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CHEMICAL TECHNOLOGY DIVISION
UNIT OPERATIONS SECTION
MONTHLY PROGRESS REPORT
FEBRUARY 1959

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UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT

February 1959

CHEMICAL TECHNOLOGY DIVISION

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JUN 11 1959

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Oak Ridge, Tennessee
Operated By
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for the
U. S. Atomic Energy Commission

ABSTRACT

A gamma scintillation spectrometer was used to measure diffusivity of uranyl nitrate in water during preliminary capillary experiments. During Fluorox run FBR-22, 90.4% of the theoretical amount of UF_6 formed was collected in cold traps and chemical traps. Toroid tests of flame calcined mixed Th-U oxide showed low corrosion rates, small changes in particle size and a low solubilization of uranium, while denitration of uranyl nitrate in a fluidized bed resulted in particle growth with uniform layers of uranium oxide. A half-time of 30 min for uranium anion exchange was measured in differential bed studies of uranium sorption on Dowex 21K. The Darex Reference flowsheet operation resulted in chloride removal to less than 50 ppm in solvent extraction feed from APPR head-end treatment. Unirradiated prototype Consolidated Edison pins were dejacketed with 6 M H_2SO_4 with uranium losses to the dejacketing solution of approximately 0.2%. An optimum procedure was developed for clarifying large batches of solvent extraction feed by sand bed filtration. Sheared sections of stainless steel clad UO_2 were completely leached in one-half the time required for equal lengths of stainless tubes containing uncrushed pellets. Abrasive disc wheel to metal removal ratios were measured at cutting rates from 10 to 60 in./min. Dissolution of Zircaloy-2 dummy fuel elements in an INOR-8 dissolver with the NaF-LiF salt system resulted in vessel wall corrosion rates of 1-2 mils/run (approximately 8 hr of HF exposure). At a heat generation rate of 60 Btu/hr/gal of solid wastes, the maximum temperature rise in a 0.75 ft radius infinite cylinder ($k = 0.1$ Btu/hr sq ft $^{\circ}F$) was 1270 $^{\circ}F$ in soil, 1150 $^{\circ}F$ in rock, and 1020 $^{\circ}F$ in salt.

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SUMMARY

1.0 CHEMICAL ENGINEERING RESEARCH

A modified diffusion cell was designed for use in the measurement of diffusional resistance of an interface. The new cell has no metal-to-glass seals which have given trouble with previous models.

A gamma scintillation spectrometer was found to be a very rapid, convenient and economical means of analyzing for enriched uranium in diffusion experiments. Preliminary capillary experiments indicate that the diffusivity of uranyl nitrate in water is approximately 0.6×10^{-6} cm²/sec.

2.0 FLUOROX

During run FBR-22, 90.4% of the theoretical amount of UF₆ formed was collected in cold traps and chemical traps with a UF₆ material balance of 99.2%. Corrosion rates on the Inconel reactor were 0.14 ipy in run FBR-21 and 0.29 ipy in run FBR-22.

3.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

Additional results have confirmed the production of spherical particles of Th-U-Al oxides by flame denitration of alcohol solutions. Toroid tests of mixed Th-U oxides showed relatively low corrosion rates (about 3.4 mpy for 200 g Th-U/kg H₂O, O₂ atmosphere, stainless steel coupons), small changes in particle size, and low solubilization of uranium. These mixed oxides also had relatively high yield stresses of 0.45 to 0.94 lb/sq ft and surface areas of 2 to 3 sq m/g.

Denitration of uranyl nitrate in a fluidized bed gave particle growth with uniform layers of uranium oxides. An agitated trough calciner was operated to produce 50-500 micron ThO₂ particles. Installation of equipment to test the electrolytic removal of nickel from fuel solution was partially completed.

4.0 ION EXCHANGE

Several differential studies of the uranium sorption rate on Dowex 21K were completed. Two of the first runs gave the following results. Using approximately 1000 micron resin beads, a superficial flow rate of 1.2 cm/sec, and a uranium solution 0.005 M in uranium, the resin bed became half loading in 30 min. Performance of the experimental equipment was generally satisfactory.

A method was developed for studying the rate of sorption by analysis of the enriched uranium within individual beads as a function of time.

5.0 POWER REACTOR FUEL REPROCESSING

5.1 Darex

In continued 10-liter scale chloride removal tests, it was shown that air sparging was required to assure chloride removal by the Reflux flow-sheet to less than 350 ppm. Reproducibility runs without air sparging gave chloride removals to 351, 510, 590, and 320 ppm.

Reference flowsheet runs in which recycle HNO_3 was continuously added during the first mixed acid withdrawal step gave chloride removal to less than 50 ppm in the solvent extraction feed.

Heavily oxidized unirradiated stainless steel uranium plate type fuel assemblies were dissolved in approximately 20 min similarly to unoxidized fuel. Braze metal and oxide scale was only slightly attacked. During dissolution, foam heights of up to seven feet were attained. Dissolution rates of from 272 g/min to 278 g/min were measured in dissolvents with the composition range: 3-4 M H^+ , 1.7-2.0 M Cl^- , 1-2.6 M NO_3^- , 50-75 g SS/liter, and 5-9 g U/liter to which 5-2 aqua regia was added continuously at 4.2-4.5 liters/min.

5.2 Sulfex

Unirradiated prototype Consolidated Edison pins were dejacketed with 6 M H_2SO_4 with initial rates of 8-11 mg/cm²/min. Uranium losses to the dejacketing solution were approximately 0.2%. Addition of 0.25 M CdSO_4 and H_3BO_3 to sulfuric acid reduced the decladding rates by 20%. Batch core dissolution of the declad pellets in 13 M HNO_3 , 0.04 M F^- , and 0.04 M Al^{+++} required 16 hr at a volume ratio of 3.45 ml acid/g pellets.

5.3 Feed Clarification

An optimum procedure was developed for clarifying 300-liter batches of Darex solvent extraction feed solution of siliceous impurities using sand bed filter of limited area (approximately 1 sq ft) which involves: (a) precipitation and sedimentation of a flocculent silica-gelatin polymer, in situ, (b) addition of approximately 10 g/liter of filter aid, (c) filtration of the clear supernatant liquor followed by the thickened slurry under 5-in. Hg vacuum or 5-ft gross head. The filter cake 8 to 9 in. thick can be freed of uranium by 3-4 six gal washes with 0.05 M HNO_3 . The filter cycle requires from 2-5 hr depending primarily on the filtration rate obtained for the approximate 200 liters of supernate.

5.4 Solvent Extraction Studies

There was no effect of aqueous phase concentration on HETS in Redox solvent extraction runs where the over-all value of HETS was 2 ft or less. For larger over-all values of HETS, the "point" values varied from 1-4 ft.

5.5 Mechanical Processing

Core Leaching. Unirradiated stainless steel clad (304 L) UO_2 sheared into 1-1/2 in. lengths were completely leached free of UO_2 in 10 M acid in approximately one-half (22-25 min) the time required for equal lengths of stainless steel tubes containing uncrushed pellets. Decreasing the sheared length to 1/2 in. portions in a single run showed no significant decrease in leach time over that for 1-1/2 in. sheared lengths.

SRE Decanning. High pressure steam cleaning of a mineral oil and NaK coated uranium slug removed oil and NaK adequately to permit safe recanning of the slug in air.

Abrasive Sawing. A cutting rate of 10 in./min with a 16-in. diameter Manhattan 239 abrasion disc (10,770 surface feed per minute) cutting 0.5-in. diameter stainless steel rod gave a wheel to metal removal ratio of 1-6 (by volume). A decrease in ratio to 1/3 resulted when a cutting feed rate of 60 in./min was used. Approximately 4,500 cuts at a 1/6 ratio would halve the blade diameter. Stainless steel clad porcelain could not be cut successfully with a 24-in. abrasion disc at 11,000 surface feet per minute.

Shearing. Shearing of an entire prototype fuel bundle, 36 tube (stainless clad porcelain filled) sixty-five times at 0.3 in./sec with a 125-ton hydraulic Manco shear increased the average clearance between the "line of contact" blades from 2 mils to 18 mils, but this clearance change may have been caused by the natural displacement of the piston at its extended position. Despite the increase in clearance, the efficiency of shearing appeared to be unchanged.

Shearing of stainless steel clad UO_2 single tubes (thermal cycled five times from 20°C to 550°C) at 0.5 in./sec dislodged as much UO_2 (29%) from the sheared face as non-heat-treated specimens. In both case, 50% of the UO_2 dislodged was 150 microns in diameter or less.

Ferrule Splitting. Several unirradiated prototype Consolidated Edison fuel bundles made with solid rod stock were successfully disassembled into slabs by forcing a wedge between the layers of rods and rupturing the Microbrazed 50 bond between ferrules and rods.

6.0 VOLATILITY

Dissolution of Zircaloy-2 dummy fuel elements in a vessel constructed of INOR-8 and using the NaF-LiF salt system resulted in corrosion rates of the vessel wall at the gas-salt interface averaging about 1-2 mils/run (approximately 8 hr of HF exposure). Dissolution rates were about 0.2 lb/(hr)(sq ft), with an average HF utilization of 40%. Entrainment of unidentified solids in the off-gas was severe.

In the fused salt hydrofluorination of zirconium sub-assemblies, the section not submerged in fused salt will be exposed to a mixture of hydrogen and anhydrous hydrogen fluoride. The reaction rate under these conditions is being studied in the temperature range of 400-750°C. Two preliminary tests were made of this reaction, one at an initial temperature of 700°C and the other at 750°C. The hydrofluorination reaction under these conditions can be carried to completion but rate data were not obtained because of problems in metering the mixed gases.

7.0 WASTE PROCESSING

A sample of simulated Darex waste was evaporated in an experiment to determine the concentration of acid as a function of volume reduction. When 77% of the volume of the feed had been removed, all the free acid had been removed. The removal of an additional 10% of the volume produced an acid-deficient concentrate. Three calcination runs were made with Darex waste in an 8-in. calciner pot. Excessive entrainment occurred in two runs, but the material balance on the third accounted for 93% of the iron in the feed. The calcined cake was 7% of the original Darex waste volume.

Maximum temperature rise was calculated in an infinitely long cylinder of radioactive solid insulated from an infinite solid medium by an air space. For equal total heat generation rates but varying fission product distributions, the differences in maximum temperature rise were less than 3% between one- and three-year cooled waste and less than 7% between one- and ten-year cooled waste. At a heat generation rate of 60 Btu/(hr)(gal solid), maximum temperature rise in a 0.75 ft radius cylinder ($k = 0.1$ Btu/hr ft °F) was 1270°F in "average soil", 1150°F in "average rock" and 1020°F in salt.

1.0 CHEMICAL ENGINEERING RESEARCH

M. E. Whatley

1.1 A Modified Diffusion Cell for the Measurement of Resistance at an Interface - C. V. Chester

A program is underway to measure the resistance to diffusion at the aqueous organic interface in the Purex system. One technique being tried is to measure a steady-state concentration gradient across the interface by photographic techniques. In order to construct the gradient, a special diffusion cell was designed with provision for supplying uranyl nitrate at the aqueous side and fresh TBP at the organic side. Earlier models of the cell were unsatisfactory due to leaks.

A new cell model was designed which should circumvent the difficulties of the previous cells. The new cell shown in section in Figure 1.1 has no stresses to distort the disc and has no metal-to glass seals. All seals are metal-to-teflon or teflon-to-glass. The core of the cell is a teflon sheet held between two glass plates. The required diffusion column and chambers are cut into the teflon core. Access to the chambers in the cell is through holes drilled in one of the glass plates. The cell core and glass plates are held together between two flanges which are compressed by means of six cap screws about the periphery. In the lower flange are fittings to bring the capillary tubing to the cell and make seal between the tubing ends and teflon gasket on the lower cover plate.

