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CHEMICAL TECHNOLOGY DIVISION

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ABSTRACT

A concentration cell electrode was installed in a fritted glass surface and was used to measure the surface KCl concentration while water was being transpired through the surface into a mixed tank of 0.1 M KCl. The results from the first Fluorox run made with crude UF_4 showed that 85.3% of the theoretical amount of UF_6 was accounted for, with 17.9% being collected in cold traps and the remainder being consumed in various side reactions. Installation was completed of apparatus to study the electrolytic removal of nickel on an engineering scale from concentrated HRT fuel solution. An extremely low yield stress of 0.02 lb/sq ft was measured for a thorium-uranium slurry containing 2.5 wt per cent Al_2O_3 and spherical particles of 1.7 micron mean diameter. Preliminary data on the rate of uranium sorption on Dowex 21K from sulfate solutions were correlated with a simple spherical diffusion model. Laboratory scale studies to determine the effect of reflux time, HNO_3 concentration, and air sparge on chloride removal from APFR-type Darex dissolver product showed that an air sparge is definitely beneficial in chloride removal. Preliminary cyclic cleaning tests showed that boiling 25% caustic solution was adequate for cleaning type F (20 micron) porous metal filter elements fouled in the absence of filter aid with siliceous sludge from Darex solvent extraction feed solutions. Sections of unirradiated stainless steel-clad UO_2 , sheared into lengths of 1/2 in., 1 in., 2 in. and 2-3/4 in., were leached free of UO_2 with 10 M HNO_3 in 30, 45, 60 and 75 min, respectively. The abrasive blade cost for the removal of inert end adapters from selected reactor assemblies ranges from \$0.12 for the Gas-Cooled Reactor to \$1.19 for Consolidated Edison. A zirconium dissolution was carried to completion at 600°C in a NaF-LiF salt mixture containing initially 23 mol per cent ZrF_4 at an average rate of 1.3 mg/(cm²)(min) with an HF feed rate of 2 lb/hr. The thermal conductivity and thermal diffusivity at the center of an 8-in. diameter cake of Darex waste calcined at about 900°C were determined as a function of temperature.

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SUMMARY

1.0 CHEMICAL ENGINEERING RESEARCH

A method is under development to measure point electrolyte concentrations in a flowing system for application in a study of corrosion protection by transpiration of inert liquids. A concentration cell with an active electrode surface of 1 mm dia was constructed and tested with KCl concentrations from 0.1 M to 10^{-5} M. The Nernst equation was found to apply over the entire range. An electrode was installed in a fritted glass surface and used to measure the KCl concentration while water was being transpired through the surface into a mixed tank of 0.1 M KCl. At transpiration rates of 2 cm/min the measured wall concentration was 0.001 M.

2.0 FLUOROX

The results from the first run made with crude UF_4 (FER-23) show that 85.3% of the theoretical amount of UF_6 was accounted for with 17.9% being collected in cold traps and the remainder being consumed in various side reactions.

A crude UF_4 run of 29 hr duration (FER-24) was made in the 4-in. fluidized bed reactor. The Inconel corrosion rate was 6-7 mils/hr. A total of 7100 g of crude UF_4 was introduced to the reaction and 1180 g of impure UF_6 was collected in the cold traps.

3.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

Installation of apparatus to study the electrolytic removal of nickel on an engineering scale from concentrated HRT fuel solution was completed. Preliminary operation demonstrated the necessity of careful cell design to minimize electrolytic corrosion and stray currents. Use of thermal denitration of ThNT in an agitated trough was shown not to be a practical method of producing dense 50-500 micron ThO_2 spheres; fine ThO_2 of 0.5-20 micron diameter was produced.

Mixed oxides of U:Th = 0.08:1 and 2.5 or 5 wt per cent Al_2O_3 were prepared with spherical shapes by flame denitration of CH_3OH solutions of nitrate salts. Spheres were previously obtained for 10 wt per cent Al_2O_3 . An extremely low yield stress of 0.02 lb/sq ft was measured for a slurry of the 2.5 wt per cent Al_2O_3 spherical particles of 1.7 micron mean diameter.

4.0 ION EXCHANGE

Preliminary data on the rate of uranium sorption on Dowex 21K from sulfate solutions were correlated with a simple spherical diffusion model. Two runs made with different sized beads in the sulfate form and approximately the same solution concentrations (0.005 M in uranium, 0.020 M in sulfuric acid, and 0.20 M in total sulfate) gave essentially the same value for the diffusion coefficient (7.8×10^{-8} cm²/sec). However, when chloride beads were used the diffusion coefficient was slightly higher (10^{-7} cm²/sec).

