Al increases sharply with increasing temperature, (Fig. 3). The presence of equal molar concentrations of boric acid in solutions of uranium 235 or 233 will prevent the solution from becoming critical. Since the highest concentration of soluble uranium during the Consolidated Edison core dissolution will be about 0.05 M U , these experiments indicate that a concentration of boron five times the uranium concentration can be maintained at 23°C and 20 times the uranium concentration when the solution temperature is maintained above 80°C .

The solubility of boric acid in 13 M HNO_3 , 0.04 M F , 0.1 M $\text{Al}(\text{NO}_3)_3$ was determined by stirring an excess of the acid in the solution at the desired temperature then sampling through a glass frit. Errors are estimated to be approximately 10% because of sampling problems.

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Fig. 1. Effect of Sulfate Concentration and Time on the Dissolution of Sintered 95.5% $\text{ThO}_2\text{-U}_3\text{O}_8$ Pellets in a 200% Excess of Boiling 13 M $\text{HNO}_3\text{-0.04 M NaF-0.1 M Al(NO}_3)_3$.

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Fig. 2. Effect of Sulfate Concentration on the Amount of Thorium Dissolved in 1 hr in a 200% Excess of Boiling 13 M HNO_3 -0.04 M NaF -0.1 M $\text{Al}(\text{NO}_3)_3$. Sintered 95.5% ThO_2 - U_3O_8 pellets used in the experiments.

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Fig. 3. Solubility of H_3BO_3 in 13 M HNO_3 , 0.04 M NaF , 0.10 M $\text{Al}(\text{NO}_3)_3$.

The addition of 1.5 M boric acid to the Thorex dissolver solution did not noticeably increase the time required to dissolve ThO_2 - UO_2 pellets at the boiling temperature. As the solution cooled to room temperature crystals of boric acid precipitated and floated on the surface of the solution which then contained 236 g/l Th, 0.24 M B, and 9.4 M HNO_3 .

Steam Stripping of HNO_3 from Thorex Dissolver Solution. The amount of steam which is required to remove free acid from Thorex dissolver solution, 1 M Th, 10 g U/l, 9 M H, 0.04 M F and 0.04 M Al, was found to vary from the water equivalent of 4.5 volumes to 2.5 volumes at 120°C. The present Thorex feed adjustment for aluminum jacketed thorium slugs consists of concentrating the dissolved thorium solution to a boiling point of 150°C to remove the free acid and convert the solution to "acid deficient" conditions. This high temperature feed adjustment assures the dissolution of ThO_2 which is present in the metal, dehydration of silica to prevent emulsions, and converts ruthenium, zirconium-niobium, and protactinium to a non-extractable species. However, later experiments⁴ showed that these radioactive species could be made unextractable by lower temperature treatment of acid deficient solutions. Treatment at 150°C is a difficult operation in pilot plant equipment and results in the highest corrosion rate in the plant. In the case of Consolidated Edison fuel reprocessing, a temperature greater than 150°C (but not yet determined) would be required to convert the dissolver solution to acid deficient conditions due to its low aluminum content. The conditions for removing the free acid at lower temperatures, and an evaluation of the effect on the properties of the solution are being studied.

An efficient means of removing free acid at 120°C consisted of rapidly concentrating the dissolving solution to one third its volume while steam was being passed through the solution. The first 1.7 volumes of condensate contained 4.7 M HNO_3 . The next 0.5 volume contained 1.68 M HNO_3 . The acid content of the next volume averaged 0.32 M. The condensate³ consisted of 0.7 volumes from the dissolver solution concentration and 2.5 volumes from the steam. Steam sparging at 110°C to 115°C was not effective for the removal of the free acid.

An evaluation of the effect of steam stripping on the physical and solvent extraction properties of the solution is in progress.

1.13 Radiation-Induced Uranium Losses to Decladding Reagents (T. A. Gens)

Uranium losses from Consolidated Edison type pellets (95.5% ThO_2 - U_3O_8) to decladding reagents under Co^{60} irradiation are being investigated. The radiation-induced losses, which are smaller than non-radiation induced losses, decrease as the temperature of the decladding reagent increases.

Pellets were immersed for periods up to 150 hr in flowsheet volumes^{5,6} of two decladding reagents, 5 M HNO₃- 2 M HCl and 6 M H₂SO₄. Small aliquots of the reagent were periodically removed and analyzed for uranium. Control experiments in the absence of radiation also were performed. Differences between experimental results in the control and irradiated samples were determined from smooth curves after 3 hrs contact time and ascribed to radiation effects. In 5 M HNO₃- 2 M HCl at 35°C at radiant power densities of about 1 watt/liter (approximately the power density expected in reprocessing),⁷ the radiation-induced losses were 40% as large as losses from other sources (last column of Table 1). When the experiment was performed at 75°C, no radiation-induced losses were found. In 6 M H₂SO₄, the radiation-induced losses were proportionately higher, 70% and 40% at 35 and 75°C, respectively. An inverse temperature dependence was again evident in the radiation-induced losses.

One experiment was performed with a crushed, irradiated (5600 Mwd/T) Consolidated Edison type pellet (97.5% ThO₂-UO₂), cooled 3.8 yrs, to investigate uranium and thorium losses which might be expected under highly unfavorable conditions during Sulfex decladding. The pellet, which was clad in 304 SS and air bonded, was exposed to air about 1 week after mechanical decladding. The surface area of the oxide particles was not measured.

The crushed pellet was immersed in 6 M H₂SO₄ (flowsheet volume). Small aliquots of the sulfuric acid were periodically removed and analyzed for uranium and thorium. Uranium losses were nearly 3% after 3 hr contact time and about 15% after 50 hr (Fig. 4). Because of the low radiant power density of about 10⁻³ watt/liter, the high uranium and thorium losses must be ascribed to surface dissolution reactions and not to the irradiation.

The thorium losses observed in the above experiment were compared to those with a freshly crushed unirradiated pellet (run labelled "control," Fig. 5 - pellet was 95.5% ThO₂-U₃O₈). Precipitation of a thorium compound, probably thorium sulfate, became apparent after a few hours in refluxing 6 M H₂SO₄. In the run with irradiated material, the low level of radiation apparently helps keep thorium in solution. Since the prevention of thorium sulfate precipitation is very desirable in the Sulfex process because of possible inhibition of core dissolution by the precipitate, this experiment will have to be repeated at higher radiant power densities.

Table 1. Uranium Loss Studies - 3 hr Contact of Consolidated Edison-Type Pellets (95.5% ThO₂-U₃O₈) with Decladding Reagents (Flowsheet Volumes)

Reagent	T, °C	U Loss, %		Increase in Loss from Radiations, %
		With Co ⁶⁰	Radiations* Control	
5 M HNO ₃ - 2 M HCl	35	0.14	0.10	40
	75	0.27	0.27	0
6 M H ₂ SO ₄	35	0.11	0.065	70
	75	0.20	0.14	40

* Radiant Power Density was about 1 watt/liter in experiments performed at 35°C and about 10 watt/liter in experiments performed at 75°C.

Fig. 4. Uranium Losses from a Crushed Consolidated Edison Type Pellet to Refluxing 6 M H_2SO_4 . Burnup: 5600 Mwd/T; cooled 3.8 yr; radiant power density $\sim 10^{-3}$ watt/liter; pellet weight 2.7g (2.5% UO_2) volume 6 M H_2SO_4 , 11.5 cc.

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Fig. 5. Thorium Losses from a Consolidated Edison Type Pellet to Refluxing 6 M H₂O₄. Burnup: 5600 Mwd/T; cooled 3.8 yr; radiant power density $\sim 10^{-3}$ watt/liter; pellet weight 2.7g (97.5% ThO₂) volume 6 M H₂SO₄, 11.5 cc.

1.14 Demonstration of Sulfex Process on Irradiated Fuel (J. R. Flanary,
C. P. Johnston)

The equipment for carrying out hot cell experiments to de jacket and dissolve the U_3O_8 - ThO_2 core pellets of prototype Con-Ed fuel pins was assembled and cold tested as designed. Results of cold tests showed ~ 0.07 U and $< 0.1\%$ Th losses to the $6\text{ M } H_2SO_4$ de jacketing solution. Core pellet dissolution in $13\text{ M } HNO_3$ - $0.04\text{ M } NaF$ - $0.04\text{ M } Al(NO_3)_3$ solution was accomplished in approximately 8-10 hrs with one exception which required ~ 14 hrs.

The rate of stainless steel de jacketing was easily followed by measuring the hydrogen off gas with a wet test meter using up to 1-1/2" H_2O negative pressure on the outlet side of the meter. Thus it appears possible to use the metering device in the hot runs.

As originally designed and constructed, the dissolver head, dip tubes, transfer lines and separator head and connections were made of Carpenter-20 stainless steel. These components were replaced with glass to make the entire apparatus of glass and hence more adaptable to Darex de jacketing, as applied to Con Ed fuel, and to the Zirflex system. The corrosion rate of Carpenter-20 in either the Darex or Zirflex systems is prohibitive.

Experiments were carried out in the equipment to determine the solubility of whole unclad U_3O_8 - ThO_2 pellets in boiling $5\text{ M } HNO_3$ - $2\text{ M } HCl$ Darex solution. Losses of uranium and thorium were $< 0.1\%$ in 2-3 hrs and 0.08-0.18% in 3-7 hrs. Higher losses to both Darex and Sulfex decladding solutions will be expected if the UO_2 - ThO_2 pellets shatter as have the UO_2 pellets.