The pressure between the glass and the cell can be regulated by adjusting the torque on the peripheral cap screws. The pressure between the tubing connectors and the lower gasket can be adjusted by tightening the compression screws. In earlier models the tubing fittings were brought in to the circumference of the cell. When pressure was applied to seal the fittings, the cell was distorted and the seal between the cover glass and the cell destroyed. In this model the pressure applied by the compression screws is added to the pressure maintaining the seal between the cell and the cover glasses.

In Figure 1.1, section "A-A" shows the cell details. The arrangement of holes and chambers is similar to that of previous models. This cell differs from previous models in that the standard cells have no common sump. They will be filled by first evacuating them and then permitting the desired standard solution to fill them. By elimination of the common sump the necessity for continually applying fresh standard solution to the standard cells is eliminated and with this also are six feed tubes.

The column and equilibrium cell have hydrophillic stainless steel inserts in the aqueous portion, to control the interface by maintaining the interface at the boundary of the hydrophillic insert and a hydrophobic teflon cell wall. A flat interface can be obtained which will not distort the light passing through the cell for the photograph of the concentration gradient.

SECTION B-B

SECTION A-A
CELL ARRANGEMENT

1"

Fig.11. Compression seal diffusion cell.

1.2 Measurements of the Diffusivity of Uranyl Nitrate Using a Scintillation Spectrometer

To supplement measurements of diffusion at an interface, a series of measurements of diffusivity of uranyl nitrate in aqueous and organic solutions are being made. A convenient method of performing these measurements is the use of a convenient geometry such as that of a capillary tube, or in the case of ion exchange resins, a sphere, and following the diffusion of the uranium by a scintillation gamma counter. Counting a capillary tube or a resin bead for the uranium gamma is a very convenient method of analysis. There is often a high uranium background in many radiochemical laboratories, and there are also gamma peaks of many uranium daughters in any uranium sample. By using a spectrometer, a desired gamma peak can be examined and counted which corresponds to the uranium concentration in the object to be analyzed for uranium.

The Spectrometer - The pickup of the spectrometer is a deep well sodium iodide crystal mounted on a Dumont 6292 photomultiplier. The signal from the photomultiplier is preamplified and transmitted to a DD-2 linear amplifier equipped with a pulse height selector and an adjustable "window." The pulse height selection is varied by a small rheostat geared to the drive of a Brown recorder. Thus, a spectrogram can be traced on a Brown chart by having the Brown potentiometer connected to a count rate meter. The count rate meter is connected to the output of the DD-2 amplifier.

Figures 1.2 and 1.3 are spectrograms of natural and enriched uranium obtained by this setup. Figure 1.2 is a trace of natural uranium obtained with a gain of 20 and a slit width of half a volt. The energy scale is plotted on the abscissa, with a calibration point obtained by counting a source of cesium-137 of known energy. The low peak around 0.19 mev is from the U-235 in natural uranium. The sharp peak around 0.1 mev is due to the thorium-234 which exists in 25-day equilibrium with the uranium-238. Figure 1.3 is a trace of 92% enriched uranium with the same energy scale as in Figure 1.2. The very high peak at 0.19 mev is due to the decay of uranium-235. There are lesser peaks due to daughters of uranium-235 and probably also uranium-238. The relatively high specific activity of uranium-235 makes it possible to analyze for very small amounts of uranium in the diffusion system. As small as one milligram of uranium-235 will provide a count rate in excess of a hundred counts per min, which is a quantity that might be expected in the analysis of the uranium in a single resin bead.

Capillary Measurements - To measure the diffusivity of uranyl nitrate in aqueous solutions, a series of capillary tubes were filled with aqueous uranyl nitrate of the desired concentration (about 1 M in the first experiment) and were immersed in a bath of flowing demineralized water. After successive increments of several hours, the capillaries were removed from the bath and counted for uranium activity. By plotting the fraction of activity leaving the capillary against the time divided by the square of the length of the capillary, a roughly linear plot with a slope of $1/2$ can be obtained on log log paper. The coefficient of the time term is proportional to the integral diffusivity of the material being counted.

Fig.1.2. Gamma Spectrum of Natural Uranium.

Fig.1.3. Gamma Spectrum of 92% Enriched Uranium.

Preliminary experiments were carried out with natural uranium. The results of the experiments are shown in Figure 1.4. Deviations at the low end of the plot should be noted. This deviation may be due to the fact that thorium-234 was being counted rather than the uranium-238. The most probable value of the integral diffusivity of uranium from this series of preliminary experiments was about 0.6×10^{-6} cm²/sec.

Fig. 1.4. Fraction $\text{UO}_2(\text{NO}_3)_2$ Extracted vs Reduced Time

2.0 FLUOROX

R. W. Horton

The Fluorox program is the engineering development of processes which produce UF_6 without the use of elemental fluorine. The process under study at present is the oxidation of UF_4 with oxygen, $2\text{UF}_4 + \text{O}_2 = \text{UO}_2\text{F}_2 + \text{UF}_6$, with subsequent recycle of the UO_2F_2 .

2.1 Fluidized Bed Development - C. D. Scott, W. G. Sisson

The UF_4 oxidation process is being 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 800-850°C. The UF_6 which is produced is removed in the off-gas stream and is subsequently recovered in cold traps.

Run FBR-22. Run FBR-22 which lasted for 58.4 hr was made to test the reliability of the experimental equipment over a long period of time and to give additional operating data which could be used in a possible scale-up of equipment. Complete analytical results are available, and the run was evaluated in the same manner which was used in previous runs.

The over-all material balance of all reactor streams entering and leaving was 99.4% (material leaving/material entering) with an over-all uranium material balance of 99.0% (see Table 2.1 and Figure 2.1). The apparent loss of 528 g of material and 659 g of uranium can be partially accounted for by UF_6 losses through the Condensation Pressure Analyzer off-gas system. (UF_6 vapor was observed in the vacuum pump off-gas.)

The UF_6 balance was 99.2% complete (see Figure 2.2) with 90.4% of the theoretical amount of UF_6 formed being collected in cold traps and chemical traps. 8.8% of the UF_6 formed was consumed in side reactions: 2.3% reacted with UF_4 to form U_4F_{17} ; 2.2% reacted with reactor and thermowell walls to form corrosion products; 0.5% reacted with the uranium oxides introduced with the feed; and 3.8% reacted with the water introduced with the feed. The 90.4% UF_6 collected in cold traps and chemical traps was the highest recovery of all runs to date.

Apparent reaction rate constants were determined for three periods of reactor operation in which average bed temperatures of 812, 813 and 817°C were maintained (see Figure 2.3). The rate constants, 6.7 hr^{-1} , 8.5 hr^{-1} , and 11.3 hr^{-1} , respectively, check favorably with previous fluidized bed runs.

A significant amount of U_4F_{17} was formed and recovered in the lower part of the filter section in the reactor. The accumulation of solids in the upper part of the reactor caused a pressure buildup during the latter part of the run. The majority of the U_4F_{17} formation was during the last

Table 2.1. Change in Amounts of
Individual Compounds in Run FBR-22

Compound	<u>Entering Reactor, g</u>		<u>Leaving Reactor, g</u>		<u>Change, g</u>	
	Total	Uranium	Total	Uranium	Total	Uranium
UF ₄	80,802	61,248	8,627	6,539	-72,175	-54,709
UO ₂ F ₂	8,554	6,610	43,102	33,305	+35,548	+26,695
UO ₂	264	233	0	0	-264	-233
U ₃ O ₈	6	5	0	0	-6	-5
U ₄ F ₁₇	0	0	6,352	4,739	+6,352	+4,739
UF ₆	0	0	33,803	22,858	+33,803	+22,854
Metal F	30	0	556	0	+526	0
H ₂ O	144	0	0	0	-144	0
O ₂ *	3,488	0	0	0	-3,488	0
HF**	0	0	320	0	+320	0
Totals	93,288	68,096	92,760	67,437	-528	-659

*The amount of O₂ entering the reactor was calculated to be the theoretical amount necessary for oxidation in the various reactions occurring.

**The amount of HF leaving the reactor was calculated to be the theoretical amount which resulted from the hydrolysis of UF₆.

Over-all material balance (material leaving/material entering) = 99.4%.

Over-all uranium material balance (uranium leaving/uranium entering) = 99.0%.

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Fig. 2.1. Material Balance of the Constituents of Each Stream from Run FBR-22.

Fig.2.2. Disposition of UF_6 Which was Formed in Run FBR-22.

13.3 HOURS OF OPERATION AT AN
AVERAGE BED TEMPERATURE OF $812^{\circ}C$.

13.5 HOURS OF OPERATION AT AN
AVERAGE BED TEMPERATURE OF $813^{\circ}C$.

22.7 HOURS OF OPERATION AT AN
AVERAGE BED TEMPERATURE OF $817^{\circ}C$.

REACTION RATE CONSTANT,

$$k = \frac{1472g/hr}{221g} = 6.7 \text{ hr}^{-1}$$

REACTION RATE CONSTANT,

$$k = \frac{1484g/hr}{174g} = 8.5 \text{ hr}^{-1}$$

REACTION RATE CONSTANT,

$$k = \frac{1490g/hr}{132g} = 11.3 \text{ hr}^{-1}$$

Fig. 2.3. Apparent Reaction Rate Constants for Three Periods of Run FBR-22.

few hours of operation when there was a static bed of high UF_4 content at a high temperature. A failure of the powder feeding system occurred at the time of a forced shutdown due to a broken solids discharge line, resulting in abnormally high UF_4 feed rates with insufficient bed agitation. The run was terminated shortly after these occurrences.

Two UF_6 samples were submitted for chemical and spectrographic analysis. The following impurities were found:

Sample No.	Impurities, ppm							Total
	Al	Ca	Cr	Cu	Fe	Mg	Ni	
X-25	10	15	20	8	125	16	45	239
X-38	5	11	12	3	95	11	55	192

A UF_6 sample was also submitted to the Oak Ridge Gaseous Diffusion Plant for specification analysis.

Inconel corrosion coupons were attached to the thermowell during run FBR-22 in three positions: gas phase, interface, and in the fluid bed. The coupons will be checked for the type and amount of corrosion.

Corrosion Rates in FBR-21 and FBR-22. Apparent corrosion rates of the Inconel reactor were determined at steady-state operating conditions during runs FBR-21 and FBR-22. It was assumed that (1) corrosion occurred only in the fluid bed area of the reactor and (2) at steady-state operation, the corrosion products in the overflow and cold traps represented the only corrosion taking place. On this basis, the apparent corrosion rates at $8100 \pm 15^\circ C$, based on a 360-day year, were: Run FBR-21 - 0.145 ipy and Run FBR-22 - 0.289 ipy.

2.2 Allied UF_4 Run - C. D. Scott, D. H. Newman, L. M. Ferris (Chemical Development Section B)

The fluidized bed reactor system is being prepared for a run in which crude UF_4 (produced from unpurified mill concentrate) will be used as the feed. Approximately 100 lb of such a material was received from Allied Chemical Corporation.

Initial tests indicate that this impure material has a melting point of $730-740^\circ C$ and appreciable sintering occurs at $690-700^\circ C$. The low melting point will necessitate a fluid bed temperature less than $730^\circ C$ with the resulting decrease in reaction rate. Further tests will be made on the crude UF_4 mixed with UO_2F_2 .

3.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

P. A. Haas

Process and equipment development studies are necessary for the preparation and processing of aqueous homogeneous reactor fuel and blanket fluids. These studies include direct denitration of thorium and/or uranium nitrates in high temperature flames to prepare less than 20 micron dia material or denitration in mechanically agitated or fluidized beds to prepare over 50 micron dia material. Other engineering studies include those required for electrolytic removal of nickel from fuel solution, for high capacity hydroclone processing of fuel solution, and for special hydroclone classifications of ThO_2 .