5.0 POWER REACTOR FUEL REPROCESSING

5.1 Darex

A Reference flowsheet run was made with APPR dissolver product in the 4-in. I.D. equipment using dissolver product to which soluble sodium silicate solution (equivalent to 5 g/liter SiO₂ in the solvent extraction feed) was added to aid the precipitation of silica as SiO₂. The presence of the sodium silicate did not effect operations, and chloride was removed to 39 ppm in the solvent extraction feed. The silicate addition did not improve the removal of silica in a subsequent feed clarification step.

An over-all heat transfer coefficient of 450-500 Btu/hr-ft²-°F was measured in a titanium feed adjustment tank of the proposed APPR pilot plant design at a boiling water to steam temperature difference of 40-55°F.

Laboratory scale studies to determine the effect of reflux time, HNO₃ concentration, and air sparge on chloride removal from APPR-type Darex dissolver product showed that (a) an air sparge is definitely beneficial in chloride removal. The effect of a sparge rate of 7.9 liters air/hr liter dissolver product was approximately equivalent to refluxing at 0.4 liters condensate/(hr)(liter DP) with a nitric acid strength higher by two moles per liter; (b) a nitric acid concentration of 9 M or greater was required to reduce the chloride content to 50 ppm or less with or without sparging; and (c) no significant reduction in chloride resulted from sparge times in excess of 6 hr for acid strength above 9 M.

5.2 Sulfex

A survey of uranium loss data from 15 tests of decladding unirradiated SS-clad ThO₂-UO₂ pellets (Consolidated Edison) with 6 M sulfuric acid showed the soluble uranium loss varied from 0.02-0.24%. The average loss value was 0.08% with 80% of the samples 0.10% or less. The loss values reported are probably high since the contained uranium oxide in the prototype fuel used analyzed approximately UO_{2.75}. The fuel pins had been sealed in air rather than in helium.

5.3 Feed Clarification

Preliminary cyclic cleaning tests showed that boiling 25% caustic solution was adequate for cleaning type F (20 micron) porous metal filter elements fouled in the absence of filter aid with siliceous sludge from Darex solvent extraction feed solutions. When a porous metal filter which had not been backwashed was permitted to dry for four days without backwashing, severe fouling occurred which could be corrected by the caustic treatment.

5.4 Solvent Extraction Studies (Hanford Assistance)

Flooding determinations made with acid-deficient Darex-Redox type feeds (containing soluble silica) fed to a packed solvent extraction column showed that: (1) reducing the soluble silica content by a factor of 4 (0.016 M to 0.004 M SiO_2) increased the column throughput at flooding by a factor of 1-1/2 (333 GSFH to 484 GSFH), and (2) the addition of 100 ppm Mistron (insoluble calcium-magnesium silicate powder) to a feed containing 0.015 M soluble silica increased the throughput by a factor of 2-1/2 (333 GSFH to 815 GSFH).

5.5 Mechanical Processing

Core Leaching. Sections of unirradiated stainless steel-clad UO_2 , sheared into lengths of 1/2 in., 1 in., 2 in. and 2-3/4 in., were leached free of UO_2 with 10 M HNO_3 in 30, 45, 60 and 75 min, respectively. Seventy per cent was dissolved in 5, 23, 30 and 37 min. The over-all leaching rates were 0.033, 0.0225, 0.0166 and 0.0133 g/min/g of original U present. It appears that chopped lengths greater than 2-3/4 in. long will give greatly increased leach times.

SRE Decanner. The SRE decanning unit being fabricated by the Southern Machine Company of Chattanooga, Tennessee is approximately 75% completed. Several pieces of auxiliary equipment were designed, and a contract for fabricating a steam cleaning unit to remove NaK and oil from de jacketed slugs was let to the Brinkman Tool and Die Company, Inc., Dayton, Ohio.

Abrasive Sawing. The abrasive blade cost for the removal of inert end adapters from selected reactor assemblies ranges from \$0.12 for the Gas-Cooled Reactor to \$1.19 for Consolidated Edison. The measured volume of cutting waste (metal plus saw blade) produced for each assembly was 16.3 and 184 cubic centimeters, respectively. Cutting time, not including set-up or positioning of the blades, was approximately 1 min/assembly.