In order to check the effect of prolonged exposure of U_3O_8 - ThO_2 pellets to $6\text{ M } H_2SO_4$ on subsequent pellet dissolution, an experiment was carried out in which the pellets were boiled in $6\text{ M } H_2SO_4$ for 2 hrs, thoroughly washed in H_2O , and dissolved in $13\text{ M } HNO_3$ - $0.04\text{ M } NaF$ - $0.04\text{ M } Al(NO_3)_3$ solution. Pellet dissolution progressed smoothly and at a rate equivalent to that found in the usual procedure of de jacketing followed by core dissolution. In the event that a sulfate film had formed on the ThO_2 in the pellets it was evidently removed by thorough washing.

Another set of experiments was carried out in which U_3O_8 - ThO_2 pellets were placed in two vessels containing the standard core dissolving solution. One of the solutions was spiked with H_2SO_4 to make the solution 0.03 M in $SO_4^{=}$. While the pellets in the standard core dissolvent were dissolved in ~ 8 hrs, the pellets in the solution containing $0.03\text{ M } SO_4^{=}$ required ~ 10 hrs for complete dissolution.

It appears that the inhibiting effect of residual sulfate on the core dissolution rate is not large provided that the concentration of the residual sulfate in the core dissolvent can be reduced to 0.03 M or less by efficient washing.

1.2 Yankee Atomic Fuel (J. R. Flanary, J. H. Goode)

The PRFR flowsheet demonstration program was continued with a number of additional Sulfex head end experiments using prototype Yankee Atomic fuel specimens which had been irradiated from 1000-1440 Mwd/Ton of uranium. Three runs were made to determine uranium and plutonium losses under a variety of Sulfex head end conditions along with tests on chemical methods for initiating dissolution of passive stainless steel jackets in the decladding medium, boiling 6 M H_2SO_4 . Tests were also made on methods of decontaminating the "hot" solids and filter aid resulting from filtration of decladding solutions and feed solutions through a sand filter.

1.21 Depassivation of Stainless Steel with Chromous Sulfate

Previous results⁸ indicated that making the Sulfex decladding solution, 6 M H_2SO_4 , 0.1 M in chromous sulfate partially initiated the dissolution of a passive irradiated fuel Yankee Atomic specimen, UO_2 pellets clad in 304L stainless steel. However, the reaction ceased after 7% of the stainless steel had been dissolved. The experiment was repeated with another passive irradiated fuel specimen by pipetting concentrated chromous sulfate solution under the surface of the 6 M H_2SO_4 in the nitrogen-blanketed dissolver, and boiling for 1 hour. No reaction was observed or weight loss of the specimen measured, although the surface of the specimen had been brightened. The 0.1 M CrSO_4 -6 M H_2SO_4 solution was discarded, and the cleaned specimen was immersed in fresh boiling 6 M H_2SO_4 to determine whether the cleaning action had destroyed the passivity of the specimen. No dissolution occurred, even after the specimen was scratched with a file and reimmersed in the boiling acid. Wrapping the pin with iron wire, however, initiated the complete dissolution of the cladding.

Rapid oxidation of the reducing agent, chromous sulfate, was believed responsible for its failure to depassivate the stainless steel. Experiments were made to determine the "half-life" of the reagent in nitrogen-blanketed boiling 6 M H_2SO_4 with and without actively dissolving stainless steel. Table 2 indicates an effective "half-life" for 0.1 N CrSO_4 in nitrogen-blanketed, boiling 6 M sulfuric acid of approximately 3 hours.

Table 2. Stability of Chromous Sulfate in Nitrogen-Blanketed Boiling 6 M H_2SO_4

Sample No.	Time, min.	Cr ⁺⁺ Conc., N
1	1	0.084
2	10	0.080
3	20	0.076
4	30	0.076
5	40	0.074
6	50	0.070
7	60	0.068

The experiment was repeated in the presence of actively dissolving stainless steel by pipetting 75 ml of the concentrated reagent (0.8 M) under the surface of 500 ml of boiling 6 M H_2SO_4 in which 28 g of 304L stainless steel was dissolving. Table 3 shows that the reducing normality, or chromous concentration, was only 0.032 N at the time the 1 minute sample was taken, indicating almost instantaneous oxidation of the reagent to chromic sulfate in the presence of stainless steel. It is interesting to note, however, that the reducing normality increases linearly with time as the stainless steel dissolves in the sulfuric acid; this fact may account for the low losses of uranium and plutonium to the decladding solution in the presence of actively dissolving stainless steel.

Table 3. Stability of Chromous Sulfate in Boiling 6 M H_2SO_4 in Presence of Dissolving Stainless Steel

(500 ml, 6 M H_2SO_4 , 28 g 304L SS, ca. 0.1 N $CrSO_4$, N_2 Blanket)

Sample No.	Time, min	Reducing Normality, N
1	1	0.032
2	5	0.058
3	10	0.122
4	15	0.162
5	20	0.204
6	25	0.246
7	30	0.286
8	40	0.356
9	50	0.424
10	60	0.460

This experiment was then checked in the hot cell using a totally passive (as determined by boiling 1 hr in 6 M H_2SO_4) irradiated fuel specimen by blanketing the dissolver with nitrogen, introducing chromous sulfate under the surface of boiling 6 M H_2SO_4 , and immersing the passive fuel specimen in the 0.1 N $CrSO_4$ -6 M H_2SO_4 decladding solution. No reaction occurred or weight loss was measured after 1 hour of boiling. A solution sample taken after 15 minutes showed that the chromous concentration had been reduced to less than 0.001 N, indicating complete oxidation in the presence of the passive stainless steel.

The passive fuel specimen was then immersed in 0.8 M $CrSO_4$ -0.5 M H_2SO_4 , at 85°C, for a period of 15 minutes, under a nitrogen atmosphere, in an attempt to activate the stainless steel in a separate depassivation step. No reaction was observed and no weight loss was detected. The fuel specimen was then placed in boiling 6 M H_2SO_4 , and after a 30 minute induction period began to dissolve at a slower rate than exhibited by non-passive specimens. Total dejacketing time was 2 hours as compared with 1.2 hours for a non-passive specimen of the same type.

From these results, it remains uncertain whether chromous sulfate has useful application as a depassivating agent in the Sulfex process. Although the dilute reagent has been shown to be reasonably stable in boiling 6 M H_2SO_4 in an inert atmosphere, the reagent is rapidly dissipated in the presence of actively dissolving or passive stainless steel. The use of concentrated chromous sulfate as a special depassivating solution may be feasible; the technique, however, requires more study and development. Another technique which involves production of chromous sulfate in the dissolver, is attractive since it eliminates the problem of handling the highly unstable reagent in the plant. This procedure remains to be investigated.

During the recent series of Sulfex studies with irradiated prototype Yankee Atomic fuel pins, seven of a total of nine pins were found to be totally passive to boiling 6 M H_2SO_4 . These pins were prepared at ORNL from sintered UO_2 pellets encased in 304L stainless steel tubing with welded end caps. As a test for leak tightness, the pins were autoclaved at 300°C and 1600 psig for 105 hr. During the 4 month irradiation in the MTR, the pins were continuously washed with reactor cooling water with an exit temperature of 125°F. Unirradiated fuel pins prepared in the same fashion, without autoclaving for leak tightness, were consistently de-clad (i.e., not passive) in boiling 6 M H_2SO_4 . In six, single pin, tests, no passivation was encountered. In the absence of further information, these results suggest that passivation may possibly be induced by the autoclaving treatment or by conditions associated with the irradiation. A great deal of careful investigation will be required to determine the cause of passivation.

1.22 Demonstration of Sulfex Process on Irradiated Fuel

In the event of maloperation in the Sulfex Head End plant, the core material may be exposed to fresh boiling 6 M H_2SO_4 , or perhaps to spent de-cladding solution containing dissolved stainless steel, in the presence or absence of air. The rate of dissolution of irradiated UO_2 was determined under such miscellaneous Sulfex de-cladding conditions. Figure 6 shows how the rate of dissolution, expressed as the percentage uranium loss is affected by the de-cladding solution composition and environment. The rate data used in this plot were obtained by de-cladding a simulated Yankee Atomic fuel pin, i.e., sintered UO_2 pellets canned in 304L SS and irradiated to 1040 Mwd/Ton U, in boiling 6 M H_2SO_4 . When dissolution of the clad was completed, the pellets were removed and divided into batches. Then, equivalent portions of pellets from the same 1040 Mwd irradiated pin were refluxed for 24 hr in each of the boiling de-cladding solutions under specified conditions. The uranium losses represent the cumulative loss under the conditions shown.