3.1 Flame Calcination Experiments - C. C. Haws, Jr., V. L. Fowler

An electron shadow-graph showed that rounded particulates were obtained from the firing of a thorium-uranium system containing 5 wt per cent alumina at 1400°C (see Figure 3.1). This observation confirms the spheroidizing effect first reported last month for a 10 wt per cent alumina system. Further tests have been run at alumina concentrations of 2.5, 5.0, and 10 wt per cent at temperatures above 1500°C . Aqueous feed solutions produced rounded shapes at temperature below 1000°C . Results from these latter tests are not yet available.

Corrosion rates, particle degradation and uranium solubility of flame-fired slurries were measured by toroid tests (see Table 3.1). Corrosion rates for the flame fired material were the same as those obtained for the 1050°C fired production material. For SS 347, this rate ranged from 2.7 to 7.0 mils/yr (mpy) under oxygen overpressure. Particle degradation appeared to be slight under oxygen but particle growth was experienced under deuterium. Uranium solubility in the supernate was below the limits of detectability for three of the four samples under deuterium, and low under oxygen for the same samples. Run 39 product appeared normal with respect to corrosion and particle degradation, but uranium solubility was high. The high uranium solubility of this one sample has not been explained.

Analytical results (Table 3.2) showed high values for yield stress and surface area for flame calcined mixed Th-U oxides. Yield stresses lying between 0.45 and 0.94 lb/sq ft were obtained. Surface areas ranged from 6-8 sq m/g. Equivalent values for similar furnace fired materials are 0.2-0.3 lb/sq ft and 2-3 sq m/g, respectively. Flame and furnace fired products appear equal in all other respects.

3.2 Fluidized Bed Denitration - S. D. Clinton, R. D. Arthur

A 7-hr run was made to duplicate the denitration of UNH in a fluidized bed reported by Argonne National Laboratory (see ANL-5363, 1954).

Fig. 3.1. Flame Calcination Experiments: Flame Fired Mixed U-Th Oxides Containing 5 wt % Alumina.

Table 3.1. Flame Calcining Experiments

Toroid Results on Th-U Mixed Oxides

Toroid Test Conditions:

Operating Temperature	280°C
Exposure Time	300 hr
Velocity	26 fps
Concentration	200 g Th-U/kg D ₂ O

Run No.	Average Particle Size, micron		Atmosphere	Corrosion Rate, mpy				U Loss to Supernate, g/ml	U/Th Ratio
	Pre-Run	Post Run		347SS	Ti-75A	Inconel	Zr-2		
35	1.0	1.2	O ₂	6.9	0	12.3	0.2	< 2	0.058
	1.0	2.0	D ₂	11	1.0	1.5	0.4	< 2	
36	1.5	1.3	O ₂	7.0	1.1	22	0	5	
	1.5	5.4	D ₂	14	1.6	2.4	0.5	< 2	0.075
39C ^a	1.5	0.7	O ₂	3.2	1.6	21	0.2	29	
39RC	1.0	1.0	O ₂	6.3	1.6	35	0.3	84	0.076
45	0.6	1.0	O ₂	2.7	1.5	17	+	3	
	0.6	1.0	D ₂	0.8	1.1	0.2	0.2	< 2	0.077

a. Run 34 product was classified to $d_{50} = 1.5\mu$ (39C); reclassified (39RC) to $d_{50} = 1.0\mu$.

Table 3.2. Flame Calcining Experiments
Analytical Results Th-U Mixed Oxides

Run No.	Reflector Temp., °C	Average Particle Size, μ	Yield Stress, lb/sq ft	Surface Area, sq m/g
46	1000	1.7	0.94*	7.6
47	800	2.2	0.45*	6.5
48	1440	2.5	0.8	6.2
49	1220	1.8	0.675	7.7
50	1425	1.7	-	7.7
51	1200	1.6	-	7.8
52	1425	1.5	-	2.0
53	1400	1.8	0.196*	5.7

*These values corrected to a density of 2, from a lower sample density.

This run was a test of equipment designed and installed for fluidized bed denitration of $\text{Th}(\text{NO}_3)_4$. During the run, 7.2 liters of a 2.5 M $\text{UO}_2(\text{NO}_3)_2$ aqueous solution was sprayed into a fluidized bed initially filled with sand (particle size 150-250 microns). The temperature of the bed was between 390 and 400°C, and the temperature gradient from the bottom to the top of the bed varied between +4 and +8°C. A superficial fluidizing air velocity of 1.3 to 1.4 ft/sec was maintained throughout the run. The pressure drop across the metallic bayonet filters cycled between a minimum of 3 and a maximum of 8 in. of Hg. In order to remain within this pressure drop range, the filters were blown back every 25 min.

There was no caking in the bed as indicated by temperature and pressure measurements. A 300-400 g bed sample was removed hourly through the 1/2 in. sch. 40 classifier line (see Unit Operations October monthly report, ORNL-CF-58-10-90), and the entire reactor contents was withdrawn by gravity flow through the 1/2 in. line at the end of the run. The total weight of material removed from the reactor was 8260 g of which 5180 g was UO_3 . This material was screen classified and chemically analyzed (Table 3.3).

Table 3.3. Product of Fluidized Bed UNH Denitration

Particle Size, microns	Wt % of Bed	Wt % of UO_3 in Bed	Wt % of SiO_2 in Bed
< 53	4.0	6.0	0.3
53-149	9.7	11.3	6.6
150-250	38.6	32.4	50.0
251-500	29.6	30.5	28.0
501-840	8.7	9.8	6.9
> 840	9.4	10.0	8.2

The results of sedimentation size analyses are not yet available. The UO_3 produced contained 0.26 wt per cent NO_3 .

3.3 Agitated Trough Denitration - S. D. Clinton, R. D. Arthur

Preliminary tests were made with an agitated trough calciner (see Figure 3.2) for preparation of 50-500 micron dia ThO_2 . A 1 M TNT aqueous solution was pumped into an agitated ThO_2 bed (size range < 50 microns) at a feed rate of 15 to 20 ml/min over a time interval of 8 hr. The agitated bed temperature in the vicinity of the nitrate injection line was controlled between 200 and 250°C with no evidence of bed caking. The major portion of ThO_2 removed from the trough was in the size range of 300-800 microns, but the individual particles appeared very porous. Further testing of the trough calciner is planned.

Fig.3.2. Agitated Trough Calciner For Denitration Studies

3.4 Electrolytic Removal of Nickel - E. L. Youngblood

Construction has begun on a test unit for the removal of nickel from HRT fuel solution using an electrolytic method developed by Laboratory Section A. The equipment was designed for removing nickel from approximately 30-gal batches of simulated fuel solution. The nickel will be removed by circulating the solution through an electrolytic cell operating at up to 25 volts and 400 amperes where the nickel forms an amalgam with the mercury cathode of the cell. The hydrogen and oxygen produced in the cell are diluted below the explosive limits with air before being discharged.

A regeneration system for periodic removal of the nickel from the mercury cathode will also be tested. The regeneration step will be done by draining and washing (with water distilled from the fuel solution) the fuel solution from the cell to remove most of the uranium and heavy water. An acid solution in light water will then be circulated through the cell while the polarity of the electrodes are reversed in order to put the nickel back in solution. The light water solution containing the nickel can be discarded after the regeneration step.

While the system is designed for removal of nickel from heavy water solutions, the use of light water solutions is planned for the initial tests with subsequent runs using heavy water. The installation of the HRT-CPP test nickel removal system is scheduled for completion in March.

3.5 Hydroclone Classification of Thorium Oxide - E. L. Youngblood, D. H. Newman

A 40.6 kg batch of IO-42 thorium oxide was passed through a 0.5 in. dia hydroclone in order to enrich the overflow stream in small particles (< .5 microns). Recovery in the product was over 60% of the below 0.6 micron dia material and about 6% of the over 1 micron material.

The hydroclone was operated at a feed pressure of 60 psi and a slurry temperature of 80°C in order to lower the hydroclone classification range. The feed slurry was prepared by adding 7 kg quantities of ThO₂ to 200 liters of demineralized water to which oxalic acid had been added as a dispersing agent. The underflow from the first pass was passed a second time through the hydroclone to recover additional fine particles. A total of 4.9 kg of overflow material enriched in fine particles was produced.

After the hydroclone classification, both the overflow and underflow fractions were centrifuged and then fired to 600°C to decompose the oxalic acid. The particle size distribution of a composite sample of the original feed and the overflow product shown in Figure 3.3 indicates an enrichment from about 4.4% to about 23% in thorium oxide particles below 0.6 microns. These results compare favorably with previous runs using Batch IO-42 thorium oxide (see Unit Operations January monthly progress report, ORNL CF 59-1-74).

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Fig. 3.3. Particle Size Distribution of Thorium Oxide Feed and Overflow from a 0.5-in. Diameter Hydroclone.

4.0 ION EXCHANGE

M. E. Whatley

Mechanism and Kinetic Studies - J. S. Watson

In order 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 an effort is being made to determine the equilibrium sorption isotherms and rates of sorption of uranium on Dowex 21K.

Differential bed rate studies were begun to determine the rate of sorption of uranium on Dowex 21K from sulfate solutions. For simplicity, the resin was first converted to the sulfate form with a solution having the same pH as the uranium loading solution. The apparatus and procedure were described in the Unit Operations monthly progress report for January, ORNL CF 59-1-74.

The results obtained from runs 2 and 3 have been tabulated and are shown in Figures 4.1 and 4.2. The concentration of uranium in the effluent stream is shown as a function of time. The curves and the points from which they are drawn were calculated from the readings of a colorimeter.

In Figure 4.1, the blocks of shaded area represent potentiometric analyses of the solution leaving the bed. Since each sample was taken during a finite period of time, these results essentially integrate the curve over the time interval during which the sample was taken. Very good agreement was obtained between the colorimeter results and the analyses for run 2. However, agreement was not obtained in run 3, and these results are being checked.

There is some uncertainty in the colorimeter curves during the first 20 sec of the run while the flow had not become stable, and the colorimeter chart usually showed some fluctuations. In order to obtain adequate response time for recording the transient at the start of the runs, a Sanborn recorder was used in place of the Brown for runs after No. 4.

The differences between the feed composition and the values recorded in Figures 4.1 and 4.2 are multiplied by the flow rate to give the rate at which uranium is being sorbed on the resin bed. The results of such calculations are shown in Figures 4.3 and 4.4. In run 2 there were small drifts in the flow rate, so at each point the instantaneous flow rate was used to calculate the sorption rate. The flow in run 3 was essentially constant.

The same bed of resin was used in both of these runs. When in the sulfate form, the resin beads were 1034 ± 72 microns in diameter. Between

Fig. 4.1. Results from Differential Bed Run No. 2 .

Fig. 4.2. Results from Differential Bed Run No. 3.

Fig. 4.3. Rate of Uranium Sorption in Differential Bed Run No. 2.

Fig. 4.4. Rate of Uranium Sorption in Differential Bed Run No. 3.

each run, the resin was eluted with 2 liters of 1 N NaCl solution, and then converted back to the sulfate form with 2 liters of 1 N Na₂SO₄ solution. The dry weight of resin in the bed was approximately 3 g.

One inherent difficulty arises in the use of such a differential bed. For the bed to appear truly "differential", only a small change in the solution concentration can occur across the bed. However, this change in concentration is the measure of the sorption rate. Therefore, attempts to make the bed approach "differential" conditions sacrifice accuracy in the rate measurements.