Shearing, and Solids Discharging Leachers. The experimental leacher installation in cell 4A was complete. This installation includes the spiral vibrating leacher and auxiliaries which can be used for evaluating either batch or continuous prototypes.

A calculated thrust of 270 tons based on experimental information is required for shearing all the seven fuel assemblies considered in this program providing only the Nuclear Ship Savannah fuel is quartered into subassemblies.

Preliminary data showed that a blade velocity of about 3 in./sec increased shear blade wear by increasing wiping damage to the blades. About 10% of the UO_2 dislodged from chopped single 0.5-in. dia tubes was less than 44 micron size. The use of porous bottom buckets was investigated for shearing in the presence of a spray and constantly removing the wash solution through a porous bottom collector. The addition of 13 liters of water was required to vacuum jet 192 g of stainless steel fines (1000 micron size) from a 10-in. dia round bottom tank simulating the 100 kg batch dissolver geometry. The fines were moved toward the vacuum line with directed streams of water from a header around the perimeter of the tank bottom.

6.0 VOLATILITY

6.1 HF-Fused Salt Dissolution of Zirconium

A zirconium dissolution was carried to completion at 600°C in a NaF-LiF salt mixture containing initially 23 mol per cent ZrF_4 which reduced the melting point to less than 600°C at an average rate of 1.3 mg/(cm²)(min) with an HF feed rate of 2 lb/hr. This rate is 10% higher than rates for the NaF- ZrF_4 salt at 650°C and 2 lb/hr HF rate in the same dissolver geometry.

6.2 Dry Hydrofluorination

A series of three runs were performed with 790 g Zircaloy-3 dummy fuel elements in a 66.7 mol per cent HF-33.3 mol per cent H_2 atmosphere. The results showed average gas-metal reaction rates of 1.44 mg/(min)(cm²), 2.19 mg/(min)(cm²), and 2.58 mg/(min)(cm²) with reactor wall temperatures of 550, 650, and 750°C, respectively, and an HF feed rate of 1.0 lb/hr. Maximum element temperatures remained below 925°C in all tests.

An attempt was not successful to cover an element surface with ZrF_4 reaction product at 300-500°C in order to reduce the reaction rate at 700°C and thereby control the maximum element temperature. At 700°C a rapid reaction, initiated from the center of the element, spread over the entire surface at a reaction rate of 9.7 mg/(min)(cm²) and an element temperature of 925°C.

6.3 Off-Gas Disposal Studies

Visual observations of flooding were correlated with pressure drop using a 3-in. I.D. glass column having an 18-in. packed section containing 1/4-in. fluorothene Raschig rings. A comparison of extrapolated liter-

ature data with these experimental data indicated that the gas flow rates required to flood fluorothene packing were slightly higher than the gas flow rates required to flood ceramic or metal packing. At a liquid flow rate of 537 lb/hr-sq ft fluorothene rings flooded at a gas velocity of 842 lb/hr-sq ft whereas steel rings flooded at a gas velocity of 716 lb/hr-sq ft. Experimental data for higher liquid rates must be obtained before a general comparison can be made.

7.0 WASTE PROCESSING

The thermal conductivity and thermal diffusivity at the center of an 8-in. diameter cake of Darex waste calcined at about 900°C were determined as a function of temperature. The experimental method involved following the temperature rise of an electrically heated small diameter metal tube in the center of the cake. The thermal conductivity increased from 0.042 to 0.11 Btu/hr-ft-°F when the average temperature increased from 120 to 480°F. For the same temperature range the estimated thermal diffusivity increased from 0.0037 to 0.0061 sq ft/hr, but may be in error due to a large heat transfer resistance between the heated tube and the cake.

1.0 CHEMICAL ENGINEERING RESEARCH

M. E. Whatley

Transpiration Corrosion Protection - W. M. Woods

The objective of transpirational corrosion protection is to protect a vulnerable surface from corrosion by transpiring a corrosive fluid through the porous surface to maintain a protective film on the surface.

King and Jury¹, Patrick and Bixler², Jury and Simpkins³ have reported experiments with $\text{Ni-HNO}_3\text{-H}_2\text{O}_2$ and Ni-FeCl_3 in both tubular transpirational flow and in stirred batch corrosion tests. In addition, Jury and King¹ used electrical conductivity measurements in tubular transpirational flow to measure the effective film thickness of the transpirational fluid. Corrosion rates in the Ni-FeCl_3 system were reduced by water transpiration to as low as 1/60th the rate without transpiration.