The data show that the rate of uranium loss is minimum (0.04%/hr) while the pellets are exposed to spent de-cladding solution, ~10:6 M H^+ , 6 M SO_4^{2-} containing 35 g/l dissolved stainless steel, under a nitrogen blanket. Exposure of a fresh portion of pellets to the same solution with pieces of 304L SS added periodically resulted in an accelerated rate: 0.29%/hr. The stainless steel was added to provide an actively dissolving

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Fig. 6. Uranium and Plutonium Losses Under Miscellaneous Sulfex Operating Conditions. Approximately 11 g fragmented UO_2 pellets refluxed in 6 M H_2SO_4 or spent declad solution ($\sim 10.6 \text{ M H}^+$, 6 M SO_4^{2-} , 35 g SS/liter) with N_2 Blanket, air sparge, or with SS metal present. UO_2 irradiated to 1040 Mwd/T.

metal heel; however, the heel actually dissolved quite slowly --- with little production of hydrogen. Possibly, slow oxidation of the ferrousion occurred during the previous 24 hr reflux with a gradual buildup of ferric ion whose effect on the rate becomes evident in the second 24 hr experiment. The partially dissolved stainless steel was removed and the reflux continued for 24 hr with a constant air sparge. Again, the rate increased to 0.81%/hr, undoubtedly by the mechanism of air oxidation of ferrousion. Finally, using a fresh charge of pellets and fresh 6 M H_2SO_4 refluxing under nitrogen, a rate of 0.30%/hr was established. Here, the inhibiting effect of dissolved stainless steel is absent and effect of pure boiling 6 M H_2SO_4 is exhibited.

Two additional fuel pins, irradiated to 1000 and 1440 Mwd/Ton U, were declad in separate experiments and additional loss rate data were obtained in similar fashion. Table 4 lists uranium losses, in per cent per hour,

Table 4. Uranium Losses under Sulfex Headend Conditions

(24 hour reflux periods, 10-12 g irradiated UO_2 exposed to 570 ml test solution in Pt gauze basket, N_2 blanket, air sparged, or SS present)

Approximate solution composition: 35 g/l SS, ~ 10.6 M H^+ , 6 M $SO_4^{=}$

Expt. No.	Irrad., Mwd/T	Uranium Loss, per cent/hr			6 M H_2SO_4 - 6 M H_2SO_4	
		Spent Declad + N_2	Spent Declad + N_2 + SS	Spent Declad + air	+ N_2	+ air
9	1000	0.07	0.41	-	0.16	-
10	1440	0.08	0.36	-	0.39	0.37
11	1040	0.04	0.29	0.81	0.30	0.72
Average Rate		0.06	0.35	0.81	0.28	0.55

obtained from these experiments, and shows consistently higher loss rates in all cases except where the pellets were exposed to the spent decladding solution under a nitrogen blanket.

Table 5, however, presents a more realistic picture of uranium and plutonium loss values under normal head end operating conditions. Losses are tabulated for a number of prototype fuel specimens, irradiated from 0 to 1440 Mwd/T both at the time the cladding is completely dissolved at 2 hr and after 4 hrs reflux in the spent decladding solution. Increased losses are noted at irradiation levels greater than 800 Mwd/T due to fragmentation by thermal shock during irradiation of the UO_2 pellet core material. This results in greatly increased surface areas exposed to the decladding solution.

In the subsequent core dissolution step, the fragmented pellets were dissolved by 10 M HNO_3 at a rate about five-fold that determined with unirradiated, whole pellets. Actually, the same accelerated rate was observed at the 450 to 800 Mwd level with pellets which remained intact during the decladding step. Apparently, irradiation or the conditions associated with irradiation, renders the UO_2 extremely susceptible to attack by nitric acid.

Table 5. Uranium and Plutonium During Sulfex Decladding of Irradiated Prototype Yankee Atomic Fuel Pins

Fuel Pins: 42 g. of sintered UO_2 pellets encased in 20 g of 304L SS, 30 mil wall thickness, irradiated from 150 to 1440 Mwd/Ton U and "cooled 4 months."

Decladding Solution: 570 ml of boiling 6 M H_2SO_4

Irradiation Mwd/Ton U	U Loss, %		Pu Loss, %		Pellet Form
	Clad		Clad		
	Dissolved (2 hr)	4 hr Reflux	Dissolved (2 hr)	4 hr Reflux	
0	0.005				Intact
250	(0.003)		(0.06)		Intact
450	0.003	0.005	0.04	0.05	Intact
650	0.003	0.005	0.009	0.05	Intact
800	0.005	0.03	0.02	0.07	Fragmented
1000	0.03	0.29	0.03	0.34	Fragmented
1440	0.045	1.41	0.052	0.60	Fragmented

1.23 Decontamination of Sand Filter Residues

Shielding calculations⁹ for a drum shielded with 1 ft of concrete containing 1 kg of radioactive solids in 4 liters of slurry from the Immi Mixer-Settler Facility sand filter indicated that radiation intensities of up to 1.8 R/hr would be encountered at the surface of the shielding. Since even this amount of radiation would render direct operation of the waste facility hazardous, and since several times that amount of solids is expected to be loaded in each shielded drum, a number of scouting experiments were made to determine methods of decontaminating the solids on the sand filter prior to transfer to the waste facility.

Gamma scanning of the radioactive solids indicated that Zr-Nb was the principal fission product activity present along with some ruthenium and some activated stainless steel components having a 1.1 mev gamma energy (Fe, Co, or Ni). Samples of the solids were loaded onto a small sand filter and washed downflow with various reagents to determine their effectiveness in eluting the contaminants. Table 6 summarizes details of the successive washing steps with the various reagents, and indicates that up to 90% of the activity can be removed with from 25-100 volumes of hot 25% caustic or cold 0.27 M sodium versenate- 1 M caustic and water rinsing. Hot caustic, which dissolved silica, is quite effective. However, it probably cannot be safely used with the sand filter because of plugging.

Table 6. Chemical Decontamination of Filter Solids

Expt.	Reagent	Throughput Volumes	Gross Gamma Activity Removed %	Remarks
1	0.4 M Oxalic Acid	13	38	
	"	26	38	
	Water	13	38	
	1 M NaOH-100 g/l	13	70	
	Na Versenate	26	80	
2	Water	50	16	All activities remove in same proportion
	1 M NaOH-100 g/l	25	50	
	Na Versenate	50	78	
	"	75	78	
	Water	25	88	
3	1 M NaOH	33	33	
	"	66	50	
	"	99	58	
	Water	33	66	
4	Hot 25% NaOH	25	89	Zr-Nb activity removed
	"	50	89	
5	Cold 25% NaOH	33	90	Filter plugged after 40 vols

1.3 APPR- Darex Feed Clarification (A. F. Messing, O. C. Dean)

The nature of the silica present in Darex solution immediately after dissolution was studied further. A 30-gram piece of APPR fuel prototype element was dissolved in 520 ml of 5 M HNO_3 -2 M HCl cooled to 40°C and vacuum filtered through medium fritted glass. Approximately 40% of the silica was collected as a fine 95% SiO_2 precipitate but passed through 30 mesh sand. Passing the filtrate through fine fritted glass failed to remove silica further. Allowing this filtrate to stand overnight and refiltering through fine fritted glass removed an additional 20% of the total silica.

A second APPR fuel element sample was dissolved as above but in the presence of 0.005 M HF . Vacuum filtration through medium fritted glass resulted in the removal of about 60% of the silica as a 96% SiO_2 precipitate. The remaining silica was removed on a fine filter after standing for two days as a 9% SiO_2 precipitate.

In a third run 0.2 g of gelatin was added to the solution, after dissolution and cooling to 60°C. The solution was further cooled to 30°C and filtered through medium fritted glass. Approximately 50% of the silica was removed as a 22% SiO_2 precipitate. After standing for one day the filtrate was passed through a fine fritted glass filter. An additional 10% of the silica was removed.

1.4 Recovery of Uranium and Thorium from Graphite Fuels (L. M. Ferris, M. J. Bradley)

A general study of the recovery of uranium and thorium from graphite fuels has been undertaken. Interest in these fuels has grown with the development of gas cooled power reactor concepts such as the proposals by Sanderson and Porter (Pebble Bed Reactor), Los Alamos (Turret Reactor), and General Atomics. Mechanical grinding and leaching with nitric acid is the method currently being investigated experimentally for uranium-graphite fuels.¹⁰ Studies on the effects of initial uranium concentration and particle size on the recovery of uranium with boiling 15.8 M HNO_3 from fuels containing 5.5-14 wt % uranium have been completed. Soxhlet extraction with azeotropic nitric acid of plates of the General Atomics 1.5% uranium-7.2% thorium-graphite fuel offered no advantages over a single leach with boiling 15.8 M HNO_3 .

Leaching of 10-g uranium-graphite fuel specimens was accomplished as follows. After a 4-hr digestion with 50 ml of boiling 15.8 M HNO_3 , the residue was washed with three 25-ml portions of cold water. The residue was digested another 4 hr in 25 ml of fresh acid before the final 25-ml water wash. Washing was achieved by agitating the residue with each volume of water for 15 minutes, and then filtering under vacuum. With -200 mesh specimens containing 5.5, 9.7, and 14.0 wt % uranium, the uranium recovery was 99.9% or greater (Table 7). With a specimen containing 11.2 wt % uranium, the recovery was only 99.7%. However, the iron content of this sample was higher than the others (see below). In general, higher uranium recoveries were obtained with more finely ground material. The uranium loss to the graphite residue was reduced 0.1 to 0.2% by reducing the particle size from -4 +8 to -200 mesh (Table 7).

Significant amounts of uranium were found in the water washes after the first leach - 0.2% in the third wash of -16 mesh material and 0.6% in the third wash of -4 +8 mesh samples.