As a supplement to the differential bed studies, a method of sampling the resin beads from a stirred container at various times is being considered. This technique would yield sorption rates without the above limitation. If enriched uranium is used, enough activity for a uranium analysis by gamma counting can probably be obtained in 1 or 2 resin beads, which would allow the use of a very small quantity of beads. Also the diameter of each bead analyzed could be measured, and the uncertainties caused by size distributions in any batch of beads could be eliminated.

There are two limitations in the proposed system. In a simple mixer it would be difficult to remove a bead seconds after the run was started and have any knowledge of the flow field in which it had been contacted with the uranium solution. For this reason, these studies would be valuable primarily at moderately long contact times when particle diffusion controls the sorption rate. Also it is possible that differences between single beads would introduce some randomness in the data which could not be detected when samples of hundreds of beads are used.

5.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

5.1 Darex - B. C. Finney, F. G. Kitts, J. Beams, R. C. Early

The purpose of the Darex process is to convert SS-U and SS-UO₂ fuels into chloride-free nitrate solutions suitable for processing in existing stainless steel solvent extraction equipment. Chloride is necessary to effect dissolution of stainless steel in HNO₃ but it must be removed to avoid corrosion of process equipment. The purpose of the present investigation is to develop a batch flowsheet in which dissolution product is treated with 61 wt per cent HNO₃ to produce solvent extraction feed containing < 350 ppm chloride.

5.1.1 Flowsheet Development, Chloride Removal and Feed Adjustment

Seven batchwise Reflux runs were made in the 4-in. equipment using a standard Reflux flowsheet with an updraft condenser (see Table 5.1). Runs APPR-42, 43 and 44 were made to determine the effect of air sparge rate during the reflux step. An identical run (No. 47) was made to check the results of run 44. These runs showed that increasing the sparge rate had some beneficial effect but sparging might not be necessary to reach 350 ppm chloride.

Three runs (48, 49 and 50) were made to check the reproducibility of run 43 made without an air sparge. Chloride removal was to 351, 510, 590 and 320 ppm for runs 43, 48, 49 and 50, respectively. The Cl⁻ in the acidified concentrate (column 16) was ~ 0.8 M for runs 43, 48 and 49, and 0.62 M for run 50; this fact might account for the acceptable result of 320 ppm obtained in run 50 but it does not account for the 351 ppm result in run 43. On the other hand the high HNO₃ in the acidified concentrate (column 15) of run 48 should have produced a lower Cl⁻ content in the finished product, yet the final result was 510 ppm.

It must be concluded from these four runs that Cl⁻ removal to < 350 ppm cannot be assured without the use of an air sparge. However, the optimum amount of sparge required for maximum chloride removal in this equipment will not be determined in the present apparatus since some different amount would be required in a pilot plant. There is an apparent dependence of chloride removal by sparging on equipment size and characteristics.

Runs APPR-45 and 46 were laboratory scale flowsheet studies based on data reported last month as exploratory run APPR-29. These two runs differ in that a continuous HNO₃ addition was used during the withdrawal of the first mixed acid cut. In run 45, 13.3 M HNO₃ was used as the first addition and 12.2 M HNO₃ was recovered as the second mixed acid cut (columns 18 and 19). In run 46, 12.2 M HNO₃ was used and 12.0 M was regenerated

Table 5.1. Data of Batchwise Reflux Runs Using 61 wt % HNO₃

Run No.	Air Sparge	Condenser	Dissolution Product			Acid Waste			Add 13.3 M HNO ₃ (l)	1st Mixed Acid			Add 13.3 M HNO ₃ (l)	Acidified Concentrate			Reflux Time Hours	2nd Mixed Acid (Trace Cl ⁻)		Solvent Extraction Feed		
			Vol (l)	H ⁺ M	Cl ⁻ M	Vol (l)	H ⁺ M	Cl ⁻ M		Vol (l)	H ⁺ M	Cl ⁻ M		Vol (l)	HNO ₃ M	Cl ⁻ M		Vol (l)	HNO ₃ M	Vol (l)	HNO ₃ M	Cl ⁻ ppm
44	2 l/min reflux*	Updraft	10.0	2.92	1.75	2.0	0.75	0.25	1.8	7.5	5.95	1.70	4.0	~6.1	9.36	0.58	2	1.8	10.7	11.5	2.92	200
47	2 l/min reflux*	Updraft	10.0	2.92	1.75	2.0	0.65	0.25	1.8	7.5	5.55	1.45	4.0	~6.1	9.21	0.56	2	1.9	10.9	11.5	2.87	225
42	1 l/min reflux*	Updraft	10.0	2.92	1.75	2.0	0.60	0.25	1.8	7.5	5.70	1.53	4.0	~6.1	8.97	0.80	2	2.0	10.2	11.5	2.8	309
43	None	Updraft	10.0	2.92	1.75	2.0	0.67	0.20	1.8	7.5	5.70	1.55	4.0	~6.1	8.88	0.83	2	1.9	10.8	11.5	3.1	351
48	None	Updraft	10.0	2.92	1.75	2.0	0.70	0.25	1.8	7.5	5.80	1.45	4.0	~6.1	9.26	0.82	2	1.9	10.7	11.5	2.9	510
49	None	Updraft	10.0	2.92	1.75	2.0	0.70	0.25	1.8	7.5	5.70	1.50	4.0	~6.1	8.98	0.80	2	1.9	10.6	11.5	2.9	590
50	None	Updraft	10.0	2.92	1.75	2.0	0.70	0.27	1.8	7.5	5.60	1.45	4.0	~6.1	8.77	0.62	2	1.9	10.7	11.5	2.7	320
45	0.12 l/min reflux*	Updraft	0.90	2.92	1.75	0.20	0.9	0.35	Contin. 0.80	0.80	6.75	1.1	0.53	1.23	11.8	0.12	2	0.83	12.2	0.99	3.75	35
46	0.12 l/min**	Updraft	0.90	2.92	1.75	0.20	0.6	0.2	Contin. 0.82 12.2 M HNO ₃	0.82	5.85	0.97	0.55	1.25	11.46	0.06	2	0.82	12.0	1.00	4.08	37

*Air sparge during reflux step only.

**Air sparge in effect during mixed acid withdrawal and reflux steps.

indicating that a steady state concentration of $\sim 12 \text{ M}$ can be maintained. Both runs gave high HNO_3 and low uranium concentrations in the acidified concentrate (columns 15 and 16) and less than 50 ppm Cl^- in the solvent extraction feed (column 22).

5.1.2 Continuous Dissolution

Two dissolution runs, GD-8 and GD-9, were made in the 6-in. ID glass dissolver. Run GD-8 was made using a prototype APPR weighing 5440 g, including 296 g U, that had been heated in air at 1200°F for 16 hr to oxidize the surface. The purpose in oxidizing the surface was to determine whether or not this treatment would have a detrimental effect on the dissolution rate. The fuel element was dissolved in 20 min at an average aqua regia (5 N HNO_3 -2 N HCl) flow rate of 4.2 liters/min with a resultant dissolution rate of 272 g/min, yielding a product 2.95 M H^+ , 1.92 M Cl^- , and a total metal loading of 79.5 g/liter. This run was comparable to previous runs that have been made using unoxidized fuel elements. There was evidence of only slight attack on the oxide coating (which flaked off the surface) and braze metal (Coast Metals-NP).

Run GD-9 was made using a special "heat" fuel element weighing 5900 g, including 1000 g uranium, that had been oxidized in air at 1675°F for 69 hr. The dissolver was operated for 21 min at an average 5-2 aqua regia flow rate of 4.5 liters/min. At shutdown, the uranium-bearing portion of the fuel element had completely dissolved but the rails, spacers, and weld metal were virtually untouched. The total weight of the undissolved metal was 459 g.

The dissolution rate based on the dissolved portion of the fuel element was $8.5 \text{ mg/cm}^2\text{-min}$ or 278 g/min yielding a product 4.21 M H^+ , 1.65 M Cl^- , and a metal loading of 60.2 g/liter. The maximum foam height produced during the run was 7 ft.

5.2 Sulfex - J. B. Adams

Batch decladding and core dissolution runs were made on unirradiated prototype Consolidated Edison pins*. The pins used had been heated to 1100°F and quenched in cold water through 5 cycles to build an oxide coating and simulate pellet breakage due to thermal stressing. Little or no breakage of pellets occurred.

*0.3125 in. O.D., 20 mil wall x 7-3/8 in. long, 304 ELC stainless steel tubing with 1/2 in. long solid end caps; loaded with $\text{UO}_2\text{-ThO}_2$ pellets containing 1.72 g U and 37.75 g Th. About 9 g of stainless steel is in the end caps and 16 g in the tube.

Hydrogen evolution curves for several runs are given in Figure 5.1. Most curves are for the reaction of 250 ml of 6 M H_2SO_4 on a single pin. One curve was for the dissolution of 304 stainless steel 1/4 in. tubing. The dissolution rates varied relatively little over the range 4 M and 6 M H_2SO_4 during a batch dissolution. In one run the rate obtained with 165 ml of 6 M H_2SO_4 on a single pin was only slightly less than the rate when 250 ml was used. The rates are best compared by the slope of the straight line portion of hydrogen evolution curves after the reaction is fully developed, the clad is still intact, and the original area of stainless steel is still exposed. Based on the area of the Con Ed pins used, reaction rates of 8-11 mg/cm²/min were obtained. However, the end caps were not completely dissolved.

Preliminary analytical results indicated that the losses of uranium from the pellets to the sulfuric acid decladding solution were approximately 0.2%. Microbraz 50, a braze used in fabricating Con Ed fuel elements, dissolved only very slowly in sulfuric acid. In one decladding run, where 6 M H_2SO_4 contained 0.25 M CdSO_4 and 0.25 M H_3BO_3 (nuclear poisons), the rate of dissolution of stainless steel was only slightly reduced.

Batch core dissolution in boiling 13 M HNO_3 , 0.04 M F^- , 0.04 Al^{+++} solutions required 16 hr for completion with a volume ratio of 138 ml for 40 g pellets. The dissolution time could be reduced to approximately 8 hr by using more acid and/or by removing partially spent acid and charging fresh acid to the dissolver. Variation of the Al^{+++} concentration from 0.00-0.1 M progressively reduced the dissolution rate to a moderate extent. No brown oxides were noted visually during dissolution, and only traces of nitrogen were found in a caustic scrubber used with the system.

5.3 Feed Clarification - J. B. Adams, G. B. Dinsmore

Dissolver solutions from fuel reprocessing treatments frequently require clarification because they may contain undesirable precipitates, undissolved fissile or fertile fuel, and emulsion-forming agents (usually silica). Clarification of dissolver solutions by filtration through a sand bed is being investigated.

Test on a new batch of Darex solvent extraction feed solution (HS-4-A) showed it to be the most difficult solution to filter yet encountered. Procedures satisfactory for previous samples proved insufficient.

A complex clarification procedure was developed involving addition of small amounts of soluble silica and gelatin, digestion to form an insoluble silica-gelatin polymer, addition of filter aid and sedimentation to obtain a clear solution and thickened slurry. The supernate and slurry were filtered separately on a precoated sand filter. This procedure was a most effective method for filtration of approximately 300-liter batches on filters of limited area (1 sq ft), but the results were not as good as those from previous more easily filterable samples when the silica-gela-

Fig.5.1. Hydrogen Evolution from the Reaction of Boiling 6M H₂SO₄ with 304 SS.

tin precipitation was not used. The results indicated that to obtain adequate precipitation and flocculation of a silica-gelatin polymer from Darex solutions containing only 8-14 ppm Si up to 200 ppm of additional soluble silica must be added.

The results from filtration tests with this feed solution (HS-4-A)* are shown on Figure 5.2. All filtration tests were made using 5 in. Hg vacuum on a 1-1/2 in. dia x 8 in. deep sand bed precoated with 1 g of Celite 545 filter aid. Approximately 12 g of Celite 545/liter were added to the original solution and small amounts were added to the supernate samples before filtration. Experiments were also made using NP-10**; a flocculating agent which proved to be partially successful, causing rapid sedimentation although apparently leaving enough colloidal material in the clear supernate to hinder filtration.

