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CHEMICAL TECHNOLOGY DIVISION

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ABSTRACT

The measured diffusivity of uranyl nitrate in water at 25°C was 0.7×10^{-8} cm²/sec with about 40% average deviation. A program was started to develop nonnuclear uses for depleted uranium. Two continuous DRUM reaction runs were terminated due to erratic operation of the sodium metering system. In the second Fluorox run with crude UF₄ which lasted for 29 hr, a total material balance of 94.8% was obtained and 17.9% of the theoretical amount of UF₆ was collected in cold traps and chemical traps. Room temperature flow rate-pressure drop calibrations of a multiclone (thirteen 0.60-in. dia hydroclones in parallel) for installation with the HRT replacement circulating pump were completed. Mixed oxides of U:Th = 0.08:1 and 1, 2-1/2, 5, and 10 weight per cent Al₂O₃ prepared by flame denitration all have low yield stresses of 0.02-0.05 lb/sq ft compared to 0.2-1.0 lb/sq ft for normal Th-U or Th oxides of 1.5-2.5 micron mean diameter. The rates of uranium anion exchange from solutions containing between 0.025 and 0.20 M sulfate were measured and apparent uranium diffusion coefficients between 1.2×10^{-7} cm²/sec and 1.6×10^{-7} cm²/sec were calculated. In bench scale studies, the Darex reference flowsheet was successfully applied to stainless steel-clad UO₂ fuels (Yankee Atomic) and to aluminum-uranium foreign reactor fuels. The corrosion of titanium A-55 was measured in the vapor and liquid phases of a modified boiling Thorex dissolvent (13 M HNO₃, 0.04 M F⁻, 0.1 M H₃BO₃) containing 0.0, 0.5 and 1.0 M thorium from dissolved Consolidated Edison pellets and the maximum corrosion rate was 0.6 mils/month. Siliceous filter cakes resulting from the filtration of Darex solvent extraction feed solutions through porous metal filter elements were easily washed to a uranium loss of 0.1% in the discarded cake. A run with an acid-deficient Darex-Redox feed containing soluble silica resulted in uranium losses higher by a factor of 20 than those previously obtained in the same column with a standard Redox feed. Batch leaching of sheared pieces, 1/2 in. to 5 in. long, of FWR reject UO₂ pellets clad with stainless steel, 0.40 in. o.d. with 0.10 in. wall, in boiling 10 M HNO₃ (173% excess) was completed in 70-245 min. Dissolution test runs of Zr-2 in fused salt made at approximately 700°C under identical conditions except for HF feed rate resulted in dissolution rates of 1.87 and 2.68 mg/min-sq cm for 2.5 and 6.0 lb/hr HF feed rate, respectively. Purex and TRP-25 evaporated wastes were calcined at 900-1000°C resulting in solid wastes which had densities of 0.77-0.83 and 0.40-0.45 g/cc, respectively.

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SUMMARY

1.0 CHEMICAL ENGINEERING RESEARCH

The measured diffusivity of uranyl nitrate in water at 25°C was 0.7×10^{-6} cm²/sec with about 40% average deviation. The reason for the data scatter and poor agreement with literature values (3 to 5×10^{-6} cm²/sec) has not yet been determined.

2.0 DEPLETED URANIUM UTILIZATION

A program was started to develop nonnuclear uses for depleted uranium. Possible applications include use as an alloying metal, the production of high density materials, and for ceramic, catalytic, or pigment compounds. An ORNL project report to be issued in July will review present information and outline a development program. The report will include summaries of presently active work at other AEC and Bureau of Mines sites.

3.0 DRUM

Two continuous reaction runs were terminated due to erratic operation of the sodium metering system; however, they did demonstrate possible use of thick MgO reactor liners.

4.0 FLUOROX

In the second run with crude UF₄ which lasted for 29 hr, a total material balance of 94.8% was obtained and 17.9% of the theoretical amount of UF₆ was collected in cold traps and chemical traps.

5.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

Room temperature flow rate-pressure drop calibrations of a multiclone (thirteen 0.60 in. dia hydroclones in parallel) for installation with the HRT replacement circulating pump were completed. Tests of a cell for electrolytic removal of nickel from HRT fuel solution indicated that careful cell design will be required to avoid electrolytic corrosion of any stainless steel exposed to cell solution and to avoid excessive leakage currents.

Mixed oxides of U:Th = 0.08:1 and 1, 2-1/2, 5, and 10 wt per cent Al₂O₃ prepared by flame denitration all have low yield stresses of 0.02-0.05 lb/sq ft compared to 0.2-1.0 lb/sq ft for Th-U or Th oxides of 1.5-2.5 micron mean diameter. While the higher Al₂O₃ concentrations resulted in a large fraction of spherical particles, the 1 wt per cent Al₂O₃ material contained only a moderate amount of rounded particles and a small number of spherical particles.

6.0 ION EXCHANGE

Equilibrium uranium loadings were determined for Dowex 21K from 0.3-0.5 M sulfate solutions. The rates of uranium loading from solutions containing between 0.025 and 0.20 M sulfate were measured and apparent uranium diffusion coefficients between 1.2×10^{-7} cm²/sec and 1.6×10^{-7} cm²/sec were calculated.

7.0 POWER REACTOR FUEL REPROCESSING

Darex

In bench scale studies, the Darex reference flowsheet was successfully applied to stainless steel-clad UO₂ fuels (Yankee Atomic) and to aluminum-uranium foreign reactor fuels. Chloride was reduced to 440 ppm and 10 ppm. In a dissolver solution resulting from the total dissolution of Yankee Atomic fuel in aqua-regia and in a synthetic dissolver solution (2 M Al(NO₃)₃, 2 M HCl) simulating the total dissolution of Al-U fuel.

Over-all heat transfer coefficients were 200-300 Btu/hr-ft²-°F in a prototype titanium feed adjustment tank heated by steam during the mixed acid removal and recycle acid recovery steps for Yankee Atomic dissolver solution.

The removal of chloride from Darex APPR solutions at room temperature by air sparging was shown to be relatively ineffectual as the chloride was reduced only by 37 mol per cent after a sparge time of 12 hr.

Sparging Darex APPR solution at boiling temperature in the presence of 8 M HNO₃ with air or nitrogen reduced the chloride equally well from 0.5 to 0.04 M Cl.

Darex-Thorex

Laboratory tests have shown that it may be possible to process Consolidated Edison fuel (stainless steel-clad; UO₂-ThO₂) by a Darex decladding (2 M HCl-5 M HNO₃) step followed by a Thorex core dissolution step (13 M HNO₃, 0.04 M HF, 0.1 M Al(NO₃)₃ in titanium equipment. In preliminary experiments, uranium and thorium losses to the decladding solution were consistently low--about 0.02%. Cross contamination of solutions was reduced to satisfactory levels by proper washing techniques. Cyclic corrosion of titanium specimens (44-hr test) showed a maximum rate in the vapor phase of only 0.6-0.8 mils per month, and no evidence of pitting was found. In a longer test of 253 hr, the corrosion of titanium A-55 was measured in the vapor and liquid phases of a modified boiling Thorex dissolvent (13 M HNO₃, 0.04 M F⁻, 0.1 M H₃BO₃) containing 0.0, 0.5 and 1.0 M thorium from dissolved Consolidated Edison pellets. The maximum corrosion rate was 0.6 mils/month. The boric acid may be a useful inhibitor for vapor phase corrosion since the condensate probably contained boron.

Sulfex

Experimental equipment of glass and Carpenter-20 has been fabricated at 1/25 Power Reactor Fuel Reprocessing Pilot Plant scale. Installation is scheduled to begin May 18 in cell 2, Building 4505.

Feed Clarification

Filtration. Siliceous filter cakes resulting from the filtration of Darex solvent extraction feed solutions through porous metal filter elements were easily washed to a uranium loss of 0.1% in the discarded cake. Following three washes, the uranium loss was reduced to 0.005%.

In a typical experiment with 10 liters of solvent extraction feed from APFR-type Darex head-end treatment, 3516 cubic inches of wet filter cake was collected on a 0.66 sq ft filter. The cake was washed 3 times with 5 liters of water per wash. The uranium loss after one wash was < 0.1% and after three washes, 0.005%. The use of porous metal filters for feed clarification in a large scale plant appears to be feasible, and the recovery of uranium values from the filter cake is probably not a serious problem.

Centrifugation. Preliminary tests showed that Darex solvent extraction feed solution could be clarified of siliceous solids in a solid bowl centrifuge. Feed rates as high as 300-400 cc/min were possible in a 5-in. dia solid bowl at 3000 rpm. A satisfactory method of washing the cake in the bowl has not yet been developed.

Solvent Extraction Studies

A run with an acid-deficient Darex Redox feed containing soluble silica resulted in uranium losses higher by a factor of 20 than those previously obtained in the same column with a standard Redox feed.

The extraction of uranium from a feed solution of 0.4 M uranium, 0.8 M stainless steel, 0.15 M acid deficient, 0.004 M Si with hexone in a 2-in. diameter 21.3 ft column packed with 1/4 in. x 3/8 in. stainless steel Raschig rings gave a uranium loss of 0.04%. The feed/scrub/solvent flow ratio was 1/0.24/2.5.

Mechanical Processing

Batch leaching of sheared pieces, 1/2 in. to 5 in. long, of PWR reject UO₂ pellets clad with stainless steel, 0.40 in. o.d. with 0.10 in. wall, in boiling 10 M HNO₃ (173% excess) was completed in 70-245 min. These tests compared the reaction rates obtained by the direct addition of boiling acid with that of room temperature, 10 M acid brought to boiling in about 12 min. The average reaction time for 1/2, 1, 2, 3, 4, and 5-in. sheared lengths was 40, 70-200, 110, 130-245, 100 and 100 min, respectively, which is greater than the times previously obtained by an approximate factor of 2. A factor of as much as 2 in average dissolution rate has been

measured with whole pellets so the difference measured here is probably not significant. The initial constant leaching rates were 0.08, 0.039, 0.039, 0.014, 0.016 and 0.013 g/min/g U which is similar to the rates of 0.11, 0.042, 0.027 and 0.023 g/min/g U obtained previously on the 1/2, 1, 2 and 3-in. lengths. This is to be expected since the amount of fines present in both tests was similar. It was shown that advantageous leaching rates result if the sheared length is less than 3 to 4 in. long.

A straight line on log-log paper resulted when the apparent surface area per unit weight of total UO_2 present at the beginning of the UO_2-HNO_3 reaction was plotted against the length of stainless steel-clad UO_2 rod. This apparent area varied from 1 cm^2/g of UO_2 for 0.5-in. lengths to 0.04 cm^2/g of UO_2 for an extrapolated 10-in. length of 0.4-in. dia rod. The relationship may be expressed as $A = 0.5/L^{1.06}$, where A is the apparent surface area per total weight of UO_2 expressed in cm^2/g and L is the length of the sheared rod in inches.

8.0 VOLATILITY

Fused Salt Hydrofluorination

Dissolution test runs INOR-8 -7 and INOR-8 -8 made at approximately 700°C under identical conditions except for HF feed rate confirmed the previously reported dependence of dissolution rate on HF feed rate. The dissolution rates were 1.87 and 2.68 mg/min-sq cm for 2.5 and 6.0 lb/hr HF feed rate, respectively.

Dissolution test INOR-8 -9, identical with INOR-8 -8 except for initial ZrF_4 concentration in the fused salt, indicated a dissolution rate reduction with increasing ZrF_4 concentration which has not been previously noted. The dissolution rates were 2.68 and 1.95 mg/min-sq cm for initial Zr concentrations of 0.0 mol per cent and 13.0 mol per cent, respectively.

Off-Gas Studies

Solids in the dissolution off-gas have been characterized as grayish-black in color, with 50 to 60 per cent by weight being smaller than 150 microns. The chemical composition of 6 different samples was relatively constant. The 20 to 50 per cent weight loss on heating at 110°C has not been explained. The ammonia concentration of 23 per cent found in INOR-8 -2 was probably a singularity since subsequent runs yielded analyses in the range 0.19 to 1.92 weight per cent. Changing the blanket gas from nitrogen to argon had no effect on solids formation. Two tests indicate that solids form only during the dissolution. A solid plug formed in the outlet line during run INOR-8 -8 had a high nitrate concentration of 8 weight per cent.

Dry Hydrofluorination

A dry hydrofluorination test at a reactor wall temperature of 1025°C and an HF feed rate of 1.0 lb/hr proceeded at an average rate of 5.6 mg/

min sq cm and with an average HF utilization of 44%. The highest measured temperature within the fuel element was 1155°C. Reaction product ZrF_4 was distilled away from the reaction zone and condensed in a cooler section of the reaction vessel.

9.0 WASTE PROCESSING

Reduction to Solids

Purex and TBP-25 evaporated wastes were calcined at 900-1000°C resulting in solid wastes which had densities of 0.77-0.83 and 0.40-0.45 g/cc, respectively. Four different feed rates to the calciner were used with the TBP-25 waste; the largest was 8.7 liters/hr. Feed rate had a negligible effect on solid waste density.

Darex waste containing 175-1750 ppm of HCl was calcined at 600-800°C. Only 10-15% of the Cl remained in calcined solid.

1.0 CHEMICAL ENGINEERING RESEARCH

M. E. Whatley

Diffusion Measurements - C. V. Chester

As part of a program to measure interfacial diffusion resistance, measurements of the diffusivity of uranyl nitrate in water and TBP solutions are being made. The diffusion of U-235 nitrate from 5-cm capillaries into 0.1 N HNO₃ and 30% TBP-Amsco was followed by scintillation spectrometry. The experiments were carried out in the recirculation system for diffusion experiments described in the UNOP March 1959 monthly report, ORNL CF No. 59-3-61.

The diffusivities were calculated from the relation

$$D = \frac{F^2/L\pi}{T/L^2}$$

where

D = diffusivity, cm²/sec

F = fraction diffused

T = elapsed time, sec

L = capillary length

The equation is from the first approximation to the solution of the equations for diffusion from an infinite column.¹ It is accurate to better than 1% if F is less than 0.5. The diffusivities so calculated are integral diffusivities over the range of concentration from the sink (essentially zero) to the bottom of the capillary, about 50 g/liter.