Lowering the amount of acid used in the first leach to 25 ml/10 g sample instead of 50 ml/10 g, lowered the uranium recovery after the first leach by 0.1%, but the second leach recovery increased by a corresponding amount so that the over-all yield was the same (Table 7, runs 23, 13, 17, and 20). It is doubtful whether the nitric acid volume can be reduced much below 25 ml/10 g and still completely cover the graphite matrix.

Uranium recovery from 5.5, 9.7, and 14 wt % uranium specimens increased slightly with increasing uranium concentration (Fig. 7). Uranium recoveries from the 11.2 wt % sample were consistently lower by 0.2-0.3%. The exact history of each fuel specimen is not known, but the iron content of the

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Fig. 7. Uranium Recovery as a Function of Initial Uranium Concentration after Two, 4-hr Leaches with Boiling 15.8 M HNO₃. Residue washed with cold water after each leach.

11.2 wt % specimen was 2-10 times higher than in the other specimens (Table 7). In general, the uranium concentration in the graphite residue increased with increasing iron content (Fig. 8). At low iron concentrations, the uranium concentration in the graphite residue after leaching seems to approach a limiting value which is dependent upon particle size, but independent of initial uranium concentration over the range 5.5-12 wt %. The effect may be caused by solid solution formation between uranium and iron or iron carbide (both are unreactive toward nitric acid), or variations in the iron impurity content may simply be an indication of variations in the porosity and density of the samples as manufacturing techniques were changed. Data are insufficient to draw a definite conclusion.

The uranium-graphite fuel specimens used in the study were prepared by mixing UO_2 (-325 mesh) with graphite flour and a liquid binder, pressing into plates, and then graphitizing at 2400°C . At this temperature the UO_2 is converted to UC_2 . Since uranium dicarbide reacts rapidly with moisture the uranium in the fuel samples was probably present as the oxide.¹⁰ The uranium (1.54%) - thorium (7.18%) graphite samples were prepared for the General Atomics gas cooled reactor program (see below) in a similar fashion, except that the final shape was a right cylindrical slug about 3 inches in diameter and 3 inches high. It is not known whether the original carbides converted to the oxides before the chemical studies were made.

Soxhlet Extraction of General Atomics Fuel (1.54% U, 7.14% Th)

Soxhlet extraction for 10 hr with azeotropic HNO_3 of $1/4$ in thick plates recovered 79.8% of the uranium and 67.9% of the thorium. Leaching of a similar plate with boiling 15.8 M HNO_3 for 10 hr dissolved 78% of the uranium and 58% of the thorium, so there was little gain in Soxhlet extraction. When $1/2$ in. plates were subjected to Soxhlet extraction with azeotropic nitric acid for 10 hr only 35.6% of the uranium and 26.6% of the thorium was recovered.

1.41 Dissolution of Borax-IV Fuel (L. M. Ferris)

Three alternative decladding methods are being investigated for the Borax-IV fuel (a $\text{ThO}_2\text{-U}_3\text{O}_8$ pellet core clad in 99% Al-Ni alloy and bonded with lead). These methods, which precede dissolution of the core in 13 M HNO_3 -0.04 M NaF-0.1 M $\text{Al}(\text{NO}_3)_3$, are 1) dissolution of the aluminum in boiling 2 M NaOH-1.78 M NaNO_3 followed by simultaneous dissolution of the lead and core, 2) simultaneous dissolution of the aluminum, nickel, and lead in nitric acid - mercuric nitrate solutions, and 3) a two-step decladding in which the aluminum is first dissolved in sodium hydroxide before the lead and nickel are dissolved in 1-2 M HNO_3 . In the first two cases, problems arise either from solubility considerations or kinetics.¹¹ With lead present, the rate of core dissolution is lowered markedly, and, because of the limited solubility of lead nitrate in $\text{Th}(\text{NO}_3)_4\text{-HNO}_3\text{-H}_2\text{O}$ solutions,¹² a thorium concentration in the product solution of greater than 0.2 M cannot be achieved except possibly at very low acidities. Therefore alternative 1) is undesirable.

Fig. 8. Uranium Present in Graphite Residue after Two 4-hr Leaches with Boiling 15.8 M HNO_3 as a Function of Iron Concentration. Uranium concentration before leaching 5.5-14 wt%, after leaching 0.004-0.06 wt%.

Table 7. Recovery of Uranium from 5.5-14 wt % Uranium-Graphite Fuel Specimens by Leaching with Boiling 15.8 M HNO_3

First HNO_3 leach: 50 ml acid/10 g sample
 Second HNO_3 leach: 25 ml acid/10 g sample
 Reflux time: 4 hr

Run No.	U in Fuel %	Fe in Fuel %	Particle Size Mesh	Uranium Recovered, %					
				1st HNO_3 Leach + 2 Water Washes	3rd Water Wash	Total Solubilized 1st Leach + 3 Washes	2nd HNO_3 Leach + 1 Water Wash	Graphite Residue	Total Solubilized
29	5.41	0.254	-4+8	98.04	0.50	98.54	1.24	0.231	99.77
24	5.49	0.240	-16+30	99.67	0.06	99.73	0.13	0.138	99.86
23	5.47	0.243	-16+30	99.43 ^a	0.20 ^a	99.63 ^a	0.22 ^a	0.148 ^a	99.85 ^a
30	5.33	0.268	-200	99.81	0.04	99.85	0.08	0.077	99.92
26	9.46	0.068	-4+8	98.31	0.69	99.00	0.82	0.18	99.82
14	9.76	0.065	-16+30	99.59	0.10	99.69	0.20	0.121	99.88
13	9.73	0.070	-16+30	98.87 ^a	0.72 ^a	99.59 ^a	0.31 ^a	0.132 ^a	99.87 ^a
31	10.51	0.167	-200	99.71	0.07	99.78	0.13	0.098	99.90
18	11.06	0.761	-4+8	98.19	0.38	98.57	0.87	0.51	99.49
15	11.14	0.694	-16+30	99.10	0.23	99.33	0.19	0.43	99.57
16	11.20	0.668	-16+30	99.20	0.21	99.41	0.15	0.43	99.57
17	11.16	0.681	-16+30	99.01 ^a	0.16 ^a	99.17 ^a	0.32 ^a	0.49 ^a	99.51 ^a
27	12.43	1.038	-200	99.39	0.15	99.54	0.19	0.27	99.73
25	13.84	0.452	-4+8	98.30	0.59	98.89	0.95	0.16	99.84
19	14.12	0.418	-16+30	99.79	0.03	99.82	0.07	0.097	99.90
20	14.29	0.414	-16+30	99.37 ^a	0.28 ^a	99.65 ^a	0.22 ^a	0.105 ^a	99.90 ^a
22	14.15	0.409	-16+30	99.51	0.14	99.65	0.25	0.105	99.90
28	15.19	0.471	-200	99.65	0.17	99.82	0.14	0.033	99.97

a 1st leach, 25 ml acid/10 g sample

At present, decladding in two steps is the preferred method. The uranium content in the sodium hydroxide decladding waste solution is so low that this solution may be discarded.¹³ In the second decladding step, removal of lead and nickel with 1-2 M HNO_3 , uranium losses are expected to be less than 0.5%. Recovery of uranium from this solution by solvent extraction should not be difficult.¹⁴ Lead is readily dissolved in dilute nitric acid. The initial dissolution rate of 0.04 cm thick lead foil in boiling dilute nitric acid increased from 3.3 to 15.9 mg/min/cm² as the nitric acid concentration increased from 0.5 to 2.0 M (Table 8). In these experiments, the initial HNO_3 /Pb mole ratio was 3. Complete dissolution was achieved in about 1 hr with 1-2 M HNO_3 at HNO_3 /Pb mole ratios of 2 and 3.

Decladding with mercury-catalyzed nitric acid does not appear attractive in that a mercury concentration of about 0.5 M is required to insure a suitable rate of dissolution when lead is present (Fig. 9). In these experiments, 0.95 cm dia, 2.5 cm high right cylinders of aluminum were digested with boiling 4 M HNO_3 (4 moles of HNO_3 per mole of aluminum) in the presence of lead (8.77 moles aluminum per mole of lead). In general, the rate of dissolution of aluminum increased with increasing mercury concentration, but in no case was dissolution as rapid as when no lead was present (compare upper and lower curves in Fig. 9).

Fig. 9. Effect of Mercury Concentration on the Rate of Dissolution of Aluminum in Boiling 4 M Nitric Acid in the Presence of Lead. Al/Pb mole ratio = 8.77; HNO_3 /Al mole ratio = 4, Aluminum specimens were 0.95 cm dia., 2.5 cm high right cylinders.

Table 8. Initial Rates of Dissolution of Lead Foil in Dilute Nitric Acid

Conditions: Dissolution Time = 10 min
Temperature = boiling point

HNO_3 Conc., M	Initial HNO_3/Pb Mole Ratio	Rate, mg/min/cm ²
0.5	2	3.1
1.0	2	7.7
1.5	2	11.0
2.0	2	13.1
0.5	3	3.3
1.0	3	9.3
1.5	3	13.2
2.0	3	15.9

1.5 Radiation Damage to Solvents and Diluents (W. Davis, Jr.)

(Work Performed at Stanford Research Institute on Subcontract 1081)

Di-sec-Butyl Phenylphosphonate Systems. Di-sec-butyl phenylphosphonate was irradiated to the 200 watt-hr/liter level as the pure extractant and as a 1 M solution in a diluent composed of 20 vol % o-xylene in Amsco 125-82. Yields of monobasic acid from these irradiations were 0.54 and 0.25 molecules/100 ev, respectively (Table 9). These values are similar to those obtained with n-butyl phenylphosphonate (Table 9) and are considerably smaller than corresponding yields from tributyl phosphate.