An understanding of transpirational corrosion protection involves an analysis of (a) the flow dynamics under transpiration; (b) the molecular and eddy diffusion of the corrodant (i.e., the transport relationships) and (c) the chemical kinetics of the corrosion reaction at the wall.

The first two are functions of system geometry, bulk Reynolds number, transpirational flow rate, properties of the two fluids, and the diffusivity of the corrodant. The last is a function of the material of the wall, the nature of the corrodant, the temperature, and the actual concentration of corrodant at the wall. This report describes a preliminary study to reduce the complexity of the entire problem by experimentally solving the flow dynamics and transport relations independently of the corrosion kinetics. The technique described involves the measurement of the concentration of a diffusing salt at a porous wall under transpiration conditions using a concentration cell.

1.1 The Potential of a Concentration Cell

For a uni-univalent electrolyte in a potential cell with the concentration C_1 at one electrode and C_2 at the other, and with identical rever-

¹King, C. J. and Jury, S. H., ORNL CF 57-9-32, Feb. 24, 1958, "Preliminary Studies of Transpirational Corrosion Protection."

²Patrick, S. B. and Bixler, H. J., KT-315, Dec. 20, 1957, "Transpirational Corrosion Protection."

³Jury, S. H. and Simpkins, G. R., ORNL CF 59-1-18, Oct. 23, 1958, "A Study of Transpirational Corrosion Protection in Porous Nickel Tubes."

sible electrode reactions involving the anion, the cell potential is given by the Nernst equation:

$$E = \frac{2t_+xRT}{F} \ln \frac{\gamma_1 C_1}{\gamma_2 C_2}$$

where

E = concentration cell potential, volts

t_+ = transference number for cation

R = gas constant

T = absolute temperature

F = Faraday's constant

γ = mean activity coefficient

C = concentration, molal

For the case of KCl at 298.16°K with a cation transference number, t_+ , taken as 0.490⁴ equation (1) reduces to:

$$E = 0.05797 \log \frac{\gamma_1 C_1}{\gamma_2 C_2}$$

Values of γ vs. concentration for KCl are shown in Table 1.1. Values of E_{CELL} , calculated from these data for various pairs of concentrations are shown in Table 1.2.

1.2 The Measurement of Wall Concentrations with a Concentration Cell

If a reversible electrode is placed in the bulk flow during a transpiration experiment, and the other is mounted exactly on the surface of a porous wall, it is possible to measure a potential between the electrode and calculate the concentration at the wall.

The major requirements for applying the concentration cell method are:

1. The development of a suitable reversible electrode having good reproducibility and an active surface of such a small size that it may be considered a point.

⁴Glasstone, Samuel, Elementary Physical Chemistry, Van Nostrand Co., New York, 1946, pp 410 and 484.

Table 1.1. Mean Activity Coefficients, γ
and Activities for Aqueous KCl Solutions
at 298.16°K⁴

<u>C, molal</u>	<u>γ (mean)</u>	<u>(C)(γ)</u>
0.001	0.966	0.000966
0.005	0.927	0.004635
0.01	0.902	0.00902
0.02	0.869	0.01738
0.05	0.816	0.0408
0.10	0.770	0.0770
0.50	0.652	0.326
1.00	0.607	0.607
2.00	0.577	1.154
3.00	0.572	1.716

⁴Glasstone, Samuel, Elementary Physical Chemistry, Van Nostrand Co., New York, 1946, pp 410 and 484.

Table 1.2. Concentration Cell Potentials
for KCl at 298.16°K

(Calculated from equation (1) using activities in Table 1.1)

C _W , molal	Cell Potential for Concentration Pairs, Volts							
	C _B , molal	3.0	2.0	1.0	0.5	0.1	0.05	0.01
0.001		0.18840	0.17840	0.1622	0.1466	0.1102	0.0943	0.0563
0.005		0.1489	0.1389	0.1227	0.1071	0.0707	0.0548	0.0168
0.01		0.1321	0.1221	0.1059	0.0903	0.0539	0.0380	0.0000
0.02		0.1156	0.1056	0.0894	0.0738	0.0374	0.0215	
0.05		0.0941	0.0841	0.0679	0.0523	0.0159	0.0000	
0.10		0.0782	0.0682	0.0520	0.0364	0.0000		
0.50		0.0418	0.0318	0.0156	0.0000			
1.00		0.0262	0.0162	0.0000				
2.00		0.0100	0.0000					
3.00		0.0000						

C_B = bulk concentration (C₁)

C_W = wall concentration (C₂)

2. The procurement of suitable instruments for measuring small voltages at essentially zero current flow through the meter.
3. The development of a method of installing the electrode at the surface of the porous wall.