Run 1-3 were made with well mixed feed samples. Filtration rates were very low. Extrapolation of the data indicated that it would take approximately 25 hr to filter a 4-liter batch on the 1-1/2 in. dia filter (equivalent to approximately 325 liters on a 1 sq ft filter). In runs 4-9 the sample was allowed to settle with or without reagents and the supernate filtered first followed by the slurry (split feed). Runs 8 and 9, with the steepest slopes, obtained when a silica-gelatin treatment was used.

Runs 4-7, with which the flocculating agent NP-10 was used, had slower filtration rates. The curved portion of the curves for runs 4-9 with lesser slope resulted from the filtration of the slurry. Excess liquid was mixed with the slurry in run 9 which extended the length of the cycle. With careful separation of supernate and slurry it was estimated that a 4-liter batch could be filtered in a minimum of about 2 hr. Filtration at elevated temperatures might also reduce the length of the filtration cycle by a factor of 2. The over-all filtration cycle probably would vary from 2-5 hr.

However, the cycle would be extended considerably by an excess of clear liquor with the thickened slurry; the solids settle rapidly on the filter bed leaving the excess liquor to pass through the thick filter cake. For filters of the type used during these experiments, each doubling of the available filtration area reduces the cycle time by a factor proportional to (area)⁻² or by a factor of 4. A unit with a large area or multiple units of maximum allowable area (dependent on criticality requirements) would be desired for optimum design. Increases in washing, cake removal and equipment installation problems must be balanced against the gain in shorter, more reliable filtration cycles.

*At 23°C the clear solution analyzed 5.02 g U/liter, 32.5 g Fe/liter, 2 N H⁺ and 11 ppm Si. Solution specific gravity was 1.22 and viscosity 1.97 cp. Wet silica cake associated with 1 liter was 16.7 g, analyzing 5.69% SiO₂.

**Dow Chemical Co.

All tests at $\sim 25^{\circ}\text{C}$, 5 in. Hg vacuum on 1-1/2 in. dia x 8 in. deep and bed precoated with 1 g Celite 545; 10-12 g Celite 545 added per liter of feed solution (HS-4-A).

Test No.	Method of Feeding	Other Reagent Treatment
HS-4-A-1	Mixed slurry	None
2	Mixed slurry	None
3	Mixed slurry	0.3 mg NP-10/liter
4	Split feed ^a	0.5 mg NP-10/liter
5	Split feed ^a	0.5 mg NP-10/liter
6	Split feed ^a	200 ppm soluble SiO_2 , 100 ppm gelatin and 0.5 mg NP-10/liter
7	Split feed ^a	0.3 mg NP-10/liter
8	Split feed ^a	200 ppm soluble SiO_2 , 100 ppm gelatin
9	Split feed ^a	200 ppm soluble SiO_2 , 100 ppm gelatin

^aClear supernate and thickened slurry filtered separately.

Fig. 5.2. Filtration Tests on Darex Solvent Extraction Feed Solutions.

The major difference between various runs using the split feed filtration technique was the rate of filtration of the apparently clear supernate. If free of colloidal particles, more than 200 liters of hot liquor can be filtered on a 1 sq ft precoated sand filter in 10 min. If colloidal material is present, a very thin layer on the filter bed can retard filtration rates so that it takes several hours to filter 200 liters. Differences in filtration rates for various samples of thickened slurry are relatively insignificant. The rates are uniformly slow because of the resulting thick cakes.

5.4 Solvent Extraction Studies - R. J. McNamee, F. L. Rogers

A series of HETS calculations were made for the Hanford assistance runs 1, 3b, and 3e (previously reported) in order to determine the effect of aqueous concentration on HETS. The results are tabulated in Table 5.2. It was found that there was more concentration dependence in the runs with higher HETS. The aqueous phase concentration decreased progressively down the column as shown in Figure 5.3.

"Mistron", a commercially available finely divided magnesium silicate, was added to the extraction feed in an attempt to increase column capacity. A Milton-Roy feed pump could not be used due to plugs in the check valves, but feeding was accomplished by the use of a Signamotor pump.

Table 5.2. HETS Calculated Over
Various Sections of Extraction Column

Run No.	Over-all (21.3 ft)	Top Foot	1-2.8 ft Below Feed Pt.	1-4.5 ft Below Feed Pt.	2.8-6.3 ft Below Feed Pt.	Bottom 9.1 ft	Bottom 13.1 ft
1	2.0	0.8	-	1.9	1.9	2.2	-
3b	3.6	1.0	1.9	-	-	-	4.1
3e	1.4	0.7	-	1.2	1.1	1.2	1.6

Fig. 5.3. Uranium Profile in Aqueous Phase, Hanford Assistance
Extraction Runs.

5.5 Mechanical Processing - C. D. Watson

5.5.1 Core Leaching - G. A. West, K. Ladd

Instantaneous and complete dissolution rates of stainless steel clad unirradiated sintered UO_2 pellets in boiling 10 M HNO_3 were measured to aid in the design of experimental leachers for the Power Reactor Fuel Reprocessing program. The time required for complete dissolution (0.3-0.7 hr) varied proportionally to the extent of fracturing from the shearing operation. Sheared 1-1/2 in. lengths of 0.400 in. O.D. cladding were leached free of UO_2 in approximately one-half (22-25 min) the time required for equal lengths containing uncrushed pellets. Decreasing the sheared length to 1/2 in. resulted in no appreciable decrease in leaching time over that for the 1-1/2 in. sheared lengths.

The 1/2 in. sheared sections exhibited a greater variation of instantaneous reaction rates, 85-380 $\text{mg/cm}^2/\text{min}$, than the 1 in. or 1-1/2 in. lengths which were 85-215 and 90-155 $\text{mg/cm}^2/\text{min}$, respectively (Table 5.3). All tests were conducted at an acid volume to mass ratio of 5 ml/g. The pellets were PWR rejects, 0.360-0.370 in. O.D. x 0.375 in. long, clad with 304L stainless steel tubing, 0.400 in. O.D. w/0.010 in. wall. In the shearing operation, the amount of UO_2 dislodged was 29, 14 and 10% for the 1/2 in., 1 in. and 1-1/2 in. lengths, respectively, and the fines produced ranged from micron sized particles to 1/4 in. irregular cubes.

It was demonstrated that an increase in the nitrate concentration increases the reaction rate of UO_2 . The UO_2 dissolution rate was increased the same amount (approximately 80%) by the addition of sodium nitrate to 10 M HNO_3 as it was by the addition of nitrate as uranyl nitrate.

5.5.2 SRE Decanning - G. A. West

A cleaning procedure for the removal of oil and NaK from de-jacketed SRE fuel slugs with steam and detergent solution has been developed. A single cleaning test showed that NaK and mineral oil can be removed easily from a pitted uranium rod by steaming, thus permitting the recanning of slugs safely in air.

It is proposed to recan the twelve cleaned slugs from a single SRE fuel rod in an aluminum can sealed by a canning machine. The aluminum cans will require special fabrication since the thickness will be greater than the standard cans made by the canning manufacturers. Cost inquiries have been submitted to several canning manufacturers (George D. Ellis and Sons, Philadelphia, Pa.; Dixie Canning Co., Athens, Ga.; A. J. Arns Co., Bridgeport, Conn.) for the fabrication of the aluminum cans and a machine for sealing the 30 mil wall cans.

Table 5.3. Reaction Rate of
Stainless Steel Clad UO₂ vs. Sheared Length

Conditions: 1. Reagent: boiling 10 M HNO₃
2. Loading (volume to mass): 5 ml/g
3. Element: 304-L stainless steel
clad 0.400" O.D. w/0.010" wall;
UO₂ pellets, 0.370" O.D. x 0.375"
long.

Sheared Length, in.	Reaction Rate, ¹ mg/cm ² /min
0	290 to 330 ²
0.5	85 to 380 ³
1.0	85 to 215 ³
1.5	90 to 155 ³

1. Rate based on 1/2 the original surface area.
2. Whole unclad and undamaged pellets.
3. Reaction range due to degree of fracturing
and per cent of end closure on clad from
shearing.

5.5.3 Disassembly of Fuel Bundles

Abrasive Sawing - G. A. West, J. C. Rose

The segmenting facility for mechanical reprocessing of spent power reactor fuels will contain an abrasive saw for removing inert end adapters and other inert accessories. A Ty-Sa-Man abrasive saw with a 16 in. dia Manhattan No. 239 blade is being tested to establish optimum feed rates and design information for the collection and containment of particles.

Abrasive cutting of a bundle of three 0.5 in. O.D. type 316 stainless steel rods at 10,770 SFPM blade speed showed that the optimum feed rate was approximately 10 in./min with a wear ratio of stainless cut to wheel consumed of 5.8 by volume (Figure 5.4). The ratio decreased to 3 at a feed rate of 60 in./min which approached the maximum at which the rods could be cut without damaging the blade or producing excessive metal slivers. At the slower cutting rate, a total of 4,440 cuts through a 0.5 in. O.D. stainless steel rod could be made while consuming 8 in. of the 16-in. O.D. Manhattan No. 239 blade.

A lucite box with both a water spray on its sides and a vacuum system was used to collect the sawed particles. It was concluded that the vacuum system alone would be advantageous since deposits formed under the saw and in the discharge line while using the water spray. A water flush of extremely high velocity would probably remove the particles but the water would be difficult to contain without severe contamination. Additional tests are being made on other methods of particle containment while cutting longitudinally by moving the work into the saw.

5.5.4 Shearing - G. K. Ellis, D. E. Willis

Mark I Assembly. When a Mark I prototype assembly filled with porcelain rods was sheared into 0.75-in. lengths with a "plane of contact" blade in the 125-ton Manco, 33% of the porcelain was dislodged from the sheared face. The corresponding separation using a "line of contact" blade was 27%. The size distribution of the dislodged porcelain is shown in Table 5.4. Only 4.8% of the porcelain was less than 150 micron size, while "line of contact" shearing produced 37% in this size range. After 65 cuts were made, the clearance between blades of the Manco increased from the original 0.002 in. to an average of 0.018 in., perhaps caused by the displacement of the piston in its housing at the extended position of its travel.

UO₂-Filled Stainless Steel Tubes. Thermally cycling stainless steel-clad UO₂ fuel (5 cycles from 20-550°C, 30 min at temperature followed by an air quench) did not increase the amount of UO₂ dislodged during shearing over that for nonthermally cycled fuel. A 29% separation of UO₂, 50% of which was less than 150 micron size, resulted when four 12-in. long, 0.5-in. dia stainless steel tubes filled with UO₂ were sheared (Table 5.5).

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Fig. 5.4. Wear Ratio for Abrasive Disk Cutting of Stainless Steel vs Feed Rate.