Table 9. Data on Irradiation of Phenylphosphonates and TBP

	Normal Ester ^a	Secondary Ester ^b	1.15 M Normal Ester ^a in Diluent ^c	1 M Secondary Ester in Diluent ^d	TBP
Dose, watt-hr/liter	400	200	210	200	300
G for Monobasic Acid	0.78	0.54	0.22 ^e	0.26	2.07
G gas	0.49	0.33	1.67	1.01	1.87

a. Normal ester is di-n-butyl phenylphosphonate.

b. Secondary ester is di-sec-butyl phenylphosphonate.

c. Diluent was Amsco 125-82.

d. Diluent was 20 vol % o-xylene in Amsco

e. This is the yield of total acid of which the monobasic acid is the predominant component.

1.6 Corrosion Studies (W. E. Clark)

(Work done by Battelle Memorial Institute under Subcontract No. 988 and by members of REED, ORNL.)

1.61 Darex-Purex

Tests have been concluded on specimens of Type 347 stainless steel in Darex-Purex solutions. Two types of solution were used as follows:

- (1) 2 M HNO_3 - 60 g/l dissolved stainless steel - 5 g/l UO_2^{++} .
- (2) 2 M HNO_3 - 27 g/l dissolved stainless steel - 320 g/l UO_2^{++} .

The aqueous solution was mixed with an organic phase in the ratio of 2 to 3, the organic phase consisting of one part, by volume, of tributyl phosphate to two parts of Apco 125. Chloride contaminations from 2 ppm to 1.00 w/o in the aqueous phase were studied in separate experiments.

Specimens in the form of disks, coupons stressed to 90 per cent of their yield strength, and coupons bent past their elastic limit into the shape of horseshoes were exposed. These were submerged in the aqueous phase of the system contained in long, stoppered tubes. The tubes were kept at room temperature and, during the first few weeks, the specimens were removed daily while the two-phase system was intimately mixed by vigorous shaking.

When no attack developed during the first few months, the specimens were inspected at 6-month intervals. After 2 years of exposure, the study was discontinued. No sign of attack was observed on any of the specimens except for a slight brightening of the surfaces. The weight changes were insignificant. No cracking or other localized attack could be found even upon a metallographic study of the specimens from the solution containing the highest chloride contaminations.

Under the conditions of these experiments, there is no indication that even large chloride contaminations will cause corrosion of Type 347 stainless steel Purex extraction system equipment.

1.62 Darex-Thorex and Sulfex-Thorex

The exposure of butt-and lap-welded titanium specimens to boiling 13 M HNO_3 - 0.04 M F^- with and without Al^{+3} and Th^{+4} has been continued for a total of 1000 hrs. The results (Table 10) show little change from those reported for an exposure time of 736 hr.¹⁵ Relatively high rates (5-10 mils/mo) of uniform attack were observed in the absence of any complexing agent whereas in the presence of more than 0.04 M Al^{+3} much lower rates of attack were observed but these were accompanied by pitting. In the presence of 0.04 M Al^{+3} rates were relatively low ($\leq$ 1.6 mils/mo) and no localized attack was observed. Representative specimens showing the change in the nature of the attack are shown in Fig. 10.

Ca. 4X

Fig. 10. Vapor-Phase Titanium Specimens Following 1000 hr of Exposure to Various Thorex Solutions. (See Table 10 for specimen designation)

Table 10. Corrosion Rates and Weight Losses for Welded Titanium 75A
in Boiling Thorex Solutions
(1000-hr Exposure, Good Weldments)

Solution (a)	Addition	Specimen Position	Corrosion Rate, mils per month		
			Designation in		
			Butt Weld	Figure 1	Lap Weld (b)
Initial	--	Vapor	7.3	A	10.
		Interface	5.8		7.4
		Liquid	5.1		5.9
Initial	0.04 M Al ⁺³	Vapor	1.6	B	1.4
		Interface	0.43		0.45
		Liquid	0.36		0.38
Initial	0.09 M Al ⁺³	Vapor	0.39	C	0.81
		Interface	g(c)		0.10
		Liquid	g		g
Initial	0.15 M Al ⁺³	Vapor	0.75	D	3.2
		Interface	0.01		g
		Liquid	g		g
Initial	0.20 M Al ⁺³	Vapor	3.4	E	0.76
		Interface	0.40		0.04
		Liquid	g		g
Initial	0.04 M Th ⁺⁴	Vapor	7.2	H	-
		Interface	2.6		-
		Liquid	1.7		-
Middle	0.04 M Al ⁺³ (0.5 M Th ⁺⁴)	Vapor	2.7	F	1.5
		Interface	0.13		g
		Liquid	g		g
Final	0.04 M Al ⁺³ (1.0 M Th ⁺⁴)	Vapor	1.5	G	-
		Interface	0.61		-
		Liquid	0.19		-

(a) Thorex solution compositions: Initial - 13.0 M HNO₃, 0.04 M F⁻.
Middle - 10.8 M HNO₃, 0.04 M F⁻, 0.5 M Th⁺⁴.
Final - 8.5 M HNO₃, 0.04 M F⁻, 1.0 M Th⁺⁴.

(b) Based on an approximate area of 1.3 sq. in. neglecting area inside crevice.

(c) g indicates a small gain in weight.

Other investigators¹⁶ have reported failure of RC 55 Titanium in the presence of fluoride and chloride contaminations together. In this case, no aluminum additions were made and the rates quoted were not appreciably higher than those occurring during studies at BMI with fluoride alone. However, since chloride carry-over is possible in the core dissolution by the Darex-Thorex route, two duplicate studies are under way to determine its effect. Both plain and welded Titanium 75A specimens are being exposed to boiling initial Thorex solutions (13.0 M HNO₃, 0.040 M F⁻, 0.10 M Al³⁺, and 100 ppm Cl⁻). Fresh solution has been used after each weekly inspection (Table 11). These specimens in general, show much less attack after 669 hr than the titanium exposed in the absence of chloride ion after a similar period. Occasional pitting was noted on the liquid-phase specimens, while the specimens exposed to the vapor phase showed somewhat more pitting concentrated on the lower edge of the specimen where liquid may have formed. The specimens were lightly etched and slightly discolored. The exposure will be continued.

Table 11. Exposure of Titanium 75A To Boiling Initial Thorex Solution⁽¹⁾ Contaminated with 100 ppm Chloride

Specimen Type	Specimen Position	Corrosion Rates, mil per month							
		168 hr		339 hr		500 hr		669 hr	
		A ⁽²⁾	B ⁽²⁾	A	B	A	B	A	B
Plain	Vapor	0.01	0.07	0.12	0.03	0.11	0.02	0.09	0.01
	Interface	g ⁽³⁾	0.03	g	0.01	g	0.01	0.00	0.02
	Liquid	g	0.03	g	0.03	g	0.02	0.00	0.01
Butt welded	Vapor	-	0.04	-	0.02	-	0.01	-	0.05
	Interface	-	0.06	-	0.05	-	0.11	-	0.17
	Liquid	0.05	0.05	0.02	0.04	0.20	0.06	0.22	0.07
Lap welded ⁽⁴⁾ (2 beads)	Vapor	0.08	0.00	0.22	g	0.27	0.02	0.30	0.03
	Interface	-	0.00	-	0.01	-	0.03	-	0.06
	Liquid	0.00	0.00	0.02	0.00	0.06	0.02	0.11	0.04

- (1) Composition: 13.0 M HNO₃, 0.040 M F⁻, 0.10 M Al(NO₃)₃, 100 ppm Cl⁻.
 (2) A and B denotes duplicate specimens exposed in separate containers.
 (3) g indicates a small gain in weight.
 (4) Based on approximate area of 1.5 sq. in., neglecting area inside crevice.

After 25 Darex-Thorex dissolutions of Consolidated Edison fuel pins in a titanium dissolver, the generalized corrosion rate based on the weight loss of the dissolver was 0.2 mils/mo. The conditions were: 1st cycle; boiling 2 M HCl-5 M HNO₃ for 2 hours. 2nd cycle; 1st pass, boiling 13 M HNO₃-0.04 M F⁻-0.09 M Al⁺³ for 5 hours; 2nd pass, 13 M HNO₃-0.04 M F⁻-0.09 M Al⁺³ for 3 hrs. Titanium coupon specimens exposed in the dissolver show slightly lower rates (Table 12).