It was found that a suitable electrode could be made from a No. 18 gauge pure silver wire completely covered with Eastman 910 adhesive except at the tip. No. 18 gauge wire is 1 mm in diameter. The uninsulated tip was then chlorided by electrolyzing in HCl. The resulting Ag/AgCl/Cl⁻ electrode is reversible, reproducible, and has been used extensively for chloride concentration measurements.

The major problem in instrumentation was to obtain a meter with a high sensitivity and a very high d.c. input impedance. Because of the small size of the electrode and the expected low concentration at the porous wall, the experimental concentration cell basically has a high internal resistance.

A bridge circuit and a slide wire potentiometer with a suspension type galvanometer to read the unbalance current was found to be unsuitable. A Leeds and Northrup K-3 potentiometer with a Leeds and Northrup Microvolt galvanometer was capable of reading potentials at concentrations as low as 10⁻⁴ molal within ± 0.05 millivolt. The rated input impedance of the Microvolt galvanometer is 1.8×10^7 ohms.

A Keithley Model 610 vacuum tube electrometer with a d.c. input impedance of 10¹⁴ ohms was the most satisfactory instrument tested. It was capable of reading potentials down to concentrations of 10⁻⁴ molal within ± 0.5 millivolt with the electrodes connected directly to the instrument. When used as a null galvanometer in conjunction with a potentiometer, potentials could be read down to 10⁻⁵ molal concentration. The electrometer has the advantage that its time constant is smaller than that for the Microvolt galvanometer so that more fluctuations in potential in flowing systems may be measured with it.

Figure 1.1 is a plot of potentials obtained vs. concentration along with the theoretical curve. These potentials were measured in a cell with a salt bridge in the absence of transpiration flow. There was a 10% deviation from the theoretical potential at $C_B/C_W = 10^4$ and essentially no deviation for ideality at $C_B/C_W < 10^2$.

The electrodes used to measure surface concentrations during transpiration were installed at a porous glass surface through small drilled holes. They were sealed in and secured with Eastman 910 adhesive with the tips uncoated. Figure 1.2 shows a schematic of an electrode installed in a porous glass disc.

Fig. 1.1. Cell Potential for Cell: $\text{Ag}, \text{AgCl} | \text{KCl}(0.1M) | \text{KCl}, C_K | \text{AgCl}, \text{Ag}$ at 298°K.

Fig. 1.2. Silver-Silver Chloride Electrode in Porous Glass Disk.

1.3 Experimental Results with Porous Glass Discs

All measurements were made with slab geometry in a batch of KCl electrolyte. A schematic representation of the apparatus is shown in Figure 1.3. The volume of the large battery jar was sufficiently large so that less than 10% dilution of the bulk electrolyte concentration occurred during a run.

Both electrodes were calibrated in a static salt-bridge concentration cell and they behaved normally. A preliminary transpirational run was made in which the transpirational fluid was 0.1 molal KCl, the same as the bulk concentration. The potential was essentially zero at zero transpiration flow and was independent of disc speed.

Transpirational flow produced a potential on the order of 0.0001 to 0.0002 volts at transpirational flows of 700 cc/hr. This potential varied directly with transpirational rate but was independent of disc speed. The cause of this small potential is not fully understood, but is probably associated with the streaming potential caused by flow through the porous glass. At any event, the effect was small compared to the concentration cell potentials that were expected.

The results of the first water transpiration runs are shown in Figure 1.4 where the EMF measured between the electrode in the transpiring surface and the electrode in the 0.1 molal KCl bulk solution is plotted as a function of the transpiration rate with the disc rotation speed as a parameter. These data vary as would be expected and show that the surface concentration decreased with transpiration flow rate and increased with disc rotation rates. Approximate wall concentrations may be obtained from Figure 1.1. For example, the KCl wall concentration was 0.001 molal for a disc speed of 246 RPM run and a 700 cc/hr transpiration flow rate, compared to a bulk concentration of 0.1 molal. This transpiration rate was equivalent to a linear velocity normal to the surface of 2 cm/min. Thus there was a 100/1 dilution at the wall. For 630 RPM at the same transpiration rate, the wall concentration was 0.03 molal, a dilution at the wall of 3/1.