Table 5.4. Porcelain Size Distribution

From Shearing a 36-Tube 0.5-in. Dia

Stainless Steel, Porcelain Filled Prototype Fuel Bundle

- Conditions: (a) Shear type, 125-ton Guillotine Manco
 (b) Blade type, "plane of contact"
 (c) 65 0.75-in. cuts at a blade velocity of 0.33 in./sec
 (d) Physical properties of porcelain simulating UO₂
Tensile strength	5-10,000 psi
Compressive strength	90,000 psi
Flexural strength	10-20,000 psi
Hardness	7-9 Moh scale
Porosity	< 10%
Modulus of elasticity	20-30,000 psi

Porcelain Particle Size, (microns)	Porcelain Size Distribution, (wt %)
> 1680	3.2
> 840 < 1680	12.5
> 297 < 840	51.3
> 149 < 297	28.2
< 149	4.8
	100.0
Total porcelain dislodged from sheared faces	33%

Table 5.5. UO₂ Size Distribution From Shearing
a Single 0.5-in. Dia UO₂ Filled Stainless Steel Tube

Conditions: (a) Shear type, 1-1/2 in. Guillotine Manco

(b) Blade type, "line of contact"

(c) Cuts at 0.5 in./sec blade velocity at L/D ratios of unity

(d) Physical properties of UO₂

Tensile strength 5-10,000 psi

Compressive strength 90,000 psi

Flexural strength 10-20,000 psi

Hardness 7-9 Moh scale

UO ₂ Particle Size, microns	UO ₂ Size Distribution, %	
	Thermal Cycled	Not Thermal Cycled
> 1680	0.2	0.7
> 840 < 1680	3.4	4.1
> 297 < 840	18.1	16.1
> 149 < 297	30.9	16.7
< 149	47.4	62.4
Total UO ₂ dislodged from sheared faces	29%	29%

Surplus Press. A new HPM* surplus 200-ton thrust vertical hydraulic press with a 60-in. ram travel and 30-in. x 24-in. bed has been obtained for use in the Mechanical Processing program. This press will be used with a die set accommodating different shear blade shapes to evaluate the effect of blade shape and velocity on blade wear and shearing effectiveness for Mark I prototype fuel assemblies.

The currently available pressing velocity of 2.8 in./sec of the HPM press will be increased by adding another hydraulic pump in parallel with the HPM pump. A pressing speed of 25 in./sec would require an additional pump capable of delivering an estimated 900 gpm at the 2600 psi operating pressure of the press. The pressing speed could be increased to only about 3.8 in./sec if the existing variable displacement Oil Gear pump were used.

125-Ton Manco Shear. Installation drawings were completed and auxiliary parts have been received for attaching an Oil Gear pump to the 125-ton Manco shear to increase the blade velocity from 0.33 to about 3 in./sec. The total thrust in this combination will be decreased to about 80 tons because of the difference in operating pressure of the original Manco power unit and the new Oil Gear unit. The 80 tons of thrust can be obtained only by enlarging the oil entry and exit ports of the Manco plus operating the Oil Gear unit 23% in excess of its rated pressure. In any case, there will be only a marginal excess thrust since calculations based on Hanford's data indicate a thrust of 70 tons is required to shear the Mark I prototype. The actual thrust requirement will be checked with a pressure gauge before the hookup is made between the Oil Gear and Manco units.

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Solids Discharging Dissolvers - Batch. Construction drawings for all major auxiliary batch components and a dissolver concept have been completed (Figure 5.5). In the dissolver, there are two 9-in. dia cylindrical dissolver tanks of critically safe dimensions attached to a central slab acid containment tank. Mesh size of the baskets are such that all solids which drop from it into the three tanks may be jetted from the tanks. Burns and Roe, Inc., in conjunction with REED have begun engineering drawings for the dissolver and also concept and engineering drawings for the material transfer cycle from shear to dissolver to clad disposal and back to the shear.

Solids Discharging Dissolvers - Continuous. The auxiliary components of the batch dissolver will be installed in cell 4A of Building 4505 in advance of the batch dissolver for initial use in testing and evaluating the four different concepts of continuous dissolvers. Later, the batch dissolver tanks will be installed and tested in cell 4A or 2. These auxiliary components are being fabricated. The off-gas condenser is 90% completed on an outside contract. Construction of the scrubber for removing NO and NO₂ noncondensables has begun. Other units such as feed and pro-

*Hydraulic Press Manufacturing Company.

Fig. 5.5. PRFR Batch Dissolver for Mechanical Reprocessing of Spent Reactor Fuels.

duct tanks, and heat exchangers used in maintained feed and recycle acid at the boiling temperature will be salvaged from existing equipment.

A construction drawing for the first of the continuous dissolvers, the spiral vibrating continuous dissolver including the batch auxiliaries has been completed (Figure 5.6 and 5.7). Fabrication of the dissolver is completed and installation in cell 4A has commenced.

Ferrule Splitting. Die Set - A die set has been completed for the purpose of disassembling a fuel bundle by pushing the bundle through the die which cuts the ferrules and swages the cut ends to the side of each tube to furnish individual tubes. Test of this tool is awaiting the completion of a jig which holds the ferrules in place for cutting with the die.

Slabbing Knife - The slabbing knife is another ferrule splitting tool which cuts the ferrules at a given plane through the bundle to furnish slabs of elements. Tests of this knife are awaiting completion of a test bundle.

Microbrazed Wedge Destruction. Several prototype Con Ed fuel assemblies consisting of 100 solid stainless steel rods were successfully disassembled into slabs by forcing a wedge between tube layers and rupturing the Microbrazed 50 bond between ferrules and tubes when the 30,000 psi tensile strength of the bond was exceeded (Figure 5.8). A slab of tubes produced by splitting a bundle is shown in Figure 5.9. An air hammer is being adapted for use with a wedge to furnish a portable machine for disassembly by rupturing the assembly along the Microbrazed bonds.

Building 4505 Test Area Layout. Construction drawings were completed, shop fabrication is about 80% completed, and construction has begun to extend the existing Building 4505 Test Area by 22 ft. A top to cell 4A has been designed to replace the existing concrete top. A layout of equipment to be used in the Building 4505 Test Area was completed.

Fig. 5.6. Schematic Layout of Continuous Spiral-Vibrating and Batch Dissolvers and Dissolver Auxiliaries.

Fig. 5.7. Equipment Layout to Perform the Dissolution Step in Mechanical Processing of Spent Reactor Fuel Elements.
(Bldg. 4505, Cell 4A, Second Floor)

Fig. 5.8. PRFR - Mechanical Phase - Wedge for Disassembly of Microbrazed Fuel Element - Prototype Test Set-Up in Shop.

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Fig. 5.9. PRFR - Mechanical Phase Microbrazed Prototype Fuel Element Showing Slabs and Pins After Test of Wedge.

6.0 VOLATILITY PROCESS

R. W. Horton

Studies were continued of zirconium hydrofluorination as the dissolution step in the recovery of uranium from fully enriched zirconium fuels by the Volatility process. Data on reaction rates in the gas phase and in fused salt are reported. Corrosion data are reported for INOR-8 exposed to HF in the NaF-LiF salt system under dissolution conditions.

6.1 HF-Fused Salt Dissolution of Zirconium - E. C. Moncrief

The dissolution of zirconium metal in molten salt baths of NaF-ZrF₄ or NaF-LiF with anhydrous HF is a proposed head-end step for the reprocessing of zirconium matrix fuel sub-assemblies (e.g., PWR "seed" fuel elements). The salt product from the dissolutions will serve as feed material for the fluorination step. Dissolutions have been made using dummy sub-assemblies fabricated from Zr-2 rolled plate. The present program is directed toward: (1) corrosion studies on the newly constructed INOR-8 dissolver under dissolution conditions, and (2) the study of the effects of dissolver geometry on dissolution variables.

Three dissolution runs were completed using the NaF-LiF system with sub-assemblies 100% submerged. Runs INOR-8 -1 (800°C) and INOR-8 -2 (675-700°C) were performed at HF feed gas rates of 4 lb/hr, while run INOR-8 -3 (675-700°C) was performed at 1 lb/hr. Over-all dissolution rates of 0.210, 0.188, and 0.079 lb/hr/sq ft were obtained with corresponding average HF utilizations of 41.4, 37.5, and 63.9%, respectively. "Vidigage" measurements on the INOR-8 dissolver indicated corrosion rates of 1-2 mils per dissolution, although rates as high as 2 mils per hour were observed for INOR-8 wire and Inconel wire and tubing at the salt off-gas interface. In all runs, there was high entrainment of solid material to the off-gas.

6.1.1 Description of INOR-8 Dissolver

A schematic drawing of the INOR-8 dissolver used for the dissolution studies is shown in Figure 6.1. The dissolver was constructed entirely of INOR-8 (Ni, 70.0%; Mo, 16.6%; Cr, 7.4%; Fe, 4.8%) and consists of a top section 9-3/4 in. ID for solids entrainment separation and a bottom section 5-1/4 in. ID for dissolution. The dissolution section was designed to permit maximum submergence of fuel sub-assemblies with minimum salt charge. A removable baffle assembly consisting of a plate and a cone baffle was connected to the top flange of the dissolver. A slant baffle constructed in the shape of a frustum of a hollow cone was welded to the top section wall.

A photograph of the dissolver in operational position with the front half of the heating furnaces removed is shown in Figure 6.2. Also shown

Fig. 6.1. Schematic of Inor-8 Dissolver Showing Baffle Assembly and Draft Tube .

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Fig. 6.2. INOR-8 Dissolver.

are the resistance heated HF feed and salt discharge lines, and the bottom flange of the off-gas scrubber column. Chromel-alumel thermocouples in Inconel sheaths were welded to the dissolver at specific internal positions. Several ceramic-sheathed thermocouples are visible in Figure 6.2.

The removable baffle assembly, draft tube, and HF gas distributor plates are shown in Figure 6.3 before the start of run INOR-8 -1. The dummy sub-assemblies were stacked in the draft tube during the dissolution runs as represented in Figure 6.1. The distributor plate with the most free area (9-10%) was used for all runs.

6.1.2 Dissolution Operating Procedure

All HF-fused salt dissolution runs were performed under the same operational procedure (refer to Figure 6.4). Six dummy Zr-2 sub-assemblies were stacked in the dissolver draft tube (Figure 6.1). Corrosion coupons were secured in place, and the NaF-LiF salt charged to the dissolver. The dissolver was heated electrically until the salt charge was molten. Resistance heat was then applied to the Inconel salt discharge line and the molten salt allowed to fill the line. When the resistance heating circuit was opened, a gas tight salt "freeze valve" was formed.

To start the dissolution, the Lapp pump was adjusted to deliver the pre-determined HF liquid rate to the vaporizer. The gaseous HF was then fed through a stream-traced copper line and 3 ft of resistance heated Inconel pipe before entering the bottom of the dissolver.

The dissolution off-gas (unreacted HF and H₂) was passed through the scrubber column, the HF cooler, and the trichloroethylene condenser where the HF was condensed and collected in the liquid hold tank. The noncondensed H₂ was metered before venting to the building off-gas system. A screen filled with copper turnings was placed in the scrubber to collect entrained solids in the off-gas.

At the conclusion of the sub-assembly dissolution (as determined by the theoretical H₂ evolution) the HF flow was stopped and a freeze plug was allowed to form in the HF feed line by opening the resistance heating circuit. Resistance heat was again applied to the salt discharge line and the zirconium bearing salt was transferred from the dissolver by pressurizing with nitrogen.

6.1.3 Data and Results

The operating conditions for the three dissolution runs are reported in Table 6.1. Salt composition and weight, total sub-assembly height, and per cent submergence of sub-assemblies in salt remained constant for all runs. Complete dissolution was the goal of each run, but an HF leak terminated run INOR-8 -3 and run INOR-8 -2 was stopped with 0.273 lb of zirconium undissolved. External heat was not necessary during the first 5 hr of run INOR-8 -1 since the heat of reaction held the molten salt temperature at

Fig. 6.3. Dissolver Baffle Assembly, Draft Tube, and Distributor Plates.

Fig.6.4. Hydrofluorination Process Flowsheet.

Table 6.1. Operating Conditions
for INOR-8 Dissolver Tests

Fixed Conditions:

Salt Charge: NaF, 19.3 lb; LiF, 15.8 lb

Total Height Sub-Assemblies: 12 in.