The diffusivities of uranyl nitrate in water at 25°C averaged 0.67x10⁻⁶ cm²/sec with about 40% average deviation (Figure 1.1).

The large data scatter and poor agreement with the literature value (3-5x10⁻⁶) suggests that some process akin to hydrolysis of uranyl ion may have occurred. However, the pH of all the solutions used was kept

¹J. Crank, "The Mathematics of Diffusion", equation 4.20, p 45, Oxford Press, London (1956).

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Fig. 1.1. Diffusion of Uranyl Nitrate in Aqueous Solution From Capillary Tubes Into Infinite Sink.

below 2.0, which should completely repress uranyl ion hydrolysis. The fact that the diffusivity measured low by at least a factor of 4 rules out convection currents in the tubes as the source of error. The method of analysis for uranium and method of calculation have been checked and are not the source of error. A measurement of an ion of known diffusivity (such as cesium) will be made to check the apparatus. The complete experimental data and calculations of individual diffusivities are in Table 1.1.

Table 1.1. Diffusion of Enriched Uranyl Nitrate
from Aqueous Solution (~ 50 g U/liter)

Net Gamma cts/min			Fraction Diffused	Elapsed Time, hr t_n	Capillary Length, cm l	Diffusivity, cm^2/sec $D \times 10^5$
0.18 mev < Energy < 0.20 mev	Original	After Time t Difference				
N_0	N_t	ΔN				
Sink: 0.1 N HNO_3						
2822	2467	355	.126	23.7	5.01	.372
2290	1982	308	.135	23.7	5.04	.432
2158	1658	500	.232	48.5	5.08	.633
2630	2114	516	.196	48.5	5.04	.445
3052	2210	842	.276	70.5	5.05	.609
3042	2130	912	.298	70.5	5.06	.712
2258	1575	683	.306	90.2	5.10	.597
3102	2119	983	.317	90.2	5.10	.640
2805	1889	916	.326	90.3	4.99	.674
2222	1553	669	.301	90.3	5.03	.560
2240	1574	666	.297	90.3	5.01	.542
Sink: 30% TBP in Amco equilibrated with 0.02 N HNO_3						
2191	1770	421	.192	21.4	5.06	.975
1758	1427	331	.188	45.1	5.17	.463
2042	1579	463	.227	48.4	5.01	.591
1657	1253	404	.244	54.1	5.04	.619
1548	1123	425	.275	71.0	5.08	.608
1889	1456	433	.229	70.9	5.04	.425
2202	1652	550	.250	70.8	5.05	.497

Table 1.1. Diffusion of Enriched Uranyl Nitrate
from Aqueous Solution (~ 50 g U/liter) - Continued

Net Gamma cts/min			Fraction Diffused	Elapsed Time, hr t_n	Capillary Length, cm l	Diffusivity, cm ² /sec $D \times 10^6$
0.18 mev < Energy < 0.20 mev	Original	After Time t Difference				
N_0	N_t	ΔN				
Sink: 0.1 N HNO ₃						
1547	1280	267	.173	24.2	4.98	.676
1754	1299	455	.259	48.0	5.17	.826
1626	1150	476	.293	67.9	5.04	.708
1528	1020	508	.333	90.1	5.08	.697
1876	1266	610	.325	97.5	5.04	.608
Sink: 30% TBP in Amaco equilibrated with 0.02 N HNO ₃						
2352	1844	508	.216	40.8	5.01	.636
1922	1490	432	.225	40.7	5.04	.696
1802	1306	496	.275	73.1	5.08	.589
2199	1619	580	.264	73.1	5.04	.535
2546	1744	802	.315	90.8	5.05	.612
2538	1722	816	.322	90.8	5.06	.646
1871	1325	546	.292	89.9	5.10	.544
1842	1206	636	.345	90.4	4.99	.724
2332	1568	764	.328	90.4	4.99	.654
1861	1290	571	.307	90.4	5.03	.582
1875	1283	592	.316	90.4	5.01	.613
Sink: 0.1 N HNO ₃						
2779	1937	842	.306	72.5	5.01	.716
2258	1554	704	.312	72.5	5.04	.754
2121	1393	728	.343	89.6	5.08	.748
2595	1804	791	.305	89.6	5.04	.582
3013	1912	1101	.365	117.7	5.05	.637
3003	1866	1137	.379	117.6	5.06	.692
2213	1320	893	.403	141.4	5.10	.660
2182	1190	992	.452	141.4	4.99	.796
2758	1604	1154	.419	141.4	4.99	.684

2.0 DEPLETED URANIUM UTILIZATION

J. C. Bresee

ORNL has begun a program to develop nonnuclear uses for depleted uranium. Depleted uranium is being produced by gaseous diffusion and stored by the AEC in very large amounts. While depleted uranium may ultimately be a useful fertile material for converter (plutonium recycle) or fast breeder reactors, the nuclear consumption rate for many decades will be small compared to its present rate of production. Either nonnuclear uses must be developed or the AEC will continue to have a large and expensive uranium storage problem. The first phase of the program will end with a summarizing report to be written during July 1959. A continuation of the program will depend on the results of the first phase.

2.1 Traditional Nonnuclear Uses for Uranium

As an element uranium has had a comparatively short history. It was discovered in 1789 but for fifty years UO_2 was thought to be the pure element. Carbon was used to reduce UO_3 , and the metallic appearance of UO_2 contributed to the confusion. In 1841 the metal was prepared for the first time by reduction of the tetrachloride with potassium. The atomic weight of uranium was not measured until 1882, and it was 1896 before it was discovered that uranium was radioactive.

Prior to 1932 uranium was used primarily as a coloring agent in ceramics. During the nineteenth century, use was made of the yellow, brown, and green compounds of uranium as pigments. Certain of the salts with fluorescent properties were of special value in ornamental ceramic glazes.¹

As early as 1897 it was reported that the French Government was experimenting with ferro-uranium alloys in ordnance. The preparation of uranium steels has been studied for many years, but the high cost of uranium limited its application. As a substitute for tungsten in high speed steels, uranium is said to impart increased hardness without an accompanying increase in brittleness due to the formation of stable but dispersed carbides. Some investigators have enthusiastically claimed, "The benefits obtained from the use of uranium certainly constitute the highest attainment of the steel-maker's art."²

In Haber's original patent claims for ammonia manufacture, metallic uranium and uranium carbide were listed among the best catalysts for reaction of nitrogen and hydrogen at high temperatures and pressures. Aside from cost, the greatest disadvantage of uranium catalysis has been sensitivity to impurities, primarily in the hydrogen. Other catalytic uses for uranium include reduction, polymerization, desulfurization, and cyclization of petroleum fractions.

In the electronics industry before World War II, uranium was used as a "getter" in vacuum tubes, in photoelectric tubes for ultraviolet light detection, and as a target for X-ray tubes. Another interesting electrical application was the use of UO_2 in series with tungsten in powerful incandescent lamps to smooth out current surges and to prolong the filament life.

All commercial uses of uranium began to disappear in 1938 when the fission process was discovered. Consumption decreased from a high of 100 tons/yr to a low of 1500 lb/yr in 1955. The enormous difference between the current depleted uranium supply and past commercial demands may be visualized by simple, unclassified considerations. Because natural uranium is 99.3% U-238 and conversion of more than 1% to Pu-239 is impractical without plutonium recycle in nuclear reactors, essentially all domestic uranium mined each year is accumulated as gaseous diffusion cascade bottoms. The current domestic rate of production of U_3O_8 is 15,000 tons/yr.³

2.2 Future Nuclear Uses of Depleted Uranium

It is not sufficient to compare prewar consumption of natural uranium with postwar production of depleted uranium in order to demonstrate the need for the development of nonnuclear uranium markets. A very compelling argument is one which states that depleted uranium, like thorium, is a valuable natural resource, and should be "protected" by an artificially high price so that future generations may benefit by present conservation.⁴ In theory essentially all depleted uranium and thorium can be consumed in breeder reactors with an energy potential thousands of times that available from converter or burner reactors. But just how important is present day conservation? Most particularly, how large will the nuclear market for depleted uranium be during the next forty years?

As in all such estimates, the most important (and unknown) parameter is the build-up curve for installed nuclear power. For the purposes of this memorandum, a mean was chosen between the curves of J. A. Lane and W. K. Davis. Using this mean curve, Arnold and Ullmann predicted the total nuclear fuel requirements for consumption and inventory between now and the year 2000.⁵

A conservative estimate of the portion of the total nuclear power which will be generated by fast breeder reactors during the next forty years is 10 per cent. Based on the fertile material inventory in a well designed fast breeder reactor, Arnold has estimated that the total requirement between now and 2000 for depleted uranium will be 28,000 tons.⁶ Based only on domestic uranium production, the forty-year requirements could be supplied in approximately two years. Note that assuming all power reactors are fast breeders only increases the domestic production time to twenty years with no changes in current production rates. The country would also have to face the problem of developing nonnuclear uses for enriched uranium.

2.3 Depleted Uranium Toxicology and Radiology

Handling of depleted uranium results in two types of hazards: from external radiation and from inhalation or ingestion. Uranium with an assay of 0.2% U-235 contains a minute but important quantity of U-234 (approximately 0.0015%). Having been through chemical refining and gaseous diffusion, the uranium would be essentially free of metallic impurities and in particular it would be free of daughters of radioactive decay (except for Th-234 and Pa-234 which reach equilibria in approximately six months).

It is easy to show that depleted uranium with an assay of 0.2 is only a minor hazard as a source of external penetrating radiation. Consider an infinitely long cylinder of depleted uranium of infinite wall thickness and a two foot inside diameter chamber in which a man might be unlucky enough to find himself. The Th-234 and Pa-234 beta particle emissions make up essentially all of the penetrating radiation in the chamber. The 2.32 mev β^- from Th-234 alone contributes 240 mrem/hr while the 0.2 mev β^- from the Pa-234 adds 20 mrem/hr.¹² All gammas from all disintegrations are quite soft and add only 5 mrem/hr to the total of approximately 265 mrem/hr. A recommended maximum occupational exposure in 13 weeks of 3 rem would be accumulated in slightly over 11 hours.⁸

The dangers from inhalation or ingestion of depleted uranium depends on the solubility of the inhaled or ingested material. Soluble uranium is absorbed in the kidney and acts as a chemical poison, blocking the re-absorption of vital constituents of the blood and contributing to a loss of body fluids. The damage is reparable by the body and the biological half life for uranium removal from the kidney is only 6 days.

Insoluble depleted uranium is only dangerous to the lungs and the mechanism of damage is from alpha bombardment of the tissue. The repair of such damage is slow, and the biological half life for uranium removal is much longer (approximately 120 days).

The control of inhalation or ingestion is basically the control of air-borne uranium. According to the latest recommendations of the International Commission on Radiological Protection, the maximum permissible concentration of natural uranium (soluble or insoluble) in the air breathed 40 hr/wk is 200 micrograms/cubic meter.⁸ Since the alpha activity of pure U-238 is approximately a factor of 2 lower than that of natural uranium, there would be no substantial increase in the limitations for insoluble and no change for soluble depleted uranium.

It is instructive to compare the limitation on air-borne quantities of natural uranium to those of two other common heavy elements: lead and mercury. The maximum permissible concentrations of these materials in air are 150 and 100 micrograms/cubic meter.⁹ Thus controls normally applied to the industrial uses of these materials would be entirely adequate for depleted uranium.

2.4 Depleted Uranium Metallurgy

The ORNL program in depleted metallurgy during the remainder of the current fiscal year will be primarily to collect and analyze metallurgical data from the literature and from the Oak Ridge Y-12 and Gaseous Diffusion Plants. A representative of the ORNL Metallurgy Division, Professor Gregg of Cornell University, has undertaken a literature survey of uranium alloys. In addition, S. D. Clinton of the Chemical Technology Division of ORNL is responsible for collecting, analyzing, and interpreting metallurgical data from survey programs at Y-12 and the Gaseous Diffusion Plant.

The Y-12 survey program is under the direction of C. P. Coughlen. For several years he has collected data on uranium metallurgy and the properties of various uranium alloys. He will attempt to extract unclassified data from his notes in a form useful for the summarizing report. The ORGDP survey program is the responsibility of C. H. Mahoney and W. S. Dritt of the K-25 Metallurgy Department. Several months ago they requested the Technical Library of the ORGDP to prepare a bibliography of uranium metallurgy, and they will screen the collection for information useful to the current program. Two of the most important collections of data on uranium and its compounds have been prepared at K-25 in the past.^{10,11}

2.5 Chemical Uses of Depleted Uranium

P. A. Haas and S. Peterson of the Chemical Technology Division of ORNL share the responsibility for a thorough survey of the literature, the evaluation of available results from experimental programs conducted here or at other sites, the conducting of limited but definitive experiments during the remainder of the current fiscal year, and the preparation of a summarizing report during July.

Peterson has been studying the preparation of dense aqueous solutions of uranium halides for possible use in heavy media separations of minerals of different densities. Three grams per cubic centimeter would be a useful density at room temperature for an ore dressing heavy media. The density of individual sand particles is slightly less than 3, so it would be possible to float sand from heavier minerals with such a liquid. In a preliminary experiment, Peterson has prepared a stable uranyl bromide solution with a molarity of 6.4 and a density of 3.3 g/cc.

Another attractive chemical use for depleted uranium is as a catalyst. P. A. Haas is responsible for the ORNL program on the catalytic uses of depleted uranium. In addition to conducting a thorough literature survey, he has recently written to six large commercial catalyst manufacturers, outlining the ORNL program and soliciting expressions of interest in conducting independent research with uranium compounds provided by ORNL.

University research, particularly doctoral research, may be the most appropriate method for carrying out basic research on uranium catalysis.

In answer to an inquiry from Haas, Dr. L. Berg of Montana State College proposed an AEC-sponsored program on uranium catalysis as applied to petrochemicals, with two doctoral theses to begin next year and a total program cost of \$8-10,000. Due to the uncertainty of next year's program, it was suggested that he prepare a separate proposal to the AEC Division of Research.

Finally, a chemical use for depleted uranium might be developed by utilizing UF_6 as a source of fluorine. The ORNL fluoride recovery program is jointly the responsibility of C. D. Scott, who is studying the reduction of UF_6 to UO_2 , and S. Peterson, who is considering the use of UF_6 as an organic fluorinating agent.