If corrosion rates were linear with surface concentration, reductions in corrosion by factors of 3-100 would be expected in systems with similar flow dynamics and transport relationships. It is interesting to note that this range includes the factor of 60 previously measured by Jury and Simpkins.

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Fig. 1.3. Schematic Assembly: Slab Geometry Transpiration Experiment.

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Fig. 1.4. Concentration Cell Potentials vs Transpiration Flow Rate at Various Disk Speeds.

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 is the oxidation of UF_4 with oxygen, $2UF_4 + O_2 = UO_2F_2 + UF_6$, with subsequent recycle of the UO_2F_2 .

Fluidized Bed Development - C. D. Scott

The UF_4 oxidation process is carried out in a 4-in. fluidized bed reactor. Sized UF_4 is continuously fed into a UO_2F_2 bed which is fluidized in dry O_2 or air at 700-850°C. The UF_6 which is produced is removed in the off-gas stream and is subsequently recovered in cold traps.

2.1 UF_6 Production From Crude UF_4 Produced by Allied Chemical Corporation

The crude UF_4 from the unpurified mill concentrate produced by the Allied Chemical Corporation was used as feed material for FBR-23 and FBR-24 after screening to remove +20 mesh and -150 mesh material. A chemical analysis of this screened material showed the following composition:

UF_4	85.00%
UO_2	2.62%
UO_2F_2	2.94%
H_2O	0.52%
Other fluorides	8.92%

An analysis of the "as received" material, before sizing, was reported in the Unit Operations March monthly progress report (ORNL CF 59-3-61).

The fluidized bed throughput is dependent on reaction rate which is in turn dependent on temperature. The lower melting point of the crude UF_4 (730-740°C) as compared to purified UF_4 (> 850°C) restricted the bed operating temperature to a maximum of approximately 730°C. Test runs FBR-23 and FBR-24 were made to determine the feasibility of the production of UF_6 from impure UF_4 at "low" temperatures to observe the operation of the fluid bed reactor with a relatively high concentration of impurities.

2.2 Details of Run FBR-23

The first run with crude UF_4 (run FBR-23) lasted 13.5 hr. 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 was 97.2% (material leaving/material entering) with an over-all uranium material balance of 96.4% (see Table 2.1 and Figure 2.1). The apparent loss of 307 g of total material and 279 g of uranium may have been due to the loss of UF_6 which occurred when the thermowell and reactor developed leaks due to severe corrosion.

The UF_6 balance was 85.3% complete (Figure 2.2) with 17.9% of the theoretical amount of UF_6 formed being collected in cold traps and chemical traps. 67.4% of the UF_6 formed was consumed in side reactions: 10.9% reacted with water introduced with the feed, 3.7% reacted with oxide introduced with the feed, and 52.8% reacted with Inconel reactor and thermowell walls to form corrosion products. The apparent loss of 316 g of UF_6 from the system roughly checks with the total material and uranium unaccounted for in the over-all material balance.

The UF_6 product collected in the cold traps was contaminated with vanadium, 0.9%, which was present in the feed and chromium, 2.1%, which was a corrosion product. The analytical results also indicated that an appreciable amount of HF, 10.2%, was collected in the cold trap. The following is the probable composition of the product UF_6 :

UF_6	83.8%
HF	10.2%
Other fluorides, mainly CrO_2F_2 and VOF_3	6.0%

The apparent reaction rate constant (see Figure 2.3) as determined by:

$$k = \frac{UF_4 \text{ conversion rate}}{UF_4 \text{ inventory in the bed}}$$

was 1.3 hr^{-1} for the last 6.5 hr of operation when the average bed temperature was 723°C . This value for k is higher by a factor of 2.4 compared with laboratory data. This apparent high reaction rate may have been the result of the system not being at steady state, with the actual UF_4 concentration in the bed at the time of sampling being less than the steady state amount.