Sub-Assemblies 100% Submerged

Sub-Assembly Description: Ten 1/8"x2"x4" Zr-2
Plates with 1/8"x1/4"x4" Zr-2 Spacers

Operating Condition	Run		
	INOR-8 -1	INOR-8 -2	INOR-8 -3
HF flow rate, lb/hr	4	4	1
Run time, hr	8.02	7.88 ^a	11.28 ^b
Dissolver temperature, °C	800	675-700	675-700
Zirconium dissolved, lb	13.60	13.28	8.02
Cooling air required, ft ³ /min	-	^c	4-5
HF pressure (max), psig	-	7.5	8.5
Fused salt recovered, lb	58.5	57.0	52.0

^a0.273 lb zirconium undissolved.

^bRun terminated by HF leak.

^cCooling air used, but not metered.

800°C. Subsequent runs were made with air cooling to the lower section of the dissolver so as to maintain the operating temperature below 700°C. The weights of fused salt recovered in Table 6.1 include the salt actually transferred to the salt collector (Figure 6.4) as well as scrapings from the vessel walls and baffles.

The cumulative H₂ evolution for the three runs is plotted in Figure 6.5. The anomaly in the curve for run INOR-8 -3 at 10.5 hr is attributed to an increase in HF flow rate from 1 to 2 lb/hr prior to the termination of the run. Incremental dissolution rates and HF utilizations for the three runs are shown in Figures 6.6, 6.7, and 6.8.

The corrosion data for the runs are summarized in Figure 6.9 and 6.10, and in Table 6.2. The wall thickness readings were made on the dissolver and draft tube with the "Vidigage", an ultrasonic thickness measuring instrument. The measurement locations were marked with an "Electromark" electro-chemical etcher to permit readings at the same locations after each run.

6.1.4 Discussion of Results

The primary objective of the INOR-8 dissolution runs was to obtain corrosion data on the INOR-8 alloy under dissolution conditions. The corrosion results for the three runs are summarized in Figures 6.9 and 6.10 and Table 6.2. The static molten salt level prior to the start of the dissolutions was located approximately 2 in. below point 3 on the dissolver (Figure 6.9). When HF flow was added, the salt off-gas interface was probably between points 2 and 3.

The results of Figure 6.9 indicate that corrosion of the INOR-8 dissolver was greatest at the salt off-gas interface and at the HF gas inlet. The magnitude of the corrosion was approximately 2 mils per dissolution cycle. The draft tube corrosion results shown in Figure 6.10 substantiate the rate of 2 mils per dissolution rate, but indicate a uniform attack over the entire draft tube surface. This result might be expected, since the flow of HF bubbles through the draft tube would result in the "flow of interface" across the tube surface.

The coupon corrosion results presented in Table 6.2 illustrate two points: (1) coupons located at the salt off-gas interface (Figure 6.10) were corroded more than at any other location, and (2) molybdenum corroded slower than INOR-8 at the salt off-gas interface but faster than INOR-8 when submerged in the molten salt. However, it is felt that additional tests are necessary to substantiate these results.

Corrosion was very severe at the salt off-gas interface on Inconel wire and tubing and on INOR-8 wire. The three thermocouples (15 mil Inconel sheath) shown in Figure 6.11 were severed by corrosion during run INOR-8 -1. The INOR-8 wire which was supporting coupon 6 during run INOR-8 -2 was decreased in diameter from 38 to 19 mils at the salt off-gas in-

Fig.6.5. Hydrogen Evolution as a Function of Run Time .

Fig. 6.6. Dissolution Rate and HF Utilization During Run INOR-8-1.

Fig. 6.7. Dissolution Rate and HF Utilization During Run INOR-8-2.

Fig. 6.8. Dissolution Rate and HF Utilization During Run INOR-8-3.

MEASUREMENT LOCATIONS
READING TAKEN ON LINE BENEATH LETTERS AS INDICATED BY 0-8. WELD MIDWAY BETWEEN LOCATIONS C AND D

(READINGS IN MILS)
TIME OF VIDIGAGE READING

ORIGINAL				AFTER INOR-8-1				AFTER INOR-8-2				AFTER INOR-8-3				MAXIMUM CHANGE			
A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
249	249	250	248	248	249	249	248	249	248	249	249	248	247	249	246	-1	-2	-1	-2
250	250	250	250	249	250	250	250	251	250	248	249	248	248	249	248	-2	-2	-1	-2
251	251	252	252	249	248	248	249	248	248	246	247	247	249	246	246	-4	-3	-6	-6
251	252	251	252	249	248	248	250	249	250	248	250	252	254	249	250	-2	-4	-3	-2
236	237	238	235	234	237	-	235	236	237	237	235	233	237	-	232	-3	0	-1	-3
236	238	238	238	236	238	-	236	236	237	237	237	233	235	237	234	-3	-3	-1	-4
245	247	249	240	244	246	-	242	245	246	245	239	242	244	246	237	-3	-3	-4	-3
245	247	249	240	242	246	-	240	243	247	247	240	241	244	247	240	-4	-3	-2	0
249	248	248	238	246	246	-	-	243	248	244	235	241	242	247	235	-8	-6	-4	-3

Fig. 6.9. Summary of Inor-8 Dissolver Corrosion Measurements.

NOTE:
DIMENSIONS ARE IN INCHES

MEASUREMENT LOCATIONS

READINGS TAKEN ON LINE BENEATH LETTERS AS INDICATED BY 4-8
LINE C ADJACENT TO WELD SEAM
NUMBERS IN SQUARES REFER TO COUPON LOCATION DURING RUNS (SEE TABLE 2)

(READINGS IN MILS)
TIME OF VIDIGAGE READING*

ORIGINAL				AFTER INOR-8-2				AFTER INOR-8-3				MAXIMUM CHANGE			
A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
120	119	120	120	115	117	115	114	114	115	116	116	-6	-4	-5	-6
120	118	119	120	114	115	115	113	114	114	116	115	-6	-4	-4	-7
120	118	119	120	116	116	114	114	114	114	116	115	-6	-4	-5	-6
119	118	120	120	116	115	114	114	114	113	115	114	-5	-5	-6	-6
117	116	118	118	116	114	112	112	111	111	116	112	-6	-5	-6	-6

*DRAFT TUBE NOT VIDIGAGED AFTER RUN INOR-8-1

Fig. 6.10. Summary of Inor-8 Draft Tube Corrosion Measurements.

Table 6.2. Coupon Corrosion Data
During INOR-8 Dissolver Tests

Run No.	Coupon No.	Type of Metal	Original Weight, g	Weight Loss, g	Corrosion, g/cm ²	Support Wire	Condition of Support Wire During Run
INOR-8 -1	1	INOR-8	13.3988	0.2829	0.1546	Copper	Failed from stress
8.02 hr	2	INOR-8	13.8430	0.0952	0.0504	Copper	Failed from stress
HF exposure	3	INOR-8	13.2346	0.8467*	0.4479	Copper	Failed from stress
INOR-8 -2	4	INOR-8	11.3795	0.1230	0.0748	INOR-8	Minor uniform corrosion**
7.88 hr	5	INOR-8	11.7905	0.1103	0.0644	INOR-8	Minor uniform corrosion
HF exposure	6	INOR-8	12.4010	0.3916	0.2243	INOR-8	Heavy corrosion at interface (from 38 to 19 mils)
INOR-8 -3	4a	INOR-8	11.2564	0.6108	0.3708	INOR-8	Minor uniform corrosion
11.28 hr	5a	INOR-8	11.6802	0.0440	0.0259	INOR-8	Minor uniform corrosion
HF exposure	7	Molybdenum	8.9095	0.1697	0.1194	Molybdenum	Minor uniform corrosion
	8	Molybdenum	9.9143	0.1586	0.1029	Molybdenum	Minor uniform corrosion
	9	Molybdenum	8.7099	0.1053	0.0753	Molybdenum	Minor uniform corrosion

⁺Coupons in draft tube supported by wire from draft tube bracket; coupons at interface supported by wire from cone baffle.

*Weight loss for both runs INOR-8 -1 and INOR-8 -2.

**Minor being < 5 mils/cycle.

Fig. 6.11. Dissolver After Run INOR-8-1.

terface. Also, an Inconel liquid level dip tube (35 mil wall thickness) was severed by the end of run INOR-8 -2. Thus, corrosion on wire and tubing at the salt off-gas interface was as high as 2 mil per hour for these two runs. During run INOR-8 -3 (HF rate 1 lb/hr), however, all support wires showed only minor uniform corrosion. Since the vessel wall and draft tube corrosion rates during run INOR-8 -3 were comparable to the rates at 4 lb/hr HF flow, it appears that turbulence was not important in determining the corrosion rate of massive metal in the dissolver but that higher gas rates might produce stresses in wire and tubing which accelerate corrosion.

The baffle arrangement shown in Figures 6.1 and 6.3 was only partially effective in preventing entrainment of solids to the off-gas system. After each run large quantities of fine black powder were found in the off-gas line to the scrubber and in the scrubber column screen. In most cases the deposit was easily scraped or peeled off the metal surface. Figure 6.11 shows the deposit on the dissolver top section walls after run INOR-8 -1. The condition of the removable baffle assembly and scrubber column screen are shown after the same run in Figure 6.12. The off-gas line to the scrubber column was nearly plugged with the solids during run INOR-8 -2. However, entrainment was less severe in run INOR-8 -3 at the lower flow rate.

Accurate weights of the total amount of material entrained after each run could not be obtained. Samples of the entrained solids from run INOR-8 -1 showed 7-10% Zr, 55% F⁻, 15% Na, 2-5% Li, and approximately 2% Ni. Samples from run INOR-8 -2 checked closely with these values, and also reported entrained Mo at 1.2%. Thus, it appears that the off-gas solids consist of both entrained salt and corrosion products.

The high dissolution rates and HF utilizations obtained during the runs are noteworthy. Although somewhat erratic in nature, the curves of Figures 6.6-6.8 do seem to indicate that better gas-solid contact was obtained between the HF and zirconium in the INOR-8 dissolver than in previous dissolver geometries, perhaps a result of using a better gas distribution plate and/or the draft tube. Previous tests have indicated that diffusion and turbulence may be the controlling factors on the dissolution rate (that is, the ability to remove the ZrF₄ reaction product from the reacting surface¹). The higher dissolution rates obtained at 4 lb/hr HF flow, as compared to those at 1 lb/hr, substantiate this theory since better turbulence and surface contact were obtained in the former case.

Since the average HF utilization was lower at the 4 lb/hr rate (vessel geometry and sub-assembly height and submergence remaining constant), it appears that the dissolution may have been reaction rate controlled at these

¹Unit Operations Section Monthly Progress Report for March 1958, ORNL CF 58-3-71.

-74-

Fig. 6.12. Baffle Assembly and Off - Gas Column Screen After Run INOR - 8-1.

conditions. If this is true, operation at still higher flow rates would result in even lower HF utilizations. Thus, for a constant vessel geometry and sub-assembly height and submergence there would be some optimum HF flow rate for maintaining both high utilizations and dissolution rates. However, this theory assumes that vessel geometry and HF flow rate are not interrelated.

The satisfactory operation of the bottom inlet of the new INOR-8 dissolver was of primary concern during the dissolution runs. No difficulty in operation was experienced using the bottom inlet for the HF feed gas. Operating data indicated that at a 4 lb/hr HF rate the lower feed gas-molten salt interface was maintained at the elbow below the dissolver outlet (Figure 6.2). Thus, the possibility of plugging the feed gas line was reduced.

The "freeze valve" method of sealing the salt transfer lines proved very successful. Occasionally external heat from an acetylene torch, in addition to that produced by the resistance heating, was necessary to thaw the "freeze valves." Once the salt in the discharge line was molten, the entire molten salt charge in the dissolver was easily transferred with 5 psig nitrogen pressure.