Using existing technology, it would be relatively simple to use the dry reaction developed at ORGDP: $UF_6 + H_2 \rightarrow UF_4 + 2HF$, to recover one-third of the fluorine in UF_6 as anhydrous HF. However, recovery of the remainder in a useful form is difficult since UF_4 is a relatively unreactive compound. For example, pyrohydrolysis to UO_2 ($UF_4 + 2H_2O \rightarrow UO_2 + 4HF$) requires excess water and produces dilute hydrofluoric acid. Azeotropic distillation might be used to recover strong hydrofluoric acid.

A more interesting and potentially cheaper reaction is the one-step reduction and hydrolysis of UF_6 ($UF_6 + 2H_2O + H_2 \rightarrow UO_2 + 6HF$). It may be possible to produce greater than 90% hydrofluoric acid (above the azeotropic) by the selection of proper temperature and pressure for the reaction. The one-step reaction is currently being studied at the Paducah Gaseous Diffusion Plant, where the work began in 1958, at ORGDP, at Argonne, and at ORNL. The approach that C. D. Scott has taken at ORNL is to hydrolyze UF_6 continuously to a uranyl fluoride solution and to spray the solution into a hot fluid bed of UO_2 in hydrogen. In preliminary experiments UO_2 has been produced at 500°C with the following properties:

Surface area	1.1 m ² /g (by N ₂ adsorption)
Tap density	3.7 g/ml
Oxygen to uranium atom ratio	2.1

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3.0 DRUHM

P. A. Haas

An experimental study is being carried out of the direct reduction of uranium hexafluoride to metal, using sodium and the reaction: $UF_6 + 6Na \rightarrow U + 6NaF$. At present a semicontinuous reactor is being used to study the consolidation of reaction products and the use of an MgO reactor liner.

Reduction Experiments - C. D. Scott, W. G. Sisson

Two experimental runs, D-22 and D-23, were made in the 6-in. reactor with a gas-cooled UF_6 nozzle and a 0.5-in. MgO liner. The outer wall temperature of the induction-heated reactor was $1130^\circ C$ when each run began by the metering of reactants into the lined section of the reactor. Within a few minutes plugs formed in the sodium feed line, and the runs were terminated.

The reactors were opened and the liners were examined for damage from thermal cycling or the brief contactant with the reactants. There was essentially no damage.

There has been a report of severe damage to an MgO-lined reactor in a laboratory experiment in which a mixture of sodium metal and UF_4 was heated in the reactor from room temperature to $1200^\circ C$. Internal cracks developed and there was a surface reaction to produce traces of magnesium metal.

It is felt that a factor which contributed to both the cracking and surface reaction was the penetration of the liner wall by liquid sodium. When the liner temperature exceeds the boiling point of sodium ($880^\circ C$) as was the case in both of the runs, the concentration, penetration, and surface reaction of sodium atoms may have been reduced sufficiently to account for the lack of MgO liner damage encountered thus far in the semicontinuous reactor studies.

4.0 FLUOROX

P. A. Haas

The Fluorox program is the engineering development of processes which produce UF_6 without the use of elemental fluorine. The process under study is the oxidation of UF_4 with anhydrous oxygen, $2UF_4 + O_2 = UO_2F_2 + UF_6$, with subsequent recycle of the UO_2F_2 . The UF_4 oxidation process is carried out in a 4-in. fluidized bed reactor. Sized UF_4 is continuously fed into a UO_2F_2 bed which is fluidized in dry O_2 or air at 700-850°C. The UF_6 which is produced is removed in the off-gas stream and is subsequently recovered in cold traps.

4.1 Evaluation of Run FBR-24 - C. D. Scott

The second run with crude UF_4 (run FBR-24) lasted for 29 hr at a bed temperature of $710 \pm 25^\circ C$ (UNOP monthly report for April 1959, ORNL CF 59-4-47). Complete analytical results are available, and the run was evaluated in the same manner as previous runs.

The over-all material balance of all reactor streams was 94.8% (material leaving/material entering) while the over-all uranium material balance was only 81.7% (Table 4.1). This reflects a loss of 709 g of total material, probably the result of the hole which was corroded in the reactor. The apparent greater loss of uranium from the system probably reflects nonhomogeneous sampling of solids.

The UF_6 balance was 54.6% complete (Figure 4.1) with only 17.9% of the theoretical amount of UF_6 collected in cold traps and chemical traps and 36.7% consumed in parasitic side reactions. The apparent loss of 45.4% of the theoretical amount of UF_6 formed may have been due to the hole corroded in the reactor and volatilization from the reactor.

The UF_6 product collected in the cold trap was contaminated with vanadium (2.5%), chromium (1.3%), and HF (37.0%). The probable composition of the product UF_6 was:

UF_6	55.2%
HF	37.0%
Other fluorides (mainly CrO_2F_2 and VOF_2)	7.8%

The apparent Fluorox reaction rate constant was 0.39 hr^{-1} (Figure 4.2) during a 4-hr period of approximate steady state operation at an average bed temperature of $717^\circ C$. This rate was about 20% lower than previous values obtained at these temperatures but probably within experimental error.

Table 4.1. Change in Amounts of Individual Compounds in Run FBR-24

Compound	Entering Reactor, g		Leaving Reactor, g		Change, g	
	Total	Uranium	Total	Uranium	Total	Uranium
UF ₄	6001	4549	663	503	-5338	-4046
UO ₂ F ₂	5975	4617	8773	6779	+2798	+2162
UO ₂	255	225	-	-	- 255	- 225
U ₃ O ₈	-	-	28	24	+ 28	+ 24
H ₂ O	24	-	-	-	- 24	-
UF ₆	-	-	536	362	+ 536	+ 362
HF	-	-	760	-	+ 760	-
O ₂ ^a	351	-	-	-	- 351	-
Inconel	337	-	-	-	- 337	-
Other ^b	766	-	2240	-	+1474	-
Totals	13709	9391	13000	7668	- 709	-1723

^aAmount of O₂ theoretically necessary for the various reactions occurring.

^bOther metal fluoride, oxides and oxyfluorides.

Over-all material balance (material leaving/material entering) = $\frac{13000}{13709} = 94.8\%$.

Over-all uranium balance (uranium leaving/uranium entering) = $\frac{7668}{9391} = 81.7\%$.

Fig. 4 1. Disposition of UF_6 Which was Formed in Run FBR-24.

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Fig. 4.2. Apparent Reaction Rate Constant for Run FBR-24.

4.2 Corrosion in FBR-24

The apparent high corrosion rate in run FBR-24, 6-7 miles/hr, resulted in a 1/2-in. dia hole in the reactor (UNOP monthly report for April 1959, ORNL CF 59-4-47). The fluid bed section of the reactor was sectioned and cleaned for visual observation. It shows that the corrosion was uneven with some severe pitting (Figure 4.3).

4.3 Fluorox Reaction Rate Data in Fluidized Bed Reactors

A comparison of reaction rate constants has been made for the Fluorox reaction determined from both laboratory and fluidized bed reactor data. (Figure 4.4). The data from batch fluidized bed, continuous fluidized bed, and laboratory thermobalance tests are presented as three Arrhenius plots with least square curve fitting. The slopes which correspond to activation energies are similar for the batch fluidized bed and thermobalance tests although the lines are displaced slightly. The continuous fluid bed data are correlated with a line of greater slope, but there is good agreement between the laboratory and continuous fluid bed data in the temperature range 700-800°C. There was probably a consistent error introduced equivalent to 20-40°C in reaction temperature in the calculation of rate data from the batch reactor.

From the above information, it is felt that the available reaction rate data are sufficiently precise for design of larger fluid bed reactors.

Fig.4.3. Sectioned and Cleaned 4-in. Fluidized Bed Reactor from Run FBR-24.

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Fig. 4.4. Comparison of Reaction Rate Constants for the Reaction,
 $2\text{UF}_4 + \text{O}_2 = \text{UO}_2\text{F}_2 + \text{UF}_6$, Determined from Laboratory and
Fluidized Bed Reactor Data.

5.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

P. A. Haas

The objective of these studies is to develop processing and preparation methods as required for aqueous homogeneous reactor fuel and blanket fluids. A multiple hydroclone and an electrolytic process for removal of nickel are being tested for application to HRT fuel processing. A flame denitration process is being developed for production of thorium particles for circulating slurries or fluidized beds.

5.1 HRT Multiple Hydroclone Test - E. L. Youngblood, D. H. Newman

Pressure drop and flow rate measurements were made on a multiple hydroclone assembly which is to be installed in a by-pass stream of the HRT primary system (Figure 5.1). The underflow from the multicloner system will provide the feed stream for the present HRT-CPP hydroclone. The multicloner system consists of thirteen 0.6-in. dia hydroclones in parallel (Figure 5.2).

Pressure drop and flow rate measurements were made for conditions under which 0, 10 and 20 per cent of the feed stream was discharged through the underflow line. Water at 18°C was used to obtain the pressure drop vs. flow rate data (Figure 5.3).

5.2 Flame Denitration - C. C. Haws, Jr., V. L. Fowler

A program was completed for producing large samples of flame denitrated mixed thorium-uranium oxides containing different percentages of aluminum oxide (U/Th ratio = 0.08). A minimum of 120 g of classified product (95% < 5 micron) was obtained with 1.0, 2.5, 5.0 and 10.0 wt per cent alumina concentrations.

The physical properties of the resulting aqueous slurries were measured. Yield stresses remained uniformly low, ranging from < 0.02-0.05 lb/sq ft. Low surface areas were also obtained with a range of 2.0-3.1 sq m/g.

The individual particles were examined with an electron microscope. Spheroids with smooth surfaces were found with alumina concentrations of 2.5, 5., and 10 wt per cent. At 1 per cent alumina, a partially rounded shape was obtained but a "blackberry" surface appeared in the electron micrograph (Figure 5.4). Otherwise the 1 per cent material had equal properties compared with the other concentrations (Table 5.1). All samples described in the table have been submitted for toroid tests.

A 24-hr run was made to produce a 200-g (minimum) sample of flame denitrated mixed thorium-uranium oxides (U/Th = 0.08) for evaluation by the REED Division. This sample contained 2.5% alumina by weight and was classified to the size range of 1-10 micron.

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Fig. 5.1 Simplified Flow Diagram Showing HRT Multi-Clone Location.

ALL DIMENSIONS
ARE IN INCHES

Fig. 5.2. HRT Multi-Cone Assembly.

Fig. 5.3. Pressure Drop vs Flow Rate for HRT Multi-Cone.

RUN 63- 2.5 wt% Al_2O_3

RUN 66 - 1 wt% Al_2O_3

1 micron
|-----|

U/Th wt RATIO, BOTH SAMPLES ≈ 0.08
FIRING TEMPERATURE, BOTH SAMPLES $= 1500^\circ\text{C}$

Fig. 5.4. Flame Calcination Experiments: Electron Micrographs of Particulates of Uranium-Thorium Oxides Containing Different Percentages of Alumina.

Table 5.1. Flame Calcination Experiments
Slurry Characteristics of Flame De-nitrated
Thorium-Uranium Oxides Containing Alumina

Run No.	Firing Temp., ^a °C	Nominal ^b Alumina Conc., wt %	Mean Particle Size, micron	Yield Stress, lb/sq ft	Surface Area, sq m/g
62	1500	5	1.5	< 0.02	2.0
63	1500	2.5	1.7	0.02	2.4
66	1500	1	2.0	0.026	2.6
69	1500	10	1.6	0.05	3.1

^aFiring temperature refers to the outer temperature of the magnesia reflector.

^bUranium-thorium wt ratio = 0.08 for all samples.

An improved aspirating-type feed nozzle was designed, built and tested (Figure 5.5). This device is capable of maintaining the maximum permissible operating temperature of the reflector (1500°C) and has shown a 35 per cent yield of particles within the usable size range (< 5 micron).

The new nozzle also may be operated at higher nitrate feed rates compared with the previous nozzle (1.1 vs. 0.4 g moles/hr). In the past only 10 per cent of the feed was collected within the proper size range (< 5 micron). The potential production rate of flame calcined particles has thus been increased from 11 to 100 g ThO₂/hr.

5.3 Nickel Removal - E. L. Youngblood, D. H. Newman

The electrolytic cell for the removal of nickel from a simulated HRT fuel solution¹ was modified to permit circulation of a portion of the fuel solution under the mercury cathode to provide agitation of the mercury. Run 3 was made using the revised system and a light water fuel solution containing copper, nickel and manganese sulfates without uranium (Table 5.2).

Table 5.2. Conditions and Light Water Analyses
for Electrolytic Nickel Removal Test (Run 3)

Cathode current density	0.15 amperes/sq cm
Cell temperature	20°C
Cell voltage	~ 6 volts
Cell current	~ 212 amperes
Cell current efficiency	17%
Uranium concentration	None
Volume of fuel solution	25 gal
Volume of mercury cathode	0.63 gal

Ampere Hours	"Fuel" Analyses, g/liter			
	Cu	Ni	Mn	SO ₄
0	13.5	1.09	1.54	0.57M
730	12.0	1.07	1.60	-
1511	10.1	0.86	1.60	-
2347	9.0	0.72	1.60	-
3150	7.2	0.74	1.63	0.60

¹Flow diagram in UNOP March 1959 monthly report, ORNL CF 59-3-61.

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Fig. 5.5. Burner-Aspirating Type Center Section.

The run was stopped after 3150 ampere hours of operation because of an amalgam formation, similar to that observed in runs 1 and 2, which caused an electrical short circuit in the cell. The amalgam contained about 2 per cent copper and nickel when the short circuit occurred. The current efficiency of 17 per cent obtained in run 3 was somewhat lower than that of previous runs. The system was not operated long enough to reduce the copper and nickel concentrations of the fuel solution to an acceptably low level (80 per cent removal of nickel).

The amalgam formed in run 3 was used to test a proposed mercury regeneration procedure in which a 1 M HNO_3 and 1.5 per cent H_2O_2 solution is circulated through the cell to remove the metals deposited in the mercury cathode. In this regeneration run, the nitric acid solution was circulated from the regeneration tank through the cell at periodic 8-hr intervals. During the remaining periods of the run the regeneration solution remained stagnant above the amalgam in the cell.