Table 12. Titanium 75A Corrosion Specimens from Darex-Thorex Dissolver (25 Darex-Thorex Cycles)

Specimen	Approximate Area, Sq. In.	Specimen Position	Weight Change, mg						
			Number of Cyclic Dissolution						
			5	10	11	12	15	20	25
			36 hr	81 hr	91 hr	99 hr	126 hr	171 hr	216 hr
Butt Welded	1.2	Liquid	-0.7	-0.5	+0.2	+0.3	+0.6	+0.2	+1.0
Butt Welded	4.2	Liquid	+1.6	+2.9	+5.5	+6.7	+10.1	+9.9	+11.2
Plain	4.2	Liquid	+2.8	+4.4	+6.3	+4.9	+9.1	+9.2	+10.9
			18 hr	26 hr	53 hr	98 hr	143 hr		
Lap Welded, two bead	1.4	Vapor ^(b)	-	-	-0.2	+0.3	-0.2	-1.0	-0.5
Butt Welded	1.2	Vapor ^(b)	-	-	-1.3	-1.2	-1.1	-1.9	-1.3 ^(c)

(a) Cycle 1: Boiling 2 M HCl-5 M HNO₃ for 2 hours
 Cycle 2: Boiling 13 M HNO₃-0.04 M F⁻-0.09 M Al⁺³ for 5 hours followed by fresh boiling 13 M HNO₃-0.04 M F⁻-0.09 M Al⁺³ for 3 hours

(b) Vapor specimens were put in after 9 cycles. Each complete dissolution cycle requires 9 hr.

(c) A weight loss of 1.3 mg at 143 hr equals 0.08 mil per month.

After 15 Sulfex-Thorex dissolutions in a Ni-o-nel dissolver (1st cycle: 3 hours in boiling 6 M H₂SO₄. 2nd cycle same as for Darex Thorex above) the weight loss of the dissolver indicated an over-all corrosion rate of 2.3 mils/mo. Coupon specimens of Ni-o-nel exposed in the dissolver showed rates varying between 1.5 and 4.5 mils/mo depending upon the prior treatment of the specimen and its location in liquid or vapor phase (Table 13).

After 25 cyclic dissolutions have been completed, both dissolvers will be sectioned for metallographic examination.

1.63 Nitric Acid-Mercuric Nitrate (for dissolution of Al-Clad fuels in Darex dissolver)

Microscopic examination of lap-welded titanium specimens revealed a possibility that intergranular penetration of the metal may have initiated during a 288-hr period in boiling 8.0 M HNO₃, 0.05 M Hg(NO₃)₂. An

Table 13. Ni-o-nel Corrosion Specimens from Sulfex-Thorex Dissolver^(a)

Specimen	Area, Sq. In.	Specimen Position	Corrosion Rates, mils per month					
			Number of Cyclic Dissolutions					
			1	7	9	10	15	17
			8 hr	80 hr	102 hr	121 hr	176 hr	198 hr
A (Unwelded, heat treated) ^(b)	4.8	Liquid	3.1	1.9	1.8	1.9	1.7	1.7
B (Heat treated ^(b) after welding)	4.4	Liquid	4.7	2.8	2.6	2.7	2.4	2.2
C (Heat treated ^(b) before welding)	4.8	Liquid	3.8	2.1	1.9	2.1	1.8	1.7
			11 hr	36 hr	55 hr	110 hr	132 hr	
D (Heat treated ^(c) after welding)	1.2	Vapor ^(d)	-	2.5	2.3	3.4	4.2	4.5
E (As received)	1.4	Vapor ^(d)	-	2.0	1.4	1.7	1.5	1.4

(a) Cycle 1: Boiling 6 M H_2SO_4 for 3 hours

Cycle 2: Two successive passes of 5 and 3 hours respectively in boiling
13 M HNO_3 -0.04 M F^- -0.09 M Al^{+3} .

(b) Heat treated at 1950°F, 2 hr; air quenched, sandblasted, then pickled.

(c) Heat treated at 1850°F, 1/2 hr; air quenched, surface ground.

(d) Vapor specimens were put in after the sixth pin.

additional 168-hr exposure did not reveal any more positive evidence of intergranular attack, and the specimens were similar in appearance to a group exposed to boiling 8.0 M HNO_3 containing no $\text{Hg}(\text{NO}_3)_2$. These tests will be continued several more periods after which the specimens will be examined metallographically for intergranular corrosion and crevice attack. Results obtained to date are given in Table 14.

Table 14. Titanium Crevice-Weld Specimens in Boiling
8.0 M HNO_3 , 0.05 M $\text{Hg}(\text{NO}_3)_2$

Specimen Position	Corrosion Rates, mils per month				
	72 hr	144 hr	216 hr	288 hr	456 hr
(V)	neg	neg	gain	0.0	gain
	neg	neg	gain	0.0	gain
(I)	0.3	0.3	0.4	0.3	0.3
	0.6	0.5	0.5	0.4	0.3
(S)	0.4	0.5	0.7	0.7	0.8
	0.4	0.5	0.7	0.7	0.5

1.64 Hydrofluoric Acid-Hydrogen Peroxide System (Perflex Process)

The conclusion reached last month¹⁵ that monel is not a satisfactory container material for the dissolution of Zr in 1 M HF-0.06 M H_2O_2 has been confirmed by further tests. The data (summarized in Tables 15-18) indicate that the corrosion rate drops off sharply with time, doubtless corresponding to the decomposition of H_2O_2 . In the absence of further additions of H_2O_2 maximum rates over a 4 hour exposure are as high as 157 mils/mo. This was decreased to 57 mils/mo by contact with dissolving Zr and blanketing with N_2 (Table 18).

Table 15. Corrosion Rates of Monel (ASTM B-127, Hot-Rolled, Annealed Descaled, Class A) in 1.0 M HF, 0.06 M H_2O_2 at 100°C (a)

Specimen Position	Corrosion Rates, mils per month				
	24 hr	48 hr	72 hr	96 hr	160 hr
(V) Vapor	13.4	13.1	15.2	15.7	16.2
(I) Interface	24.2	22.4	23.9	22.0	17.1
(S) Solution	20.7	21.2	19.4	20.8	16.5

(a) Fresh solution was used for each 24 hour exposure.

Table 16. Corrosion Rates of Monel in 1.0 M HF at 100°C

Specimen Position	Corrosion Rates, mils per month						
	24 hr	48 hr	114 hr	138 hr	166 hr	190 hr	24 hr*
(V)	9.6	7.6	8.7	9.4	9.7	10.2	0.2
(I)	3.5	3.5	2.1	2.1	2.0	2.5	0.4
(S)	0.9	1.0	0.9	0.9	0.9	0.9	0.4

* In presence of dissolving Zircaloy-2.

Table 17. Corrosion Rates of Monel in 1.0 M HF at 100°C
With Air Excluded by Condenser Seal and N₂
Passed Over the Solution

Specimen Position	Corrosion Rates, mils per month	
	24 hr	48 hr
(V)	0.9 0.0	0.4 0.3
(I)	1.5 1.1	1.1 1.0
(L)	1.9 2.5	2.4 2.4

Table 18. Effects of Air Exclusion and Dissolving Zircaloy-2
on Corrosion Rates of Monel in 1.0 M HF, 0.06 M H₂O₂ at 100°C

Specimen Position	Corrosion Rates, mils per month			
	Condenser Open	4 hr	10 hr	
		Condenser Sealed, N ₂ Passed	Condenser Open	Condenser Sealed, N ₂ Passed
(V)	2.93	1.6 1.7	2.31	0.9 0.9
(I)	157.0	91.7 96.7	111.0	67.8 58.0
(L)	143.0	109.0 100.0	100.0	95.3 87.8
(C) Zr contact (solution phase)	92.8	57.1	69.0	62.0

Scouting tests on INOR-8 gave a maximum rate of 47.2 mils/mo over a 24-hour exposure (Table 19) compared with 24.2 for monel (Table 15). Other metals will be scouted in this solution.

Table 19. Corrosion Rates of INOR-8 in 1.0 M HF, 0.06 M H_2O_2 at 100°C^(a)

Specimen Position	Corrosion Rates, mils per month	
	24 hr	48 hr
(V)	13.7	13.6
(I)	47.2	32.0
(S)	35.2	23.9

(a) Fresh solution was used for each of the two 24-hour test periods

2.0 WASTE TREATMENT AND ION EXCHANGE (J. T. Roberts)

2.1 Characterization of High Level Wastes

2.11 Evaporation and Calcination of Acidic Wastes (H. W. Godbee, J. E. Davidson)

Batch evaporation and calcination of acidic TBP-25 waste¹⁷ to 350°C yielded a porous, crumbly off-white solid residue. The residue was not held at this temperature for any appreciable length of time but was allowed to cool to room temperature immediately. Density of the residue was approximately 0.56 g/ml at 24°C. The volume reduction factor was about 3-1/3.

The condensate volume was 95.7% of the original waste volume and contained 84.5% of the original waste weight (Table 20). The condensate, residue, and off-gas contained 81.2, 16.8, and 3.6%, respectively of the initial nitrate (Table 20). The data taken at intermediate points during the evaporation and calcination are shown in Figs. 11-14.

Table 20. Batch Evaporation and Calcination of Acidic TBP-25 Waste to 350°C

Starting Composition: 1.6 M Al^{+3} , 0.07 M NH_4^+ , 0.01 M Hg^{+2} , 0.002 M Fe^{+3} , 0.5 M H^+ , 0.026 M SO_4^{-2} , 5.35 M NO_3^- .

	Volume (ml at 24°C) and 1 atm	Weight (grams)	g-moles NO_3^-
Initial	4000	5056	21.4
Condensate	3829	4271	17.4
Residue	1200	670	3.59
Off-Gas	23456*	52*	0.77
Material Balance	-	98+%	101+%

Batch evaporation and calcination of acidic Darex waste¹⁷ to 400°C yielded a porous, crumbly, dark brown solid. The residue was not held at this temperature but was allowed to cool to room temperature immediately. Density of the residue was approximately 0.85 g/ml at 24°C. The volume reduction factor was about 8.