Some trouble was experienced in runs INOR-8 -1 and INOR-8 -2 with salt accumulating on the slant baffle of the dissolver and not being transferred at the conclusion of the runs. Figure 6.11 shows this condition after run INOR-8 -1. Operational data indicated that the dissolver top section temperature was not hot enough to maintain the accumulated salt in a molten condition to permit drainage to the bottom section. Operation of the top section at 750°C during run INOR-8 -3 eliminated this problem.

The primary objective in using the draft tube during the dissolution runs was to produce good circulation and turbulence around and through the fuel sub-assemblies. Good circulation was indicated in run INOR-8 -1 since the internal and external thermocouples in the bottom dissolver section reported the same operating temperature throughout the run. No trouble was experienced with plugging of the 1/16 in. diameter holes in the distribution plate during salt transfers.

6.2 Dry Hydrofluorination - L. E. McNeese, G. Jones, Jr., F. N. McLain

One step of the Volatility process for recovery of irradiated uranium from heterogeneous zirconium base fuel elements is fuel element dissolution in a bath of molten fluorides in the presence of an HF sparge. In the present pilot plant design, if a NaF-LiF bath is used as the initial salt bath, 50% of the fuel element will not be submerged in fused salt.

Recent work in the Unit Operations Section on fused salt dissolution of zirconium indicates that high HF utilizations may be obtained in the submerged section (ORNL CF 59-1-74) which would result in a comparatively high concentration of H₂ (25-70 mole per cent) in the region above the fused salt. The object of this program was to study the behavior of zirconium

base fuel elements in an HF-H₂ atmosphere in the temperature range 400-700°C.

Since the literature (NAA-SR-1508) reports extensive work on the kinetics and characteristics of the Zr-H₂ reaction, this reaction was studied only for its effect upon gas phase hydrofluorination of zirconium. A reaction system suitable for study of the gas-metal reaction has been installed and was described in ORNL CF 59-1-74. Two runs using HF-H₂ mixtures at an initial fuel element temperature of 700°C were performed.

In run DH-3, a 796 g Zircaloy-3 element was contacted with an H₂ flow of 12.2 SCFH at 700°C for approximately 70 min, during which the element was converted to the approximate composition ZrH_{1.3}. The maximum hydrogen content possible at 700°C and 1 atm H₂ partial pressure is ZrH_{1.8} (NAA-SR-1508).

The hydride was then contacted with a 33 mole per cent HF-67 mole per cent H₂ mixture at 0.39 lb/hr HF flow. This composition is equivalent to an HF utilization during the fused salt dissolution of 80%. After 8 hr the hydride was 81% hydrofluorinated to ZrF₄ with an average HF utilization of 40%.

Element temperatures, measured by three 40 mil dia sheathed thermocouples in the positions shown in Figure 6.13 are given in Figure 6.14. Approximately 94% of the solid reaction products remained on the element surface, the remainder being carried out of the reaction zone and deposited in the horizontal section of the reaction system. Solids taken from the center of the reacted element were identified by X-ray diffraction as zirconium hydride. The solids were very brittle and were cracked extensively due to the high temperature reaction conditions of hydriding.

In run DH-4, a 785 g Zircaloy-3 element was contacted with a 33 mole per cent HF-67 mole per cent H₂ flow at 700°C (0.39 lb HF/hr) for 35 min during which a maximum element temperature of 928°C was observed. Temperatures were measured at the points shown in Figure 6.13 and are given in Figure 6.15. A flow of 12.2 SCFH H₂ was continued for approximately 65 min after which the element was allowed to cool to 700°C. The element was then contacted with HF at 1 lb/hr at 700°C for approximately 4 hr which resulted in 85% hydrofluorination to ZrF₄. More than 95 wt per cent of the solid reaction products remained on the fuel element surface.

Owing to the high solubility of H₂ in Zr under the experimental conditions, calculation of reaction rate and HF utilization is not possible based solely on H₂ off-gas rate from the reaction zone. For this reason, the experimental equipment is being modified in order to meter the HF-H₂ off-gas prior to condensation of HF in addition to metering the H₂ off-gas in order to determine the simultaneous rate of reaction of HF and H₂ with a zirconium element.

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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. 6.13. Element Dimensions and Thermocouple Locations.

Fig. 6.14. Element Temperature vs Time. Run DH-3

Fig.6.15. Element Temperature vs Time. Run DH-4.

7.0 WASTE PROCESSING

M. E. Whatley

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

The purpose of the reduction to solids problem of the Waste Processing program is to provide engineering data for reduction of radioactive wastes to solids for ultimate disposal. This report contains the results and description of experiments on evaporation and calcination of Darex waste.

7.1.1 The Evaporation of Darex Waste

Synthetic Darex waste was prepared by the methods described in ORNL CF 58-4-45. The final concentration of the synthetic waste is:

HNO_3	2.95 M
$\text{Fe}(\text{NO}_3)_3$	0.68 M
$\text{Ni}(\text{NO}_3)_2$	.075 M
$\text{Cr}(\text{NO}_3)_3$	0.16 M
$\text{Al}(\text{NO}_3)_3$	0.123 M

Four hundred milliliters of Darex waste was placed in a flask and heated to boiling. The resulting vapor was condensed and collected in approximately 50 volume increments. When 312 of the 400 ml of the original waste was evaporated, the total amount of nitric acid in the condensate slightly exceeded the amount of free nitric acid in the original waste.

As the evaporation continued, more nitric acid was collected in the condensate indicating that the resulting evaporated sludge was now acid deficient. The acid-deficient point was at 77% of the original volume (Figure 7.1). The evaporation was continued to a condensate collection of 87.5% of the original volume. When the resulting evaporated sludge was cooled, it formed a solid at room temperature.

7.1.2 Calcination of Darex Waste

In three calcination experiments, concentrated Darex waste (evaporated to approximately 1/4 of its original volume) was pumped into the 8 in. dia by 18 in. deep calciner vessel described in the Unit Operations Section monthly progress report for January, ORNL CF 59-1-74. The off-gas from the calciner passed to a stainless steel condenser where nitric acid was condensed and discharged. The noncondensable gases passed through a water scrubber and through a wet test meter before discharge to the plant off-gas system.

Fig. 7.1. Amount of HNO_3 in Condensate from Darex Evaporation.

The feed for the first and second calcination run was prepared by removing the water from the original Darex waste until the waste volume was 25% of the original volume (Table 7.1). The acid concentration of this waste was 11.7 M. The liquid was fed into the calcination vessel which was $> 700^{\circ}\text{C}$ by a solenoid valve which operated from a liquid level control system. Liquid was fed into the calciner by gravity when the level dropped below 8 in. from the top. Liquid inlet to the calcination was stopped by the solenoid when the liquid was 6 in. from the top. This procedure was not satisfactory, because each time a new batch of liquid was added to the calciner violent foaming occurred which carried large amounts of original feed over into the off-gas system. This foaming and entrainment accounts for the large amount of ferric ion in the condensate and the low iron balance.

Table 7.1. Calcination of Darex Waste

Run	Feed Volume, liters	Type of Feed	Iron Balance, %	Particle Density, g/cc	Bulk Density, g/cc	In Solid		
						% N, wt %	Vol. of Original Waste, %	Maximum Temp., $^{\circ}\text{C}$
1	48.0	A	58	2.0-3.0	0.9	0.34	-	730
2	18.4	A	56	2.0-3.0	0.9	0.09	-	822
3	20.6*	B	93	-	0.9	0.07	7.2	700
	Feed A	$\text{Fe}(\text{NO}_3)_3$	1.6 M	Feed B		$\text{Fe}(\text{NO}_3)_3$	2.2 M	
		$\text{Ni}(\text{NO}_3)_2$	0.17			$\text{Ni}(\text{NO}_3)_2$	0.23	
		$\text{Cr}(\text{NO}_3)_3$	0.38			$\text{Cr}(\text{NO}_3)_3$	0.51	
		$\text{Al}(\text{NO}_3)_3$	0.29			$\text{Al}(\text{NO}_3)_3$	0.39	
		HNO_3	11.7			HNO_3	0.00	

*Gas evolved was 324 liters.

For the third calcination test, feed was made up using neutral salts and water. The amount of water added to the neutral salt was the correct volume to produce a feed that corresponds with the acid-deficient point described in the previous section, that is when 77% of the liquid has been removed during evaporation of Darex waste. This waste was continuously metered into the calcining vessel using a finger pump.

The feed rate was adjusted to the condensate discharge rates varying between 50 and 60 ml per min for the entire testing period. The acid concentration of the condensate varied from 1.3 to 15.5 M nitric acid with an average of about 10 M nitric acid. The third test was the only test

in which the wet test meter functioned successfully. During the third test, 324 liters of noncondensable gas was evolved in the calciner.

When the calciner vessel was cut open after cooling, the solid had pulled away from the side wall (Figure 7.2).

7.2 Temperatures in Stored Radioactive Solids - J. J. Perona

Estimation of temperature rise in buried radioactive solids is necessary in order to evaluate the feasibility of proposed storage methods for solid wastes. The storage model used in the following calculations was an infinite cylinder of radioactive solid insulated from an infinite solid medium by an air space.

The effect of fission product distribution on maximum temperature rise was almost insignificant as the distribution varies in waste cooled from one to eight years. The percentage of heat generation rate for the various nuclides in one-, three- and eight-year cooled waste (assuming APPR irradiation conditions) are given in Table 7.2, showing Ce-144 decreasing from 71.9% in one-year cooled waste to 1.5% in eight-year cooled waste. Using equal total heat generation rates but varying the fission product distributions, the differences in maximum temperature rise were less than 3% between one- and three-year cooled waste and less than 7% between one- and eight-year cooled waste (Figure 7.3). The specific heat generation rates were calculated assuming APPR fuel reprocessed by the Drex process with a volumetric fission product concentration factor of ten in converting the liquid waste to solid. The thermal conductivity of the waste was assumed to be $0.1 \text{ Btu/hr(ft)}(^{\circ}\text{F})$, the convection coefficient in the air space $1.0 \text{ Btu/hr(sq ft)}(^{\circ}\text{F})$, and the infinite solid medium was assumed to be salt.

The effects on temperature rise of storage in media other than salt are shown in Figure 7.4. Assuming a waste cylinder 0.75 ft in diameter with a thermal conductivity of $0.1 \text{ Btu/hr(ft)}(^{\circ}\text{F})$, maximum temperature rise was calculated for storage in "average soil" ($k = 0.56 \text{ Btu/hr(ft)}(^{\circ}\text{F})$) and "average rock" ($k = 1.0 \text{ Btu/hr(ft)}(^{\circ}\text{F})$)¹. At a heat generation rate of 60 Btu/(hr)(gal) , maximum temperature rise was 1270°F in "average soil", 1150°F in "average rock" and 1020°F in salt.

¹H. S. Carslow and J. C. Jaeger, "Conduction of Heat in Solids", Oxford University Press, 1947, Appendix VI.

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8-in.-dia POT
SOLIDS 7.2% BY VOLUME OF FEED

Fig. 7.2. Calcined Darex Waste.

Table 7.2. Percentage of Heat Generation Rate
for Various Nuclides*

Nuclide	Cooled 1 yr	Cooled 3 yr	Cooled 8 yr
Sr 89	0.7%	-	-
Y 91	1.3	-	-
Zr 95	5.7	-	-
Ce 144	71.9	45.6	1.5
Ru 106	5.1	4.7	0.4
Pm 147	1.7	3.7	2.4
Sr 90	8.2	27.7	57.7
Cs 137	<u>5.4</u>	<u>18.3</u>	<u>38.0</u>
	100.0	100.0	100.0

*The decay energy from its daughters
was attributed to the nuclide.

Fig. 7.3. Maximum Temperature Rise as a Function of Radius, Showing the Effect of Cooling Time.

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Fig. 7.4. Maximum Temperature Rise as a Function of Heat Generation Rate, Showing the Effect of Storage Medium.

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