The change in copper content of the regeneration solution during treatment (Figure 5.6) indicated that the rate of dissolution of copper was not appreciably affected by circulation of the regeneration solution; however, good agitation of the mercury was not obtained during circulation due to plugging of some of the holes in the sparge tube which extends under the mercury.

After 92 hr of contact with the regeneration solution the copper concentration of the amalgam was reduced from 2 to 1.45 per cent. The nickel content of the amalgam from run 3 was too low (< 0.1 per cent) to be used to evaluate the rate of removal of nickel from the amalgam during regeneration.

Run 4 was made using a light water fuel solution containing 0.42 M UO_2SO_4 . During the 10,046 ampere-hr duration of run 4 no amalgam bridging between the cathode and anode was observed. The amalgam concentration reached 2.6 per cent copper and nickel during the run (Table 5.3). The addition of UO_2SO_4 to the fuel solution was expected to reduce somewhat the cell efficiency for copper and nickel removal because of the reduction of uranium from the six to four valence state.

In run 4 at 100 per cent current efficiency, 1,005 ampere hours would have been required for the complete removal of copper and nickel from the fuel solution and 1,260 ampere hours would be required to reduce completely the uranium from the +6 to the +4 valence state. The current efficiency for run 4 for copper and nickel removal ranged from about 56 per cent at the beginning of the run to less than 1 per cent at the end of the run as the copper content of the solution became low.

In runs 3 and 4 anodic corrosion of stainless steel components in the vicinity of the anode was observed. The stainless steel electrode which joins the platinum screen to form the anode developed an open electrical circuit at a weld and had to be replaced. The stainless steel thermocouple well extending between the cathode and anode developed a leak and was removed. A platinum plated stainless steel electrode is now being tested as the cell anode.

Fig. 5.6. Regeneration of Mercury Cathode by Nitric Acid-Hydrogen Peroxide Treatment, Copper Content of Aqueous Regeneration Solution vs. Time. (Solution Volume-15 gal).

Table 5.3. Conditions and Analyses for
Run 4 Electrolytic Nickel Removal Test

Cathode current density	0.16 amperes/sq cm
Cell temperature	30°C
Cell voltage	~ 10 volts
Cell current	223 amperes
Volume of fuel solution	15 gal
Volume of mercury cathode	0.63 gal

Ampere Hours	Solution Concentrations, g/liter				
	Cu	Ni	Mn	U	SO ₄
0	17.3	3.64	1.85	97	1.04 M
873	7.0	3.88	1.88	-	-
1567	2.89	3.55	1.82	-	-
2224	1.67	3.20	-	-	-
5792	0.10	2.42	1.83	86	0.88
10046	0.11	1.66	1.68	83	0.95
<u>Amalgam Analysis at End of Run 4, wt %</u>					
	Hg	Cu	Ni	Mn	U
	96.95	2.53	0.12	< 0.005	0.0006

6.0 ION EXCHANGE

M. E. Whatley

To make rational predictions of the operating characteristics of uranium anion exchange contactors, an understanding of the mechanism and kinetics of the exchange is necessary. Toward this objective the equilibrium sorption isotherms and rates of sorption of uranium on Dowex 21K are being determined.

6.1 Equilibrium Studies - J. S. Watson, W. E. Dunn

The equilibrium loading of uranium was determined on Dowex 21K at room temperature from solutions 0.3 M and 0.5 M in total sulfate. These data are shown in Figure 6.1 along with similar data at lower sulfate concentrations which had been obtained previously. In all of the solutions the sulfuric acid concentration was 0.02 M and the uranium concentration was 0.005 M or larger. The desired total sulfate concentration was obtained by adding the required quantity of sodium sulfate.

A flow technique was used to contact the resin and solutions since it was desirable to specify the composition of the solution with which the resin approached equilibrium. From 4 to 8 liters of the solution was passed slowly through a packed bed containing approximately 1 g of resin. This method of contacting required from 3 to 5 days. The resin was centrifuged to remove any solution remaining on the surface of the beads and eluted with a liter of 1 N NaCl solution. The resin loading was determined by analyzing the eluate. The resin was finally washed with water and dried in an oven at 55°C before weighing.

6.2 Kinetic Studies - J. S. Watson, W. E. Dunn

A series of kinetic runs have been made to determine the effects of the solution sulfate concentration on the uranium loading rate. A few resin beads were contacted with an enriched uranium solution in a stirred bath. Beads were removed from the bath at various times after the start of contact, and the uranium loading on each bead was determined by counting in a gamma spectrometer. Sulfate concentrations between 0.0258 M and 0.206 M were used, and the uranium and sulfuric acid concentrations were maintained at 0.0058 M and 0.020 M, respectively.

The results of these runs are shown in Figures 6.2, 6.3, 6.4, 6.5 and 6.6. The data were correlated with the simple model of single ion diffusion into a sphere with constant surface concentration. The correlating equation¹ may be written as:

$$\frac{M_t}{M_\infty} = 6 \left(\frac{Dt}{a^2} \right)^{1/2} \left\{ \pi^{-1/2} + 2 \sum_{n=1}^{\infty} \text{ierfc} \sqrt{\frac{na}{Dt}} \right\} - 3 \left(\frac{Dt}{a^2} \right)$$

¹Crank, J., The Mathematics of Diffusion, Oxford Press, (1956), pp 85-91.

Fig. 6.1. Equilibrium Sorption of Uranium on Dowex 21K From Sulfate Solutions at 25°C.

Fig. 6.2. Uranium Loading on Dowex 21K From 0.025 M Sulfate Solutions.

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Fig. 6.3. Uranium Loading on Dowex 21 K From 0.051M Sulfate Solutions.

Fig. 6.4 Uranium Loading on Dowex 21K From 0.075 M Sulfate Solution.

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Fig. 6.5. Uranium Loading on Dowex 21K from 0.101M Sulfate Solutions

Fig. 6.6. Uranium Loading on Dowex 21 K From 0.151 M Sulfate Solutions.

where

M_t = loading, mg/cm³

M_∞ = equilibrium loading, mg/cm³

a = bead radius, cm

t = contact time, sec

D = diffusion coefficient, cm²/sec

The diffusion coefficient was calculated from values of $(t/a^2)^{1/2}$ at $M_t/M_\infty = 0.50$.

The "apparent" particle diffusion coefficients calculated from these data are listed in Table 6.1. The coefficients do not vary in a systematic manner, probably due to errors in the measured equilibrium loadings. Several beads were left in the bath for 3 to 5 days after each run to approach equilibrium with the solution. In the first four runs, too few beads were left to give an accurate value for the equilibrium. A fairly large number of beads are required for good statistics because of nonuniformity of the beads.

To obtain better values for the diffusion coefficient, more beads must be left in the bath for equilibrium determination and existing, independently-obtained, equilibrium data must be used to correlate those runs where too few beads were used. A difficulty in calculation arose in that the independent equilibrium data were correlated on the basis of grams of dry chloride resin. In the kinetic studies it is difficult to weigh a single resin bead, so the bead volume was used instead (which varied slightly during the loading because of swelling effects). Regardless of which basis is used, the shape of the loading curves should be the same.

Table 6.1. Apparent Diffusion Coefficient
for Uranium in Dowex 2LK from Solutions
0.0058 M in Uranium and 0.020 M in Sulfuric Acid

<u>Solution Total</u> <u>Sulfate Conc.,</u> <u>moles/liter</u>	<u>Apparent Diffusion</u> <u>Coefficient,</u> <u>cm²/sec</u>
0.026	1.50x10 ⁻⁷
0.051	1.20x10 ⁻⁷
0.076	1.45x10 ⁻⁷
0.101	1.20x10 ⁻⁷
0.151	1.25x10 ⁻⁷

7.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

7.1 Darex - F. G. Kitts, B. C. Finney, R. C. Early

The primary purpose of the Darex process is to convert SS-U and SS- UO_2 fuels into chloride-free nitrate solutions suitable for processing in existing stainless steel solvent extraction equipment. The presence of chloride is necessary to effect dissolution of stainless steel in HNO_3 but it must be removed to avoid corrosion of process equipment. In the present investigation, a batch flowsheet is being studied in which dissolution product is treated with 61 wt per cent HNO_3 to produce solvent extraction feed 2-3 M in HNO_3 containing less than 350 ppm chloride.

The Application of a Darex Head-End to Chloride Removal and Feed Adjustment. Eight chloride removal and feed adjustment runs were made using three different fuel types and the reference flowsheet without reflux or sparging. The following steps comprise the reference flowsheet (refer to column headings in Table 7.1):

1. Distillation of an acid waste cut (principally H_2O) from the dissolution product as received from the dissolver.
2. At constant level, metering in HNO_3 at the same rate at which aqua regia recycle (used as dissolver feed in the following run) is removed.
3. Addition of 13.3 M HNO_3 batchwise, yielding acidified concentrate.
4. Recovery of recycle HNO_3 (used at step 2 in the following run).
5. Dilution of the remaining heel with water to produce solvent extraction feed.

Run no. APFR-59 (Table 7.1) was a 4 per cent plant scale run made in the 10-in. titanium feed adjustment tank using APFR-type dissolver product. Chloride removal was satisfactory but some trouble was encountered with the liquid intermittently "bumping" up into the vapor line (the vessel was not equipped with splash plates or liquid separator). Run APFR-60 was similar to 59 except that a smaller batch size was used; "bumping" was reduced but not completely eliminated. No explanation can be offered for the high chloride value in the product (see column 22, Table 7.1) except the slightly shorter cycle time. Should such values be obtained repeatedly in future tests, a reflux period and/or air sparging should be incorporated into the flowsheet.

Runs BYA-1 through 4 were laboratory scale adaptations of the reference flowsheet to Yankee Atomic fuel dissolver product. The final pro-

Table 7.1. Data and Results from Darcex Runs

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Run No.	Dissolution Product					Acid Waste			At Constant Level				Add 13.3M HNO ₃ l	Acidified Concentrate			Recycle HNO ₃ (Trace Cl ⁻)		Solvent Extraction Feed		
	Vol	H ⁺	Cl ⁻	U	SS	Vol	HNO ₃	Cl ⁻	Add	Aqua Regia Recycle				Vol	HNO ₃	Cl ⁻	Vol	HNO ₃	Vol	HNO ₃	Cl ⁻
	l	M	M	g/l	g/l	l	M	M	12M HNO ₃ l	Vol	HNO ₃	Cl ⁻		l	M	M	l	M	l	M	ppm
APPR-59	10.8	2.92	1.75	5½	55	3.0	0.63	0.27	9.4	9.4	5.68	0.67	6.6	~14.4	11.13	0.14	9.4	12.0	12.4	3.23	235
APPR-60	8.7	2.92	1.75	5½	55	2.4	0.50	0.25	7.5	7.5	5.70	0.75	5.3	~11.6	10.86	0.30	7.5	11.9	9.8	3.53	845
YA-61	10.8	2.3	1.1	130	35	3.0	0.25	0.10	9.4	9.4	5.47	0.53	5.0	~12.8	11.12	0.14	9.4	12.2	10.8	1.38	440
BYA-1	0.54	4.1	1.7	73	40	0.15	1.12	0.73	0.47*	0.47	7.43	0.67	0.33	~0.72	12.05	0.074	0.47	13.0	0.54	3.65	28
BYA-2	0.54	3.1	1.4	73	40	0.15	0.83	0.57	0.47	0.47	5.75	1.15	0.33	~0.72			0.47	12.7	0.54	3.77	18
BYA-3	0.97	3.24	1.53	130	36	0.30	0.15	0.20	0.83	0.83	5.85	0.95	0.50	1.17	11.49	0.22	0.83	12.3	0.97	2.3	610
BYA-4	0.97	3.24	1.53	130	36	0.25	0.11	0.30	0.85	0.85	5.45	1.05	0.47	1.20	11.38	0.18	0.85	12.3	0.97	2.7	250
AI-1	0.50	1.76	1.75	0	AI 61				0.25*	0.40	5.75	1.25		0.35	1.56	<6			0.50	1.09	<6

*13.3M HNO₃

cedure, BYA-4, differed from the APPR flowsheet only in that less 13.3 M HNO_3 was added and the heel after recycle HNO_3 recovery had a slightly lower volume. Run YA-61 was the first Yankee Atomic run made in the 10-in. titanium equipment; chloride removal was to 440 ppm, slightly above the specification of 350 ppm.

Run Al-1 shows that chloride can be easily removed from solutions containing aluminum, using an abbreviated reference flowsheet requiring neither a waste cut nor HNO_3 recycle.

Over-all Heat Transfer Coefficients. Over-all heat transfer coefficients from the heated legs to the boiling solution in the 10-in. titanium feed adjustment tank were determined for four different periods during run YA-61; two were measured during the mixed acid removal and two during the recycle acid recovery. The heat transfer data and over-all heat transfer coefficients are presented in Table 7.2. Most coefficients ranged from 200-300 Btu/hr sq ft $^{\circ}\text{F}$ but there appears to be an error in the third over-all heat transfer coefficient based on the acid vaporization. An attempt will be made to measure over-all coefficients at temperature differences in excess of 49°F .

Gas Sparging Studies. A laboratory scale chloride removal run was made using an APPR type Darex dissolver product containing 100 g/liter metal loading, 12.74 M initial HNO_3 , and 0.65 M initial chloride to determine the effect of a room temperature air sparge on chloride removal. Nine hundred ml of the test solution was placed in a 2-liter distillation flask and sparged with air at a sparge rate to liquid volume ratio of 8.5 hr^{-1} . After 12 hr sparging the chloride concentration was reduced from 0.65 M to 0.41 M (Figure 7.1). A room temperature air sparge does not appear to be an effective method for chloride removal.

A run was also made using an APPR type Darex dissolver product containing 100 g/liter metal loading, 8.0 M initial HNO_3 , and 0.26 M initial chloride to determine the effect on chloride removal of sparging with nitrogen. After 6 hr of boiling at total reflux and sparging at a sparge rate to liquid volume ratio of 8.5 hr^{-1} , the chloride concentration in the dissolver product was reduced to .04 M ($\sim 1420 \text{ ppm}$). A comparison of this run and similar runs made without sparging and using an air sparge are presented in Figure 7.2. The use of nitrogen as a sparge gas is more effective in chloride removal than no sparge but nitrogen is not quite as effective as air, indicating that there is some merit in having oxygen present.