* Calculated assuming composition is stoichiometric NO_2-O_2 mixture and that perfect gas law applies.

Fig. 11. Batch Evaporation and calcination of Acidic TBP-25 Waste to 350°C. TBP Waste: 1.6M Al³⁺, 0.07M NH₄⁺, 0.01M Hg²⁺, 0.002M Fe³⁺, 0.5M H⁺, 0.26M SO₄²⁻, 5.35M NO₃⁻.

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Fig. 12. Batch Evaporation and Calcination of Acidic TBP-25 Waste to 350°C.
TBP-25 Waste: 1.6 M Al^{+3} , 0.07 M NH_4^+ , 0.01 M Hg^{+2} , 0.002 M Fe^{+3} , 0.5 M H^+ ,
0.026 M SO_4^- , 5.35 M NO_3^- .

Fig. 13. Batch Evaporation and Calcination of Acitic TBP-25 Waste to 350°C.
TBP-25 Waste: 1.6 M Al^{+3} , 0.07 M NH_4^+ , 0.01 M Hg^{+2} , 0.002 M Fe^{+3} , 0.5 M H^+ ,
0.026 M SO_4^- , 5.35 M NO_3^- .

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Fig. 14. Batch Evaporation and Calcination of Acidic TBP-25 Waste to 350°C .
TBP-25 Waste: 1.6 M Al^{+3} , 0.07 M NH_4^+ , 0.01 M Hg^{+2} , 0.002 M Fe^{+3} , 0.5 M H^+ ,
 $0.026 \text{ M SO}_4^{=}$, 5.35 M NO_3^- .

The condensate volume was 99.1% of the original waste volume and contained 91.3% of the original waste weight (Table 21). The condensate, residue, and off-gas contained 94.6, 0.81, and 4.27%, respectively, of the initial nitrate (Table 21). The data taken at intermediate points during the evaporation and calcination are shown in Figs. 15-18.

Table 21. Batch Evaporation and Calcination of Acidic Darex Waste to 400°C

Starting Composition: 0.075 M Ni^{+2} , 0.68 M Fe^{+3} , 0.16 M Cr^{+3} , 0.123 M Al^{+3} , 2.95 M H^{+} , 6.0 M NO_3^{-} , 30 ppm Cl^{-} .

	Volume (ml at 24°C) and 1 atm	Weight (grams)	g-moles NO_3
Initial	4000	5040	24.0
Condensate	3963	4602	22.7
Residue	~500	424	0.19
Off-Gas	31376*	69*	1.03
Material Balance	-	101+%	99+%

* Calculated

In Tables 20 and 21 it is shown that about 4% of the nitrate reported to the off-gas, giving a calculated volume of 6-8 liters of uncondensed NO_2 - O_2 per liter of initial waste. Both the NO_2 and O_2 were readily absorbed in water bubblers to form nitric acid, so that the final off-gas volume was negligible. In these experiments a simple downdraft condenser was used. By condensing and scrubbing the evaporator vapors in a refluxing multiplate column the vapors should be quantitatively condensed without using additional water.

Batch evaporation to 136.8°C of acidic Darex waste containing 45 ppm chloride yielded a residue and a condensate containing 22 and 11%, respectively, of the initial chloride. The residue and condensate contained 19.4 and 80.5%, respectively, of the initial weight of waste.

2.12 Thermal Conductivity of Calcined Waste (H. W. Godbee)

Calculations have shown that none of the theoretical equations currently available for calculating the thermal conductivity of composite gas-solid materials fit exactly the experimental data obtained for a calcined TBP-25 waste (Fig. 19). These equations calculate the thermal conductivity of such a two phase material from the properties and volume fractions of the component substances.

Fig 15. Batch Evaporation and Calcination of Acidic Darex Waste to 400°C. Darex Waste: 0.075M Ni⁺², 0.68M Fe⁺³, 0.16M Cr⁺³, 0.123M Al⁺³, 2.95M H⁺, 6.0M NO₃⁻, 30ppm Cl⁻.

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Fig. 16. Batch Evaporation and Calcination of Acidic Darex Waste to 400°C.
Darex Waste: 0.075 M Ni^{+2} , 0.68 M Fe^{+3} , 0.16 M Cr^{+3} , 0.123 M Al^{+3} , 2.95 M H^{+} ,
6.0 M NO_3^- , 30 ppm Cl^- .

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Fig. 17. Batch Evaporation and Calcination of Acidic Darex Waste to 400°C.
Darex Waste: 0.075 M Ni^{+2} , 0.68 M Fe^{+3} , 0.16 M Cr^{+3} , 0.123 M Al^{+3} , 2.95 M H^+ ,
6.0 M NO_3^- , 30 ppm Cl^- .

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Fig. 18. Batch Evaporation and Calcination of Acidic Darex Waste to 400°C.
Darex Waste: 0.075 M Ni⁺², 0.68 M Fe⁺³, 0.16 M Cr⁺³, 0.123 M Al⁺³, 2.95 M H⁺,
6.0 M H⁺, 6.0 M NO₃⁻, 30 ppm Cl⁻.

Fig. 19. Comparison of Experimental and Calculated Thermal Conductivity for a Calcined TBP-25 Waste.

The best fit thus far has been given by an equation¹⁸ of the form

$$\frac{1}{k_p} = \frac{1-P}{k_s} + \frac{P}{k_g + \frac{4E\sigma T^3}{d_p}}$$

where k_p is the thermal conductivity of the granular porous body, k_g is the conductivity of the gas phase, k_s is the conductivity of the solid phase, E is the effective emissivity ($E/2-E$), σ is the radiation constant, T is the mean absolute temperature, d_p is the pore length, and P is the porosity.

The empirical fit obtained with this equation, using an effective mean pore length of 11.4 mm, is compared with the experimental results for a calcined TBP-25 waste and with the results obtained by P. N. Kelly at the Idaho Chemical Processing Plant on fluid bed calcined aluminum nitrate waste in Fig. 19.

2.13 Volatility of Ruthenium During Evaporation of Radioactive Wastes (L. L. Ennis)

Batch evaporation to dryness of simulated Darex and Purex wastes¹⁷ to study ruthenium volatility was performed in a glass evaporator and condenser with a silica gel bed and caustic scrubber in series for treating non-condensibles. Evaporations were made under a vacuum of a few inches of water to avoid contamination of the operating area. Feed for all runs had about 10^6 c/m/ml of β activity from ruthenium-106 tracer and runs 6 and 7 contained in addition approximately 0.03 g/l of stable ruthenium. Clean equipment was used in all runs except for 1 and 2. Table 22 shows the feed and the special conditions used in several runs in an attempt to suppress ruthenium evolution. Table 23 shows the distribution of ruthenium with maximum evaporator temperatures. It was found that the addition of a small volume of 30% TBP-Amsco was more than five times as effective as stainless turnings in suppressing the ruthenium level in the condensate. Very little ruthenium was volatilized in any run until the evaporator acidity reached 9 N or above. Oxidation conditions at this normality are thought to be strong enough for the rapid formation of the volatile tetroxide. Two additional runs are being made to study the effect of 30% TBP-Amsco in fission product-spiked feeds. The amount of ruthenium reporting to the silica gel traps and caustic scrubbers was too low for accurate counting or for silica gel saturation and regeneration studies. Considerable plating of ruthenium at the condenser inlet was evident in all runs. The material balance shows that 20-30% of the ruthenium is unaccounted for in analyses of condensate, cake, and off-gas traps.

A stainless calciner is ready for ruthenium volatility studies at higher temperatures.

Table 22. Feed for Ru Volatility Studies

Run Feed

1. 6 M HNO_3
2. 6 M HNO_3
3. Purex concentrate
4. Darex
5. Purex concentrate-Stainless rings and turnings in evaporator and condenser inlet
6. Purex concentrate - Stainless turnings in evaporator and condenser inlet
7. Purex concentrate - 3 ml 30% TBP-Amsco added to 200 ml feed

Table 23. Ruthenium Distribution

Run	Time Hours	Final Pot Temp °C	Ru-106, % of Feed		
			Condensate	Silica Gel and Caustic Bubbler	Product
1	3-1/2	126	12	<0.01	*
2	2-1/2	126	49	<0.01	*
3	3-1/2	165	41	<0.01	28
4	2-1/2	160	36	<0.01	54
5	2	180	35	<0.01	39
6	1-1/2	170	23	<0.01	52
7	2	170	4	0.02	47

* not measured

2.14 Pyrolysis of Waste Solids (J. E. Savolainen)

Nitrates can be converted to oxalates and the nitrate values recovered as nitric acid. The residue obtained on pyrolysis of the oxalates consist of granular products. Apparently the trivalent cation salts form oxides, while divalent salts are reduced to the metallic state.

Pyrolysis at 400°C of the oxalate salts of stainless steel components yields the oxide of iron, Fe_3O_4 , chromium, Cr_2O_3 , and nickel, NiO . Ferrous oxalate presumably would form metallic iron on pyrolysis¹⁹ while ferric oxalate appears to form magnetite. The low temperature pyrolysis products of the oxalate salts were subjected to a further reduction treatment at 500°C in an atmosphere of carbon monoxide. Nickel was the only metal which was reduced by carbon monoxide at 500°C. Some of the iron may have been reduced but presumably it reoxidizes back to magnetite, Fe_3O_4 , heat was evolved when the specimen was exposed to air.