There was a greater initial reduction in the chloride concentration when using air, but this difference decreased as the reflux time increased. There was relatively little difference in the chloride concentration after 6 hr refluxing when either nitrogen or air was used as the sparge gas.

Table 7.2. Heat Transfer Data and Over-all Heat Transfer Coefficients
for 10-in. Dia Titanium Feed Adjustment Tank (Run YA-61)

Heat Transfer Area = 2 sq ft

No.	Acid Collection Rate, lb/hr	Acid Composition			Lv Weight Average, Btu/lb	Time to Collect 1 Liter of Acid, min	Liquid Temp., °F	Steam Pressure, psia	Steam Temp., °F	Temp. Difference, °F	Steam Condensate Collection Rate, lb/hr	Over-all Heat Transfer Coefficient U, Btu/hr-ft ² -°F	
		H ⁺	Cl ⁻	NO ₃								Based on Acid Collected	Based on Steam Condensate
1	17.85	4.55	.95	3.60	780	8.48	237	46	275.5	38.5	21.4	207	258
2	27.1	8.5	.3	8.2	665	6.11	248	56	288	40	28	226	322
3	29.4	11.35	-	11.35	555	5.95	251.6	66.5	299.5	48	24	170	228
4	50.7	13.65	-	13.65	484	3.6	257	73.5	306.2	49.2	-	250	-

Fig. 7.1. Chloride Concentration in Darex Dissolver Product as a Function of Air Sparging Time.

Fig. 7.2. Chloride Concentration in Darex Dissolver Product as a Function of Refluxing Time.

7.2 Darex-Thorex - J. B. Adams, F. G. Kitts

Aqua regia decladding followed by Thorex dissolution has been proposed as an alternate process to Sulfex decladding and Thorex dissolution for Consolidated Edison head-end treatment. The use of a single titanium vessel for decladding and dissolution may be feasible, provided the Thorex dissolvent (13 M HNO_3 , 0.04 M F^-) contains an excess of fluoride complexing cations (e.g., 0.1 M Al^{+3}). Preliminary experiments have been carried out to test alternate complexing cations such as boron, to measure corrosion under standard Darex-Thorex flowsheet conditions, and to develop a general flowsheet for cyclic operation of the decladding and dissolution steps.

Boron as a Complexing Cation. The primary concern about the use of titanium for the Darex-Thorex process is the danger of vapor phase attack of the fluoride ion (plus chloride from cross contamination), since the complexing action of aluminum could only be extended to the vapor phase by entrainment. On the other hand, boron may be an effect complexing agent in both the liquid and vapor phase, since H_3BO_3 and BF_3 both would be expected to be volatile in 13 M HNO_3 containing catalytic quantities of fluoride ion.

A ten-day test was carried out with three boiling Thorex dissolver solutions: fresh dissolvent and dissolvent in which $\text{ThO}_2\text{-UO}_2$ pellets had been dissolved to 0.5 M Th^{+4} and 1.0 M Th^{+4} (approximately the initial, middle and final solution concentrations during a batch Thorex dissolution of Consolidated Edison pellets). In each case, the standard Thorex dissolvent was replaced by 13 M HNO_3 , 0.05 M F^- , 0.10 M H_3BO_3 . Four titanium A-55 corrosion specimens were hung in the liquid and vapor spaces of each container, and the three liquids were refluxed in glass equipment with updraft condensers.

The results of the tests are presented in Table 7.3. The average corrosion rates during 253 hr for the fresh dissolvent were 0.58 and 0.33 mils/month in the liquid and vapor phases, respectively. A maximum rate of 1.3 mils/month was measured in the liquid phase during the last ninety hours of the test, perhaps indicating an accelerated attack.

The corrosion rates were very small when dissolved thorium was present. The average and maximum corrosion rates for liquid and vapor phases were all less than 0.07 mils/month during the 229-hr test period, and in most cases weight gains were registered.

The dissolution rate for thorium-uranium pellets was between 2.2 and 2.5 mg/sq cm-min (based on the initial pellet area) using the Thorex dissolvent containing boron. The corrosion and dissolution rate data are sufficiently encouraging that boron should be considered as a possible replacement for aluminum in the Thorex dissolvent. Further corrosion tests will be carried out at Battelle.

Table 7.3. Corrosion Rates of Titanium (A-55)
in Boiling Thorex Solutions with 0.1 M H_3BO_3

		Corrosion Rate, mils/month			Average
		0 - 89-1/4 hr	89-1/4 - 163-1/4 hr	163-1/4 - 253-1/2 hr	253-1/2 hr
<u>Initial Dissolvent</u>					
13 M HNO_3	Liquid	0.35	0.025	1.18	0.55
0.05 M NaF		0.36	g	1.38	0.60
0.10 M H_3BO_3	Vapor	g	0.99	0.12	0.30
		0.04	0.88	0.25	0.36
		0 - 65 hr	65 - 139 hr	139 - 229-1/4 hr	229-1/4 hr
<u>Middle</u>					
135 g UO_2-ThO_2 /liter dissolved in initial dissolvent	Liquid	g	g	0.032	g
		0.00	0.00	0.032	0.013
	Vapor	0.15	g	0.063	0.058
		0.12	g	0.010	0.029
<u>Final</u>					
270 g UO_2-ThO_2 /liter dissolved in initial dissolvent	Liquid	g	0.013	g	g
		0.03	0.013	0.011	0.017
	Vapor	g	0.026	0.00	g
		g	g	0.011	g

g = weight gain

Corrosion Under Standard Conditions. Six consecutive Darex decladding and Thorex core dissolution cycles were carried out with unirradiated stainless steel-clad $\text{UO}_2\text{-ThO}_2$ pins during a 44-hr period. Titanium specimens were suspended in both the liquid and vapor phases to check corrosion rates.

Corrosion rates corresponding to 0.6 to 0.8 mols/month were measured on the titanium specimens in the vapor. Companion specimens in the liquid gained weight very slightly. The results of these preliminary tests indicate the process may be satisfactory from the standpoint of corrosion. However, extensive tests are needed and are underway at Battelle.

Flowsheet Under Cyclic Operations. Uranium and thorium losses to the decladding solution were consistently low, averaging 0.21% and 0.019%, respectively. There appeared to be no increase in losses in several runs when a small heel of pellet fragments were carried from an incomplete core dissolution to the next decladding cycle.

A general flowsheet (Figure 7.3) shows the quantities of chemicals used and analytical results derived from the average of data for the six cycles. Only slight differences in data were encountered between the cycles. Washing with water three times (total water volume was 40-50% of dissolvent volume) after decladding with aqua regia reduced the chloride content from 1.8 - 2 N in the declad solution to 0.003 N chloride in the last wash which resulted in a chloride cross contamination of 90-300 ppm in the core dissolution solution. Washing following the removal of the core dissolvent solution was less effective; however, only one-half the volume of wash water was used.

Uranium and thorium losses in the decladding wash solutions were negligible - about 1/20th of that in the decladding product (0.21%) was found in the first wash. A heel of stainless steel (~ 7.5 g) had accumulated in the dissolver after the six cycles. It is estimated that about 10 g of stainless steel would be present at steady state in the dissolver. This quantity might vary depending primarily on the design of the dissolver. The mass of the heel of $\text{ThO}_2\text{-UO}_2$ pellet fragments will be dependent upon the amount of dissolvent used and exposure time allowed.

A typical chemical declad and core dissolution procedure for a cycle is as follows: Decladding - An unirradiated fuel pin* was charged to the

*0.311" dia x 7-3/8" long with 2-1/2" end caps weighing a total of 9 g; the clad weighs ~ 16 g. The core pellets contain 42.9 g ThO_2 (37.75 g Th) and 1.95 g UO_2 (1.72 g U). Recent analyses indicate that the pellets were of a poor quality, enough excess oxygen being present for the uranium to be present as ~ $\text{UO}_{2.75}$ or ~ U_3O_8 .

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Fig 7.3 General Flowsheet from Cyclic Dorex Decladding - Thorex Core Dissolution of Consolidated Edison Fuel

glass dissolver and 250 cc of cold 4 M HNO_3 -2 M HCl aqua regia was added. On heating to $\sim 85^\circ\text{C}$, a vigorous foaming reaction was initiated dissolving the clad within 2-3 min. When the intense foaming subsided an additional 250 cc of 4-2 aqua regia was added. The total aqua regia used was sufficient to produce a decladding product 0.9 M in stainless steel. Most of the solid end caps were consumed after boiling about 1/2 hr.

The dissolver was cooled and emptied. Three batch water washes were used; the first of 100 cc, the second and third, 50 cc. Each was allowed to remain 5 min before removal. It was noted that a small amount of stainless steel fines had been accumulating in the dissolver during the six cycles. This accumulation was attributed to physical shielding of fines rather than passivation since they dissolved readily in 4-2 aqua regia when removed from the dissolver at the end of the test. The heel of fines and small pieces of end caps was carried from decladding to core dissolution after washing. Core Dissolution - 200 cc of core dissolvent (13 M HNO_3 , 0.04 M F^- , 0.1 M Al^{+++}) was added to the ThO_2 - UO_2 pellets and boiled for 5-6 hr. Over 95 per cent of the pellets dissolved in 5 hr, with approximately 99 per cent being dissolved after 5.5 hr. Sufficient core dissolvent was used to result in a product solution analyzing 0.8 M Th. In several runs a heel of small pellet fragments was carried to the next decladding cycle after washing to remove soluble uranium and thorium values. Three batch water washes were used; the first of 50 cc, the second and third, 25 cc. Each was allowed to remain 5 min before removal.

7.3 Sulfex - J. B. Adams, B. C. Pinney, J. P. Nichols (Design Section)

Stainless steel-clad ThO_2 - UO_2 and UO_2 power reactor fuel may be reprocessed by the Sulfex process. The clad metal is dissolved in boiling 4-6 M H_2SO_4 ; the core is dissolved in nitric acid (for UO_2) or fluoride catalyzed nitric acid (for ThO_2 - UO_2 mixtures). The application of the Sulfex process to Consolidated Edison fuel is being investigated.

The Sulfex process (chemical dejacketing of stainless steel-clad power reactor fuels, Yankee Atomic and Con Ed types, with boiling 6 M H_2SO_4 followed by core dissolution) is to be investigated at 1/25 the proposed interim pilot plant scale. Engineering studies, both semicontinuous and batch, will be made to determine the feasibility of a Sulfex head-end treatment and to aid in the final design of the Interim Pilot Plant. Experimental equipment of glass and Carpenter-20 has been fabricated and installation of the equipment in cell 2 of Building 4505 is scheduled to begin May 18.

Schematic diagrams of the engineering scale semicontinuous and batch Sulfex equipment are presented in Figures 7.4 and 7.5. The evaluation of the equipment and processing method will be divided into a two-phase program. The first will involve the dissolution of stainless steel plate-type fuel elements and the second will involve chemical dejacketing and core dissolution of Con Ed prototype assemblies (36 assemblies have been ordered for delivery in June).

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Fig. 7.4 Schematic Diagram of Semi-Continuous Sulfex Equipment.

Fig 7 5 Schematic Diagram of Batch Sulfex Equipment

The evaluation will include a thorough study of the following:

(1) foaming characteristic of semicontinuous and batch dissolution of stainless steel in boiling 6 M H_2SO_4 ; (2) passivation of stainless steel in boiling 6 M H_2SO_4 ; (3) maximum metal loading obtainable from the standpoint of solution stability; (4) removal and recovery of fissile and fertile particulates in a settler; (5) feed clarification, which will involve clarifying both the decayed and core dissolution solutions; (6) uranium and thorium losses to the decayed solution; and (7) dissolution rates of both cladding and core.

7.4 Feed Clarification - J. B. Adams, G. B. Minsmore

Clarification of dissolver solutions by filtration through sand beds or micrometallic filters is being investigated. Dissolver solutions from fuel reprocessing treatments frequently require clarification because they may contain undesirable precipitates, undissolved fissile or fertile fuels, and emulsion forming agents (usually silica). The present investigation is concerned primarily with the development of a positive cleaning method for micrometallic filters once they are fouled with siliceous material.

Washing of Darex Filter Cakes. Recovery of soluble uranium from siliceous Darex filter cakes* deposited on porous metallic filter elements was accomplished successfully by washing with water. Filter cakes deposited on both star-shaped and horizontal flat plate elements remained intact during three wash steps and could be washed to a uranium cake analysis of 0.001% (Table 7.4). Cakes were washed excessively because the experimental equipment was too large in proportion to the Darex slurry available.

After the third wash, the uranium loss was of the order of 0.005%. However, after the first wash it was estimated that the uranium loss had been reduced to less than 0.1%. These results indicate that uranium can be essentially completely recovered from Darex filter cakes by simple wash procedures.

In these tests, two filter elements were used, a 0.66 sq ft star-shaped element and a 0.16 sq ft -3 element flat disk-type.*** Previous tests with cylindrical and bayonet types had shown there was some difficulty in maintaining a siliceous filter cake (with or without filter aid) from Darex solutions on a vertical surface. Heavy cakes containing filter aid became brittle after being freed of interstitial liquor by air flow at the end of a batch filtration cycle. These cakes cracked and sometimes collapsed under their own weight. The open star shape eliminated these difficulties.

*About 20 g wet cake with 10 g of Celite 545 filter aid added per liter of Darex solution.

**Micrometallic Corp. no. OS-1-6 Open Star (Type F, mean pore size 20 micron); the filter cake was held vertically. (Figure 7.6)

***Micrometallic Corp. 3-1/4" dia Gravitain unit (Type F, mean pore size 20 micron) with 1" spacing to hold filter cake, porous on top side only; filter cake is held horizontally. Filter elements are drained through and supported by a common central manifold. (Figure 7.6)

Table 7.4. Uranium Removal by
Washing of Darex Filter Cakes

Star Filter Element			GravitaIn Filter Element	
Wash Volume, ¹ cc	Uranium, g/liter		Volume, ¹ cc	Uranium, g/liter
-	4.06	Original filtrate		4.06
5650	0.364	1st wash	1500	0.684
5700	0.017	2nd wash	1650	0.049
5525	0.005	3rd wash	1600	0.020
-	0.001%	Washed cake (dry basis)	-	0.001%

¹Excessive wash volumes relative to original filtrate and filter cake were required in the equipment used in these tests; the 3/8 in. cake on the "Star" element represented 10 liters of Darex solvent extraction feed solution and the 1/2 in. cake in the GravitaIn unit, 36 liters. Filter cakes were therefore "overwashed."

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Fig 76 Porous Metal Test Filter Elements

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Thin (less than 3/8 in.) siliceous filter cakes (without filter aid) tended to warp and peel after being freed of interstitial liquor by air flow at the end of a batch filtration cycle. This problem could be reduced by providing a spray mist around the cake to keep it damp at the end of a cycle. The volume of mist water would be small compared to other water requirements (e.g., washing).

A star filter provides concave cylindrical filtering surfaces. The resultant arched filter cake adds sufficient strength to allow an air-purged cake to support its own weight. The filter element could be handled with normal care and several washing steps carried out with no danger of losing the cake. The most effective use of wash water was by washing of a thick filter cake in place on the filter. Repulping procedures, although possible, would require more water to obtain the same degree of solute removal. The cake could be discharged easily by backwashing.

Horizontal filter surfaces, such as are available with the Gravitain filter, remove the requirement that the cake support its own weight. Filter cakes remained in place and could be washed easily several times. Cake deposition, washing, and discharge were satisfactory on a 6-in. dia flat porous plate (mean pore size 20 micron) and no difficulty is envisioned in possible use of larger Gravitain units.** One disadvantage of using larger flat areas for filters is that backwashing pressures are limited by the relative weakness of porous metal plate. Carefully designed instrumentation would be needed to eliminate any possibility of breakage.

Centrifuge Tests. Tests with a 5-in. solid bowl centrifuge*** showed that Darex solvent extraction feed solutions could be clarified completely at rates of 300-400 cc/min. At higher feed rates, from 500-1000 cc/min, solids appeared in the overflow, gradually increasing as the flow rate was increased. Based on the assumption of an effective particle density of 2.2 g/cc, a liquid density of 1.2 g/cc, known bowl dimensions and bowl speeds (2500-3500 rpm) measured with a Strobotac, it was estimated that essentially complete separation had been obtained when particles down to the 4-10 micron range were removed.

No effective cake washing technique has yet been found. After re-slurrying in water for washing, the solids did not compact on the wall of the centrifuge bowl but remained in part as a slurry. Flowing water con-

*The open star no. OS-1-6 was 6 in. long; further test to confirm cake adherence on an 18 in. long open star will be run.

**Larger Gravitain assemblies are available made of 9"x9" and 18"x23-1/2" rectangular plates with a 3-1/2" center manifold pipe.

***International Chemical centrifuge with a solid bowl, 5" O.D. x 3-5/8" I.D. at the overflow lip x 2.7" deep. Maximum effective bowl volume at full speed is 315 cc.

tinuously through the bowl was not effective since the less dense water flowed over the cake without mixing. A slurry made up from solids that had been through the centrifuge was almost unfilterable.

Tests on both centrifugation and washing techniques are being continued in an effort to develop effective methods of using a centrifuge for feed clarification.

7.5 Solvent Extraction Studies - R. J. McNamee, R. O. Payne, K. Ladd

A study is being carried out to assist the Hanford Atomic Products Operation in adapting the Redox process to the reprocessing of spent stainless steel power reactor fuels. The investigations being made include studying the effect of stainless steel salting strength, acidity, flow ratios, and soluble silicon and molybdenum concentrations on column capacity and uranium extraction efficiency. To increase the decontamination factor for stainless steel systems, the salting strength of the feed was reduced with a resulting increase in uranium loss (as much as a factor of 20).

A run was made with a 2-in. packed column using a 0.8 M SS, 0.15 M AD, 0.004 M soluble silicon feed and a 1 M Al, 0.12 M AD scrub. The feed/scrub/solvent flow ratio was $1/0.24/2.5$. The total column throughput was 373 GSFH, or 77 per cent of flooding. The extraction section of the column was 21.3 ft in length, packed with $1/4 \times 3/8$ SS Raschig rings.

The preliminary results of the run are given in Table 7.5. The uranium loss to the raffinate was 0.04 per cent, which may be compared with a loss of 0.002 per cent previously obtained with a standard Redox flow-sheet run in the same column. HETS calculations await equilibrium determinations.

Table 7.5. Aqueous Phase Uranium Concentrations

Solution	Concentration, g/l
Feed	99.7
1 ft below feed point	36.3
2.8 ft below feed point	12.3
4.5 ft below feed point	4.16
6.3 ft below feed point	1.31
8.3 ft below feed point	0.529
Raffinate	0.031

7.6 Mechanical Processing - J. B. Adams, G. K. Ellis, G. A. West, J. C. Rose, W. B. Sheeley, D. E. Willis

Shearing. Mechanical processing of fuel can reduce the quantity of inert structural material processed in a fuel recovery plant, resulting in increased plant capacity and a reduction of waste volumes to be stored. The purpose of this program is to evaluate mechanical methods and to demonstrate selected methods with irradiated fuel for: (1) removal of inert end adapters and other structural material; (2) the disassembly of fuel assemblies into appropriately sized subassemblies; (3) the shearing and leaching of assemblies or subassemblies; (4) the dejacketing of individual fuel elements; and (5) the disposal of jackets leached free of fissile and fertile material from the dejacketing operation.

Research and development contracts of approximately \$10,000 each to determine the feasibility of shearing spent power reactor fuel assemblies have been let to Clearing Division of U. S. Industries, Inc., Chicago, Illinois and Birdsboro Steel, Foundry and Machine Company, Inc., Birdsboro, Pa.

In the first feasibility tests, Clearing proposes to deferrule the fuel assemblies, rearrange the fuel tubes into a parallelepiped to produce minimum voids between individual tubes, and shear the entire reshaped assembly. In later tests, the shearing of fuel assemblies without prior preparation (with the possible exception of flattening the assembly) will be investigated. The Clearing program will investigate the following parameters with a 110-ton shear.

- a. Blade shape - see Figure 7.7.
- b. Blade velocity - 2 in./min at midstroke to 4 ft/sec.
- c. Blade clearance - 1 thousandth to 10 thousandths.
- d. Blade wear - Inspect blade with a profilometer after 300 cuts. Deliberately dull blade by rounding edge (1/32 radius) and continue cuts.
- e. Blade alloy - Latrobe BR-4 followed by harder alloys as indicated from test shearings.

Birdsboro's program has not yet been completely defined but it will be concerned primarily with the investigation of shearing intact fuel assemblies.

Leaching Equipment - Batch. The batch leacher to be used in cold testing is 50 per cent fabricated and will be completed June 15. A test facility to obtain design data for a conical bottom in the batch leacher for removing stainless steel fines is 75 per cent fabricated. In tests of an earlier conical design all of a sample of 200 g of 1000 micron stainless steel fines was jetted with 6 liters of water in 10 sec from

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(a)

(b)

(c)

NOTE:
THE TUBE BUNDLE BEING SHEARED
IS IN A CLOSE PACKED ARRAY,
PARALLELOPIPED FORM.

111 004 Fig 7.7 Experimental Setups To Be Used In Clearing Shear Blade Evolution.

a 60° conical shaped vessel. The 0.5-in. vacuum line was located along the vertical cone axis 0.5 in. from a 7/8 in. dia flat disc bottom.

Leaching Equipment - Continuous. Material transfer characteristics of the spiral vibratory leacher were studied in preliminary tests using pieces of sheared stainless steel-clad porcelain rod and solid stainless steel rods and flowing water down the spiral. The solids holdup was 0.6 cu ft for a single layer of 1 in. long, 0.5 in. dia cylinders and varied in weight from 53 lb for empty 35-mil wall tubing to 217 lb for UO₂-filled tubing. Liquid holdup varied from 1.5 gal to 3.0 gal for liquid flow rates from 0.5-2.0 gpm.

For a steady uniform rate of solids material transfer up the spiral, it does not appear practical to increase the solids residence time beyond 15 min. A representative from Syntrol will tune the vibrator, since it has been impossible to reproduce or maintain the same material transfer rate during most tests.

A sampler box for the purpose of taking as many as 8 samples simultaneously from various positions in the spiral leacher is being fabricated. The samples will be taken by pulling a vacuum on the sample box containing sample bottles and withdrawing samples through a set of capillary lines connecting the box to the sampling points. The pressure drop will be balanced across the lines to equalize the flow rates. A constant purge of air is expected to keep the lines clear when samples are not being taken.

High Level Segmenting Facility. Irradiated fuel assemblies of interest to the Mechanical Processing program will be sheared in cell A and leached in cell B of Building 3048. A preliminary layout of the leaching equipment for cell B is completed. The problem of material transfer between cells A and B is currently being considered by RER Division personnel. A totally enclosed automatic system for transfer from the shear to the leacher is to be designed.

A procedure for decontamination of the UO₂ leaching equipment in cell B has been proposed. The process acid feed tanks and rinse solution tanks would be used for the decontamination solution feed tanks. Two decontamination solutions and procedures were proposed: either a Turco 4501 solution of 20% caustic-2% sodium tartrate, or a solution of 20% HNO₃ with 3% HF. Penberthy jets would be used for recirculation with Bette fog nozzles in strategic locations for dispersal of the decontamination solution. Connections would be made from the decontamination solution feed tanks to the equipment being decontaminated through a quick disconnect panel board.

Sheared Fuel Leaching Studies. Batch leaching of sheared stainless steel-clad UO₂ pellets in 10 M HNO₃ (173% average excess) was continued to obtain information for the design and operation of experimental leachers. Additional runs were made to compare the effect on reaction rates of the addition of the sheared fuel to boiling acid and room temperature acid (150% excess) brought to boiling (111°C).

The reaction time for complete leaching of 1/2, 1, 2, 3, 4 and 5-in. sheared lengths was 40, 70-200, (99.5% completed in 70 min), 110 and 130-245 (99.8% completed in 130 min), 100 and 100 min, respectively (Figure 7.8, Table 7.6). The total leaching times were greater by a factor of approximately 2 than the time for leaching in acid brought to boiling from room temperature (UNOP monthly report for April 1959, ORNL CF 59-4-47).

The UO_2 leaching rates, initial and average, are presented in Figure 7.9, as a function of sheared fuel length for both preheated and room temperature leach acid. As the correlation shows, there was little difference in the initial dissolution for cold and preheated acid, but the average rates differed by the previously mentioned factor of two.

These results are unexpected, since the preheating would be expected to have the greatest effect on the initial rates and a correspondingly lower effect on the average. The main difficulty seems to lie in the definitions of the two rates. The initial rate is defined exactly as the initial slope of the uranium concentration vs. time curve. However, the average rate is the slope of a line drawn to the point on the curve where the dissolution reaction stops.

Referring to Table 7.6, variations by a factor of five in the average dissolution rate are possible, depending on whether the rate after 99.8 or 100% dissolution is calculated. Such variations are not significant but merely emphasize the uncertainties associated with the calculation of the average dissolution rates.

The apparent surface area of the sheared UO_2 (fines and bulk) clad in stainless steel reacting with nitric acid can be estimated from instantaneous dissolution rates $g/cm^2/min$ (Figure 5.7 of the UNOP January monthly report, ORNL CF 59-1-74, and Figure 7.8 of this report) of solid UO_2 of known surface area and instantaneous leach rate (g/min) of the sheared material.

The apparent surface area per unit weight of total UO_2 present at the beginning of the UO_2-HNO_3 reaction plotted against the length of stainless steel-clad UO_2 rod on log-log paper yields a straight line (Figure 7.10) where A is the apparent surface area per total weight of UO_2 expressed in $sq\ cm/g$ and L is the length of sheared fuel element expressed in inches. The relation between L and A may be expressed as:

$$A = 0.5 L^{-1.06}$$

Within the range of practical interest, the apparent area varied from 1 $sq\ cm/g$ of UO_2 for 0.5-in. lengths to 0.04 $sq\ cm/g$ of UO_2 for an extrapolated 10-in. length of 0.4-in. dia rods. These data are useful for determining the size of the off-gas process auxiliaries required for the cell 4A leaching facility.

Fig.7.8. Boiling HNO₃ Leaching of Sheared SS Clad UO₂ vs Time.

7.6

Clad UO_2 in Boiling 10 M Nitric Acid

Conditions:

- (1) Volume to mass ratio was 3 ml/g UO_2
- (2) UO_2 particles dislodged from shearing were included
- (3) End closure from shearing was 5 to 90%
- (4) 0.370 in. O.D. pellets clad with 0.400 in. O.D. x 0.010 in. wall SS

Sheared		Contact Time, min	HNO_3 , M	Initial U, g	U Dissolved, %	Reaction Rate			
						Initial Constant		Over-all Average	
Length, in.	Pieces No.					g/min	g/min/g U	g/min	g/min/g U
0.5	24	0	10.0	175	-	-	-	-	-
		8	8.35		63	13.75	0.079	-	-
		30	7.0		93.7	-	-	-	-
		40	6.9		100	-	-	4.37	0.025
1.0	12	0	10.0	180	-	-	-	-	-
		10	9.2		38.9	3.89	0.039	-	-
		70	6.7		99.5	-	-	2.57	0.014
		200	6.65		100	-	-	0.90	0.005
2.0	6	0	10.1	175	-	-	-	-	-
		30	8.6		58.3	3.4	0.019	-	-
		90	6.9		99.5	-	-	-	-
		110	6.9		100	-	-	1.6	0.0091
3.0	4	0	10.0	183	-	-	-	-	-
		40	8.3		56.4	2.58	0.014	-	-
		130	6.3		99.8	-	-	1.4	0.008
		245	6.25		100	-	-	0.75	0.0041
4.0	5	0	9.9	266	-	-	-	-	-
		45	7.2		72.3	4.22	0.016	-	-
		100	5.8		100	-	-	2.66	0.01
		160	5.8		100	-	-	-	-
5.0	4	0	9.9	259.5	-	-	-	-	-
		55	7.1		73.2	3.46	0.013	-	-
		100	6.0		100	-	-	2.6	0.01
		160	6.0		100	-	-	2.6	0.01

Fig. 7.9. Boiling 10 M HNO_3 Leaching Rates of SS Clad UO_2 Pellets vs. Sheared Lengths.