Pyrolysis of uranyl oxalate yields the dioxide according to the x-ray diffraction pattern although the product may have been U_4O_9 .

Pyrolysis of aluminum oxalate yields aluminum oxide.

2.2 Maritime Reactor Waste Disposal Studies (R. R. Holcomb)

The 304SS pressure-temperature loop (Fig. 20) for the production and study of simulated reactor cooling water has been completely rebuilt. Installation of the new Lapp LS-20 "microflo" pump, two demineralizer resin beds and conductivity flow cells has been completed. Instruments to control and record temperature, pressure and conductivity have been installed. The loop has been operated for two weeks under varying conditions for preliminary tests. Some difficulty in maintaining a constant pressure was encountered due mainly to pump failures. However, the latest runs have indicated that steady state conditions can be maintained over extended periods of time. Full design conditions, 1750 psi and 550°F, have been maintained for only two days. The best conductivity readings to date have measured ~2.0 mhos on the inlet side of the demineralizers and ~0.4 mhos on the outlet side. About one inch of the anion resin in the indicating mixed bed has changed from blue to yellow due to impurities such as CO₂ in the initial feed water.

The sea water leaching of activity from resin embedded in concrete has temporarily been discontinued. The reported²⁰ fissure in the concrete block which occurred after 28 and 44 hours of leaching resulted in an increase of activity of 25 γ c/min/ml of sea water or 0.075% of the total activity. The activity leached from the concrete block continued to increase. After 117 hours, the activity leached was 91 γ c/min/ml of sea water or 0.27% of the total activity.

3.0 FEED MATERIALS PROCESSING

(O. C. Dean)

3.1 Reduction of Uranium Fluorides with Sodium (O. C. Dean)

Small pieces of uranium metal and sodium fluoride were heated together at 1150°C in a magnesia crucible to determine the feasibility of consolidating the metal to a single mass, and also the effects of the mixture on the MgO crucible. A mixture containing 100 grams of 1/4 in. long pieces of fine uranium turnings and 107 grams of -100 mesh, dry NaF powder was heated under vacuum in a Norton Magnorite 20% porosity, 1800°C-fired, high density MgO crucible at 1150°C for 7 hr.

Sixty-four grams of the uranium was recovered in a single mass at the bottom of the crucible. The remainder had reacted with the NaF to produce UF₄ and free sodium. The sodium, and part of the UF₄ had vaporized in the vacuum and had deposited on the cooler surfaces of the inconel reactor shell. Part of the UF₄ dissolved in the molten NaF and reacted with the MgO wall at the interface to form UO₂ and MgF₂. X-ray diffraction analysis showed the brown crust on the crucible wall to be composed mainly of NaF and UO₂, with also at least 5% MgF₂ and 5% uranium metal. The series of reactions which probably occurred to give the above results was:

The crucible was cracked radially immediately above the level of the uranium metal mass. This indicated that sodium and/or sodium fluoride penetration had been the cause, and that it had occurred after the temperature had exceeded the melting point of the uranium.

3.2 Reactivity, Surface Area and Sinterability of UO_2 Powders (O. C. Dean)

Studies leading to the development of a simple test which would give surface area and predict the sinterability of a UO_2 powder were continued. In one series of experiments the procedure for determination of the acid number of UO_2 ²¹ was altered to eliminate anionic impurities since the latter give extraneous inflections in the titration curve. In the altered method, ten grams of the UO_2 sample was refluxed with 50 ml of 0.5 M NaOH-0.001 M $\text{Na}_4\text{P}_2\text{O}_7$ for 30 min under argon, centrifuged, washed and then slurried with 50 ml of boiled, distilled water. The slurry was then titrated with 0.1 N HCl to an end point at pH 2.9. The acid number was defined as the number of milliequivalents (x100) of HCl required to change the pH from 7.0 to 3.0, the two inflection points in the titration curve. The correlation of acid numbers obtained in the application of the above method with the surface area of seven ceramic grade oxides as measured by the BET method and to final sintered density was only fair. It was thought that the scatter was due to residual sodium pyrophosphate used as a dispersing agent and to aggregates in the sample which did not break down to make all surface available to the reagent.

The methylene blue test²² for surface area and sinterability of UO_2 powders was studied further. In a series of experiments with six UO_2 powders, two-gram samples were agitated with 50 ml of phosphate-buffered methylene blue solution for 10 min at room temperature under argon. The solution contained 0.16 g/l methylene blue and was buffered to a pH of 8 by 13.6 g/l KH_2PO_4 , and 86 ml of 1.1 N NaOH/liter. In addition, it contained 0.1 g $\text{Na}_2\text{P}_2\text{O}_7$ /liter as a dispersing agent. The UO_2 was separated from the slurry by centrifugation and the optical density of the supernatant liquor at 6700Å was measured. The decrease in optical density of the buffered methylene blue solution produced by 2 grams of UO_2 was plotted against the total surface area and final sintered density of the samples (Fig. 20). The correlation of the methylene blue adsorbed with final sintered density of the samples was good, but only fair with the total surface area. The test needs more study with a wider variety of UO_2 samples to define its accuracy. There is some evidence that the presence of normal phosphate inhibits methylene blue adsorption by UO_2 .

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Fig. 20. Correlation of Methylene Blue Adsorption of UO_2 Powders with BET Surface Area and Sintered Density. (Initial methylene blue optical density, 30.1; m. b. concentration: 0.16 g/liter; volume of solution, 50 ml; 13.6 g/liter KH_2PO_4 ; 0.095 M NaOH. 2g UO_2 per sample.

3.3 Thoria Coatings for UO_2 Powders (H. B. Whetsel)

In the preparation of a dispersion fuel composed of UO_2 dispersed in thorium metal, a diffusion barrier of ThO_2 is needed to prevent chemical reduction of UO_2 by thorium metal during metallurgical processing. One proposal for erecting this barrier was to coat the UO_2 with thorium perfluorobutyrate (Th PFB) and then to thermally decompose the compound to ThO_2 . Thorium PFB is very surface-active and can be readily deposited on oxide surfaces as a monolayer from ether or ether-carbon tetrachloride solutions. Subsequent treatments would increase the thickness of the layer. Thorium PFB was prepared by mixing a solution of thorium nitrate with an aqueous solution of sodium perfluorobutyrate. The ThPFB was extracted with diethyl ether and the ether was evaporated. The solid crystals of ThPFB were washed free from excess perfluorobutyric acid with CCl_4 . The salt will be deposited from ether solution onto a special dispersion grade of UO_2 powder provided by the Metallurgy Division.

3.4 Relationship of Particle Size and Sinterability of UO_2 (O. C. Dean)

The particle size distribution of eight UO_2 powders was studied by the Neutron Activation method.²³ On probability paper, the particle size in microns were plotted against percentage of particles less than the given size.

Samples of UO_2 which had higher specific surface areas and sintered to higher densities also had higher percentages of small particles. Plots of percent of particles with diameters <1 micron against specific surface and sintered densities for the powders (Fig. 21) shows that the properties correlated well. It also shows that UO_2 samples having less than 20% of particles less than 1 micron in size are unlikely to sinter well.

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ORNL-LR-DWG 39632

Fig. 21. Relation of Size Distribution of UO_2 Particles to Surface Area and Sintered Density.

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Distribution

1. J. B. Adams
- 2-3. R. E. Blanco
4. J. O. Blomeke
5. J. C. Bresee
6. K. B. Brown
7. F. R. Bruce
8. W. E. Clark
9. F. L. Culler
10. W. Davis, Jr.
11. O. C. Dean
12. L. M. Ferris
13. J. R. Flanary
14. T. A. Gens
15. D. E. Ferguson
16. H. E. Goeller
17. A. E. Goldman
18. J. M. Googin
19. A. T. Gresky
20. P. A. Haas
21. R. F. Hibbs
22. J. M. Holmes
23. R. W. Horton
24. A. R. Irvine
25. F. G. Kitts
26. Eugene Lamb
27. W. H. Lewis
28. R. B. Lindauer
29. A. P. Litman
30. J. P. Nichols
31. R. H. Rainey
32. J. T. Roberts
33. J. E. Savolainen
34. A. C. Schafer
- 35-37. E. M. Shank
38. M. J. Skinner
39. S. H. Smiley, K-25
40. E. G. Struxness
41. J. A. Swartout
42. J. W. Ullmann
43. C. D. Watson
44. M. E. Whatley
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46. F. P. Baranowski, AEC, Wash.
47. L. P. Bupp, Hanford
48. J. T. Christy, AEC, Hanford
49. V. R. Cooper, Hanford
50. R. A. Ewing, BMI
51. F. W. Fink, BMI
52. M. K. Harmon, Hanford
53. O. F. Hill, Hanford
54. F. Kerze, AEC, Wash.
55. S. Lawroski, ANL
56. J. A. Lieberman, AEC, Wash.
57. B. Manowitz, BNL
58. J. W. Morris, du Pont, Savannah River
59. D. M. Paige, ICPP
60. M. Pobereskin, BMI
61. C. A. Rohrman, Hanford
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