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Fig. 7.10. The Initial Apparent UO₂ Surface Area (Based on Kinetics Data for Whole Unclad UO₂ Pellets and Sheared Fuel) for Various Lengths of Sheared Stainless Steel-Clad UO₂ Rods.

The experimental result that the initial effective specific surface area is inversely proportional to the sheared length may be predicted by simple considerations. For cuts of cylindrical clad elements with no fines dislodged, the end areas per unit fuel mass are:

$$A' = \frac{(\pi d^2/2)}{(\pi d^2/4)L\rho} = \frac{2}{L\rho} \quad (1)$$

where

d = pellet diameter

L = sheared length

ρ = pellet density

Assuming that the mass of fines per cut remains constant and that the surface area per unit mass of fines is also constant, the additional fines specific area is:

$$A'' = D\alpha = \frac{4K\alpha}{\pi d^2 L} \quad (2)$$

where

D = fines dislodged, g/g fuel

α = surface area/g fines

K = g fines/cut

(Experimental measurement of fines dislodged vs. sheared length have indicated a roughly reciprocal relationship: $D \approx K'/L$)

The areas in equations (1) and (2) may be added if one assumes that the fuel remaining after fines are dislodged is cylindrical. The total specific area, A (sq cm/g total fuel) = $A' + A''$, is:

$$A = \frac{2}{L\rho} + \frac{4K\alpha}{\pi d^2 L} = \frac{1}{L} \left[\frac{2}{\rho} + \frac{4K\alpha}{\pi d^2} \right] \quad (3)$$

8.0 VOLATILITY

R. W. Horton

8.1 Fused Salt Dissolution and Corrosion Tests - R. B. Keely

The dissolution of zirconium metal in molten salt baths of NaF-LiF or NaF-ZrF₄ with anhydrous HF is a proposed head-end step for the reprocessing of zirconium matrix fuel subassemblies. Dissolution studies have been made using dummy subassemblies fabricated from Zircaloy-2 rolled plate. The purposes of the present dissolution program are (1) to study the corrosion of an INOR-8 dissolver under dissolution and start-up condition, and (2) to study the effects of salt composition, temperature, and HF feed rate on Zircaloy dissolution rates.

Dissolution Rate Studies. Dissolution rate data were obtained during corrosion runs INOR-8 -7, -8 and -9. The rate of dissolution increased with increased HF feed rate and decreased with increased zirconium concentration in the salt.

The effect of HF flow rate on dissolution rate was observed in a comparison of INOR-8 -7 and -8 (Table 8.1). The rate of dissolution of zirconium metal increased from 0.23 to 0.33 lb Zr/hr sq ft (1.87 to 2.68 mg Zr/min sq cm) when the HF rate was increased from 2.5 lb/hr to 6 lb/hr. There was not always a direct relation between the HF flow rate and the H₂ evolution rate which is proportional to the dissolution rate (Figures 8.1 and 8.2). The factors responsible for the effect of HF rates on dissolution rate are: (1) the "active" surface exposed to the gas, (2) the stirring effect of the gas stream, and (3) the "solubility" of the HF in fused salt as a function of flow rate.

The effect of zirconium fluoride concentration in the melt on dissolution rate was measured in runs INOR-8 -8 and -9. Higher concentration of zirconium in the salt retarded the rate of dissolution (Figures 8.3 and 8.4). The initial concentration of zirconium in the NaF-LiF melt was increased from 0 to 13 mol per cent Zr which decreased the average rate of dissolution from 0.33 to 0.24 lb Zr/hr (sq ft of original surface) (2.68 to 1.95 mg Zr/min sq cm).

Corrosion Studies. No corrosion occurred under the normal hydrofluorination conditions of runs INOR-8 -5, -6, -7, -8, -9. Severe pitting and general corrosion occurred in the zirconium barren melt used in runs INOR-8 -10.

During runs (INOR-8)-1, -2, -3, and -4 the vessel had been exposed to 700°C molten salt for 68 hr, during which HF was present for 32 hr. After oxalate cleaning, the average reduction in wall thickness measuring with Vidigage equipment was 6 mils.

Table 8.1. Operating Conditions
for INOR-8 Dissolver Studies

Fixed Conditions:

Subassemblies 100% submerged

Subassembly description: Twelve 1/8"x2-1/2"x12" Zr-2
plates with 1/8"x1/4"x12" Zr-2 spacers
(double plate on outer faces)

Argon gas blanket

No cooling air required

Operating Condition	Run			
	INOR-8 -7	INOR-8 -8	INOR -8 -9	INOR-8 -10
Initial salt composition	43 mol % NaF 57 mol % LiF	43 mol % NaF 57 mol % LiF	37 mol % NaF 50 mol % LiF 13 mol % ZrF ₄	43 mol % NaF 57 mol % LiF
Wt of subassembly, kg Zr-2	5.8791	5.8771	5.6597	None
1b Zr-2	12.96	12.96	12.48	-
HF, rate of flow, lb/hr	2.5	6.0	6.0	4.0
Dissolver temperature, °C	695-715	703-722	707-722	687-703
HF pressure, psig (at bottom inlet to vessel)	1-2	1-6	1-18.5 ^a	1-2
Run time, hr	14	9.5	12.4	11.2
Over-all dissolution rate, mg Zr/min sq cm	1.87	2.68	1.95	0.31 ^b
Lb Zr/hr sq ft	0.23	0.33	0.24	.038 ^b
Over-all utilization, %	30 ^c	29 ^d	18 ^d	3.1 ^d
HF balance, by wt	-	-	100%	-

^aDissolver vessel pressurized (obstruction in off-gas line).

^bRate of corrosion of vessel (assumed vessel pure nickel for calculation).

^cBy hydrogen evolution.

^dBy weight of HF condensed.

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Fig. 8.1. Reaction Rates for INOR-8-7.

Fig.8.2. Reaction Rates for Inor-8-8.

Fig. 8.3. Reaction Rates for Inor-8-9.

Fig.8.4. Reaction Rates of Function of Zr Concentration.

Subsequent to runs INOR-8 -5, -6, -7, -8, and -9 (Table 8.1) the oxalate cleaning procedure and Vidigage measurements were repeated. The additional 70 hr of 700°C molten salt exposure which included 37 hr of HF exposure did not product any detectable corrosion (neither uniform wall reduction nor pitting).

Runs 5 through 10 brought the total exposure to molten salt to 153 hr, of which HF was present for 80 hr.

The corrosion in run INOR-8 -10 was severe in localized and uniform attack (Figures 8.5, 8.6 and 8.7). This run was to measure the corrosion effects of HF on the dissolver in the absence of zirconium either in the salt or as a subassembly. The absence of zirconium in the melt represents a severely corrosive condition which might occur and must be avoided during plant startup; other test conditions were similar to the previous runs (Table 8.1).

Measurements with lead castings of the areas of pitting revealed a maximum penetration of approximately 65 mils. The average uniform loss of metal at the interface was 18 mils (by Vidigage surveys). The upper third of the draft tube indicated a reduction in wall thickness of 11 mils total. This total represents attack on both the inner and outer wall surfaces.

The average over-all penetration rate, assuming uniform attack, was 0.82 mils/hr for 11 hr based on the hydrogen evolution rate (Figure 8.8). However, post run examination of the vessel walls indicated a maximum corrosion rate of 6 mils/hr for 11 hr in localized areas. The corrosion decreased with time, which may substantiate the inverse dependence of corrosion rate on hydrogen concentration in the salt found by Battelle Memorial Institute. A significant observation in this run was that no solids were entrained into the off-gas.

Molybdenum and INOR-8 corrosion coupons were suspended from the baffle in the center of the dissolver at the level of the interface during runs INOR-8 -9 and -10. No visible corrosion occurred in INOR-8 -9. After INOR-8 -10 the molybdenum specimen had a 10 per cent loss weight compared with a 22 per cent loss of weight for an INOR-8 specimen of equal surface area (Table 8.2 and Figure 8.9). The dissolver was sectioned for metallographic examination after INOR-8 -10.

Equipment Performance and Modifications. A failure in the INOR-8 combination gas inlet-salt product outlet pipe from the dissolver occurred midway through INOR-8 -8; however, the run was completed without difficulty. The failure was adjacent to and above the fillet weld connecting the Inconel ground electrode to the INOR-8 pipe. The circumferential crack which developed was about 5/8 in. long. The salt leaking from the point of failure solidified and formed a "self-sealing" repair. The failed section was replaced with Inconel pipe and the ground electrode was moved to the top flange of the vessel to reduce the thermal stresses believed to be responsible for the failure.

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Fig. 8.5 View Into Dissolver.

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NOTE:

GAS FLOW IS INTO
SURFACE VIEWED

Fig. 8.6. HF Distributor Plate.

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DIRECTION OF GAS FLOW →

NOTE TYPICAL PITTING

Fig. 8.7. Exterior of Draft Tube.

Fig. 8.8. Corrosion Rate for INOR-8-10.

Table 8.2. Corrosion of Specimens
at Gas-Salt Interface (Figure 8.9)

Specimens suspended from Inconel wire during the two runs: INOR-8 -9 and -10

Metal	Original Wt, g	Wt Loss, g	% Loss ^a	Comments
INOR-8	10.8380	2.3840	22.0	Specimen and wire deeply pitted. Only one face of specimen in stream.
INOR-8	11.1823	3.2376	29.0	Specimen and wire deeply pitted. Both faces of specimen in stream.
Molybdenum	7.5275	0.7415	9.8	Specimen pitted (shallow pits). Wire deeply pitted. Only one face of specimen in stream.

^aMost of the corrosion occurred during INOR-8 -10. There was no visible corrosion after INOR-8 -9.

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Fig. 8.9. Corrosion Specimens at Salt-Gas Interface. (See Table 8.2)

Solids formed in or entrained into the vessel off-gas line during dissolution of a Zr-2 subassembly constricting the line and causing pressure increases in the system. In INOR-8 -8 the pressure rose to 6 psi in the HF supply system. Duplicate conditions in the succeeding run caused pressures of 18.5 psi within 6 hr of the start of the run. The last six hours of the run were made with the dissolver under about 10 psi pressure.

A corrugated rod was temporarily installed in the off-gas line for remote removal of solids, pending analysis of the residue which might indicate the mode of mass transfer.

8.2 Off-Gas Studies - S. H. Stanker

The purpose of this report is to summarize the current knowledge of the solids carried out of the fused salt dissolver in the process off-gas. Such knowledge is required prior to the selection of off-gas cleaning equipment.

General Characteristics. The solids have a color which ranges from gray to black and resemble a soft coal fly ash in texture. The dust loading in the off-gas was as high as 40 grains per cubic foot which represented a 1 to 2 weight per cent loss of the dissolver contents.

Particle Size. The particle size distributions for solids collected in runs INOR-8 -6, -7, and -8 (Table 8.3 and Figure 8.10) showed 50 to 60 weight per cent less than 150 micron size. These samples had a maximum variation in distribution of 220 per cent (in the greater than 590 micron fraction).

Table 8.3. Particle Size
Distribution of Off-Gas Solids

Run	Weight Per Cent in Size Fraction					
	Above 590 Microns	420-590 Microns	250-420 Microns	177-250 Microns	149-177 Microns	Below 149 Microns
INOR-8 -6	9.65	1.38	1.61	16.78	21.14	49.42
INOR-8 -7	4.89	1.01	1.66	33.69	8.05	50.69
INOR-8 -8	15.37	1.96	1.96	2.20	15.13	63.38

Chemical Analysis. The major constituents of the solids from INOR-8 runs were (Table 8.4):

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Fig. 8.10. Off-Gas Solids Particle Size

Table 8.4. Composition of Major
Constituents of Off-Gas Solids

<u>Element</u>	<u>Range of Concentration, Wt Per Cent</u>
Sodium	15-19
Lithium	5.1-7.4
Zirconium	4.0-12
Fluoride	53-61
Hydrogen fluoride	8.9-18.8

The minor constituents were (Table 8.5):

Table 8.5. Minor Constituents
of Off-Gas Solids

<u>Element</u>	<u>Maximum Concentration, Wt Per Cent</u>
Nickel	1.85
Sulfur	0.34
Copper	1.22
Molybdenum	1.22

The complete chemical analyses for all off-gas solids samples are given in Table 8.6. Phase analysis of run D-24 showed the compounds $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ and alpha quartz. The quartz was identified as the residue from a water wash of the black solids. It should be noted that the off-gas solids had a lower lithium to sodium ratio than did the salt in the dissolver. This result indicates that a sodium stripping occurred during dissolution.

The 20 to 50 per cent weight loss on heating at 110°C (Table 8.6) has not been explained. The comparisons of the loss on heating with the ammonia and HF contents (Table 8.7) demonstrates the poor material balances obtained. The deficit may be simply a variable moisture content.

Table 8.6. Chemical Analyses of Off-Gas Solids

Wt Per Cent Constituent	Run ^a							Solid Plug
	D-23	INOR-8 -1	INOR-8 -2	INOR-8 -6	INOR-8 -6 ^b	INOR-8 -7	INOR-8 -8	INOR-8 -8
Sodium	1.7	15.2	17.6	18.5	18.42	18.62	17.36	21.26
Lithium	0.44	5.1	6.59	7.0	7.37	6.69	6.70	8.49
Zirconium	1.06	10.7	11.1	4.0	3.21	9.41	6.82	7.30
Fluoride	29.8	54.9	60.3	53.5	57.45	56.42	50.91	45.17
Loss on 110°C ignition	23.4	-	-	19.96	51.48	50.63	19.83	-
Nitrogen	0.37	-	-	0.56	-	-	-	-
Ammonia	-	-	23.2	-	0.74	0.19	1.92	0.96
Nitrate	-	-	-	-	1.15	0.89	1.02	8.03
Sulfur	-	-	-	-	0.34	0.34	0.30	-
Nickel	-	-	1.85	0.18	0.94	0.83	1.12	-
Copper	11.22 ^c	-	<75 ppm	-	0.61	0.16	1.22	-
Molybdenum	-	-	1.22	-	0.29	0.45	0.70	-
HF	22.01	-	18.84	16.92	18.8	12.24	8.90	4.08

^aCertain runs yielded no off-gas data for these reasons:

INOR-8 -3: Severe off-gas leak - much ammonia used.

INOR-8 -4: Fused salt leak at start - no run.

INOR-8 -5: Resistance heating failure - no run.

D-24: Only small amount of solids.

INOR-8 -9: Plug formed - no solids sample taken.

INOR-8 -10: Only small amount of solids.

^bCheck analysis performed several weeks after initial analysis.

^cRun made in copper lined dissolver.

Table 8.7. Analyses of Off-Gas Solids

Sample	LOI, wt %	HF wt %	NH ₃ , wt %	Deficit
Recheck INOR-8 -6	51.48	18.80	0.74	31.94
INOR-8 -7	50.63	12.24	0.19	38.20
INOR-8 -8	19.83	8.90	1.92	9.01

Ammonium Compounds. A peculiar result was obtained in the analysis of solids from run INOR-8 -2. Phase analyses (Table 8.8) of these off-gas solids showed 95 per cent were ammonium compounds. Two chemical analyses showed the ammonia content was 23.2 and 23.4 weight per cent. This high ammonium salt concentration was not explained and has not been obtained since.

Table 8.8. INOR-8 -2 Phase Compositions

Compound	Weight, Per Cent
NH ₄ F	50
(NH ₄) ₃ ZrF ₇	30
NH ₄ F-HF	15
Unidentified	5

Effect of Blanket Gas on Solids Formation. Use of argon rather than nitrogen as the blanket gas did not change the composition or amount of off-gas solids produced. Because of the ammonium compounds and the high weight loss on ignition found in chemical analyses, it was decided to investigate the possibility of a reaction between nitrogen and hydrogen catalyzed by the zirconium element itself. Several authors report that a hydrogen-nitrogen reaction is possible at elevated temperatures in the presence of zirconium. Either the zirconium can react with nitrogen forming zirconium nitride, or zirconium may react with hydrogen to form zirconium hydride. These two compounds then can react with hydrogen and nitrogen, respectively, to regenerate zirconium and produce ammonia gas.

Since these reactions were possible, dissolution INOR-8 -7 was carried out to determine the effect of using argon instead of nitrogen as the blanket gas. The dissolution proceeded smoothly, but the only change in off-gas characteristics was that the solids were gray colored rather than charcoal black as seen before. There was no change in the dust loading of the off-gas. Chemical analyses showed no significant change in composition of the off-gas solids.

Effect of Dissolution Reaction. To determine if the dissolution reaction was causing the solids formation, nitrogen was bubbled through a 4-in. I.D. pot containing 12 mol per cent ZrF_4 in NaF-LiF fused salt at $750^\circ C$ (run P-1). No reaction between the fused salt, the vessel, and nitrogen occurred, and the off-gas was clean and free of solids. It should be noted that the superficial gas velocity in this test was 10 times smaller than the gas rates through the INOR-8 dissolver.

Run INOR-8 -10 was made with no element present primarily to determine a corrosion rate for the dissolver vessel. No significant amounts of off-gas solids were formed in the 12-hr run. This result may substantiate the belief that the dissolution rather than the corrosion mechanism generates the large amounts of solids found.

Solid Plug Composition. Chemical analysis (Table 8.6) of a plug (Figure 8.11) which formed during INOR-8 -8 causing a 6-lb pressure buildup, showed a nitrate concentration of 8.03 weight per cent. Since no nitrogen gas was used in this run, the presence of this ion is inexplicable.

8.3 Dry Hydrofluorination - L. E. McNeese

During studies in which the Zircaloy-3 hydrofluorination was carried out in a bath of molten fluorides, it was observed that a gas-metal reaction occurred when the metal was exposed to anhydrous HF or HF- H_2 mixtures at temperatures in excess of $600-650^\circ C$. Since gas-metal hydrofluorination appeared attractive as a method of fuel element hydrofluorination, a study of this phenomenon was initiated. The experimental work reported here deals with the hydrofluorination of a Zircaloy-3 matrix type dummy fuel element at $1025^\circ C$ with anhydrous HF.

A hydrofluorination experiment (run DE-10) was performed in the dry hydrofluorination reaction system (described in UNOP December 1958 monthly report, ORNL CF 58-12-35). A nine-plate Zircaloy-3 dummy fuel element weighing 804.6 g and having the dimensions shown in Figure 8.11 was used in the test. Element temperatures were measured by three 40-mil diameter Inconel-sheathed thermocouples in the locations shown in Figure 8.12. The test element and thermocouples are shown on the reaction system support rack prior to hydrofluorination in Figure 8.13. The element was hydrofluorinated with a reactor wall temperature (outside) of $1025^\circ C$ with an HF feed rate of 1 lb/hr for 3 hr, at which time the test was concluded in order to leave 10 to 15% of the element unreacted and to calculate the reaction rate as the hydrofluorination neared completion.

Fuel element temperatures and reactor wall temperature are given in Figure 8.14. A maximum element temperature of $1155^\circ C$ was observed. Hydrogen produced by the reaction

was metered in a wet test meter at 760 mm Hg and $26.6^\circ C$. Experimental off-gas data are given in Figure 8.15.

Fig. 8.11. Solids Buildup in Outlet of INOR-8 Dissolver.

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OUTER PLATE DIMENSIONS: 2 x 3 x 0.16 in.
INNER PLATE DIMENSIONS: 2 x 3 x 0.095 in.
SPACER DIMENSIONS: 0.25 x 3 x 0.095 in.
TOTAL SURFACE AREA: 0.721 ft²

Fig. 8.12. Element Dimensions and Thermocouple Locations for Run DH-10.

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Fig. 8.13. Zirconium Dummy Fuel Element and Thermocouples.

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Fig. 8.14. Element and Wall Temperatures During Dry Hydrofluorination Run DH-10.

Fig. 8.15. Off-gas Rate, Fraction Rate, and HF Utilization During Dry Hydrofluorination Run DH-10.

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A view of the partially reacted test element, as removed from the reactor, is given in Figure 8.16. The element surface was covered with a porous material having an ash-like appearance with the outline of the original test element. The material had the following composition:

	wt %
Ni	11.90
Sn	1.62
Zr	60.20
F	1.10
Fe	11.67
Cr	2.22
Si	0.77
Unidentified	10.52
	100.00

The partially reacted test element, after removal of the ash-like material, and an element having the dimensions of the original test element are shown in Figure 8.17. The weight of the remaining metal (124.6 g) indicated that 84.5% of the element had reacted. The remaining surface area was 0.165 sq ft.

The ZrF_4 reaction product (sublimation point $902^\circ C$) condensed in the unheated horizontal section of the reaction system. The material was crystalline and did not adhere to the walls of the system. The tap density was 3.08 g/cc (theoretical density of ZrF_4 is 4.43 g/cc).

Reaction rates, based on the initial element surface, and HF utilization were calculated from the off-gas data of Figure 8.15. Corrections were made for metering conditions, corrosion of the reactor, and inert initially in the system. The reaction rate and HF utilization varied between 8.9 to 2.7 mg/(min)(sq cm) and 68 to 23%, respectively. Average reaction rate and HF utilization were 5.6 mg/(min)(sq cm) and 44%, respectively. The reaction rate at the end of run DH-10, based on the surface area of the recovered zirconium, was 12.4 mg/(min)(sq cm). On the basis of the initial and final specific reaction rates, one may conclude that the reaction rate during the run, based on reacting surface, was 9-12 mg/(min)(sq cm).

The average reaction rate and HF utilization from run DH-10 may be compared to those of run DH-1 in which experimental conditions were identical except that reactor wall temperature was $950^\circ C$. For the first 84.5% of the hydrofluorination, average reaction rate and HF utilization were 3.75 mg/(min)(cm²) and 29.1%, respectively. Details of this experiment are given in UNOP December 1958 monthly report, ORNL CF 58-12-35.

Fig. 8.16. Partially Reacted Element and Reaction Product Coating.

ZIRCONIUM DUMMY
FUEL ELEMENT

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84.5 % REACTED
ZIRCONIUM ELEMENT

Fig. 8.17. Zirconium Dummy Element and Partially Reacted Element.

9.0 WASTE PROCESSING

M. E. Whatley

Reduction to Solids - C. W. Hancher, J. S. Taylor

The purpose of the waste processing program is to provide engineering data for design of a facility to reduce radioactive waste to solids for ultimate disposal. This report contains results of calculation tests with Purex, TBP-25, and Darex wastes containing chloride.

Calcination of Purex and TBP-25 Waste. Purex waste which had been evaporated to 40 per cent of its original weight was calcined at feed rates of 3.2 and 3.5 liters/hr in 8 and 6-in. diameter pots, respectively (Tables 9.1 and 9.2). The bulk densities of the calcined solids were 0.83 and 0.77 g/cc.

During the calcination period, as the temperature reached approximately 750°C a white powder appeared in the off-gas, coating surfaces of the condenser and gas bubbler. The white solid had the following composition: Fe - 16%, NO₃ - 12%, SO₄ - 42%. The solid was very hygroscopic as was the entire Purex calcined solid compared to Darex and TBP-25 solid wastes. Unless sulfate is eliminated from Purex waste, the calcination temperature may be limited to less than 750°C.

Four calcination runs using evaporated TBP-25 waste were completed, using the 8-in. diameter x 18 in. calciner pot. Four different concentrations of waste were used and the feed rates were varied from 1.5 to 8.7 liters/hr, but the densities of the calcined solid only varied from 0.40 to 0.45 g/cc, respectively (Table 9.1). It was difficult to pump the most concentrated 25 waste (49% of original volume) slowly even when the lines were steam-traced, because of the high freezing point of the waste (70-80°C).

A typical analysis of the off-gas from a TBP-25 calcination run (run 11-25) follows:

	<u>NO₂</u>	<u>HNO₃</u>	<u>O₂</u>	<u>N₂</u>	
Feeding	0.71	22.40	41.42	35.48	(mol %)
Calcining	12.51	24.11	14.54	48.94	(mol %)

The following decomposition and recombination reactions may account for the lack of nitric oxide (NO) in the off-gas:

Table 9.1. Per Cent Calcination of Purex and TBP-25 Waste

Run No.	Feed Conc. % of Original Waste by Weight ^a	Feed Rate (liters/hr)	Furnace Temp. During Feeding (°C)	Feeding Time (hr)	Calcining Time (hr)	Maximum Cake Temp. (°C)	Waste Volume Reduction ^b (%)	Power Usage Liters/kwh	Condensate Furnace Efficiency ^c	Calciner Diameter (in.)	Off-Gas Volume (liters)	Calcined Cake Analysis			
												NO ₃ (%)	SO ₄ (%)	H ₂ O (%)	Bulk Density (g/cc)
R-8-Purex	40	3.2	900-1000	10.0	4.0	930	10.8	0.30	20	8		0.18-0.36	1.48-1.72	1.02-1.45	0.83
R-9-Purex	40	3.5	900-1000	7.0	4.0		8.8	0.28	18	5		0.02-0.04	2.24-2.34	0.09-0.33	0.77
R-14-25	59	1.5	800-1100	22.25	4.75	1080	19.6	0.24	16	8					0.40
R-11-25	78	2.8	800-1000	9.0	3.5	900	21.0	0.26	17	8	1830				0.45
R-12-25	56	4.9	900-1000	7.0	3.5	900	16.6	0.35	23	8	1974				0.45
R-13-25	49	8.7	700-1000	3.0	7.0	900	24.6	0.36	24	8	2800 ^d				0.45

^aSee Table 9.2.^bBased on waste volume prior to evaporation.^cBased on 1000 Btu/lb condensate.^dExceeded 0.15 ft³/min (limit of ΔP CELL).

Table 9.2. Composition of
Purex and TBP-25 Wastes
(Before Evaporation)

<u>Purex Waste</u>	<u>Molar</u>
$\text{Fe}(\text{NO}_3)_3$	0.5
NaSO_4	0.15
H_2SO_4	0.60
HNO_3	5.5
<u>TBP-25 Waste</u>	<u>Molar</u>
$\text{Al}(\text{NO}_3)_3$	1.6
$\text{Hg}(\text{NO}_3)_2$	0.01
NH_4NO_3	0.03
HNO_3	0.5

Assuming there had been NO formed by nitrate decomposition, the time between sample collection and analysis was long enough for complete oxidation to NO₂ and nitrate.

Calcination of Darex Waste with Chloride. Darex waste, which had been evaporated to 27 per cent of its original weight, was spiked with varying amounts of HCl to produce solutions containing 175, 350, and 1750 ppm. A 200-ml quantity of the spiked waste was placed in a beaker and was calcined at 600-800°C. The off-gas was condensed and the noncondensable gases passed through two bubblers filled with 10 per cent NaOH and a third bubbler filled with 0.1 N AgNO₃ to detect as little as 1 ppm of Cl in the off-gas.

During the three tests the AgNO₃ bubbler concentration of Cl was always less than 1 ppm; therefore, it was assumed that all of the Cl was trapped in the system and could be accounted for. The Cl in the solid varied from 10 to 15 per cent (Table 9.3). The large percentage of Cl unaccounted for (23 to 35 per cent) may be due to the precision of analysis of aqueous chloride in the 1 to 100 ppm range which is 50 to 100 per cent.

An off-gas sample was taken after the three bubblers during the first test, and its chloride content was 0.01 micromoles/liter. This concentration times the total gas volume equalled only 0.02 per cent of the chloride in this test. Therefore, off-gas sampling was discontinued for tests 2 and 3. However, a significant quantity of chloride may have passed through the three bubblers, so better off-gas analyses will be sought.

The low retention of chloride in the calcined solids indicates that the off-gas treatment system (probably a distillation-scrubber tower) will have to be designed to concentrate and remove volatile chloride. The distillation equipment may either be operated under a vacuum to lower temperatures and corrosion rates if made of stainless steel or be constructed of titanium.

Table 9.3. Calcination of
Evaporated Waste Containing HCl

Run No.	Cl ⁻ in Feed, ppm	Cl ⁻ in Calcined Solid, %	Cl ⁻ in Condensate, %	Cl ⁻ in Caustic Trap, %	Cl ⁻ Unaccounted For, %
DC1-1	175	12	13	44	31
DC1-2	350	15	27	35	23
DC1-3	1750	10	17	38	35

Darex Evaporated Waste

(27% of original waste by wt)

Fe(NO ₃) ₃	1100 g/liter
Ni(NO ₃) ₂	80 g/liter
Cr(NO ₃) ₃	256 g/liter
Al(NO ₃) ₃	184 g/liter

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