Corrosion in Run FBR-23. There appeared to be very high localized corrosion on both the lower reactor wall and on the lower portion of the thermowell in run FBR-23. A half inch hole was formed in the reactor wall and a 4-in. section of Inconel thermowell was badly corroded. Based on the leak which appeared in the 35 mil thermowell after 9.5 hr of operation, the corrosion rate was about 4 mils/hr. From the amount of corrosion products recovered from the system, the average corrosion rate for the Inconel fluid bed reactor at $710^\circ \pm 25^\circ\text{C}$ was about 0.7 mils/hr or 5.6 ipy. Thus,

Table 2.1. Change in Amounts of Individual Compounds in Run FER-23

Compound	Entering Reactor, g		Leaving Reactor, g		Change, g	
	Total	Uranium	Total	Uranium	Total	Uranium
UF ₄	4,074	3,088	239	181	-3,835	-2,907
UO ₂ F ₂	5,862	4,530	9,062	7,002	+3,200	+2,472
UO ₂	121	107	-	-	- 121	- 107
U ₃ O ₈	1	1	5	4	+ 4	+ 3
H ₂ O	24	-	-	-	- 24	-
Metal F	418	-	978	-	+ 560	-
UF ₆	-	-	384	260	+ 384	+ 260
HF	-	-	154	-	+ 154	-
O ₂ *	304	-	-	-	- 304	-
Metal**	325	-	-	-	- 325	-
Total	11,129	7,726	10,822	7,447	- 307	- 279

*Amount of O₂ theoretically necessary for the various reactions occurring.

**Amount determined from formation of new corrosion products.

Over-all material balance (material leaving/material entering) = 97.2%.

Over-all uranium balance (uranium leaving/uranium entering) = 96.4%.

Fig 2.1 Material Balance of the Constituents of Each Stream From run FBR-23.

Fig.2.2. Disposition of UF_6 Which was Formed in Run FBR-23

ALL FLOW RATES ARE AVERAGES BASED ON
THE LAST 6.5 HOURS OF OPERATION

$$\text{REACTION RATE CONSTANT, } k = \frac{288 \text{ g/hr}}{222 \text{ g}} = 1.3 \text{ hr}^{-1}$$

Fig. 2.3. UF₄ Material Balance Across the Fluidized Bed Reactor and Apparent Reaction Rate Constant for Run FBR-23.

the corrosion rate of Inconel was higher for crude UF_4 at $710^\circ C$ by greater than a factor of 10 compared to the corrosion by pure UF_4 feed at $800^\circ C$.

2.3 Details of Run FBR-24

Run FBR-24 was made to complete the evaluation of the use of crude UF_4 as the feed material to the Fluorox 4-in. fluidized bed reactor. The run was made with dry O_2 at a bed temperature of $710^\circ \pm 25^\circ C$ and an average feed rate of 309 g/hr. The total operating time was 29.5 hr with the feed being introduced during 24 hr of this time. The experimental apparatus and the operating procedure were similar to those used in runs FBR-22 and FBR-23 (UNOP monthly report for January 1959, ORNL CF 59-1-74). There was no downtime during the run and operation was smooth with the exception of a period of about 4 hr when there was a small pressure build-up due to accumulation of agglomerates in the bottom of the reactor. The run was terminated according to schedule after 24 hr of feed time.

A total of 7100 g of crude UF_4 was introduced to the reactor and 1180 g of volatile material was collected in the cold traps. The following material balance is available from initial experimental results:

Material introduced to reactor:

Initial bed	5940 g
Crude UF_4	<u>7100 g</u>
Total	13040 g

Material removed from reactor:

Final bed	7647 g
Overflow	2317 g
Samples from bottom reactor	1764 g
Material from cold traps	<u>1180 g</u>
	12908 g

The above material balance does not include the O_2 used in reactions, the HF recovered in chemical traps, or the Inconel metal which was corroded from the reactor and thermowell. Complete analytical results are not yet available from this run.

Corrosion in Run FBR-24. It was intended that outside reactor wall temperatures would be held below $750^\circ C$ to reduce the effect of corrosion; however, two hot spots developed on the wall due to scale accumulation at which temperatures were as high as $805^\circ C$.

A 1/2-in. diameter hole and 3 small holes were corroded in the lower reactor wall at about the same place as the hot spots. These holes were not detected until the reactor was cooled (about 4 hr after the crude UF_4 feed had been stopped). The 65 mil wall thermowell was corroded through after 7 hr of operation and there were no bed temperature measurements after that time.

When the reactor was opened, evidence of severe corrosion was found. The lower 6 in. of the thermowell and the two Inconel corrosion samples attached to the thermowell had totally disintegrated. From the above data Inconel corrosion was at a rate of 6-7 mils/hr.

After the hole in the reactor occurred, the part of the fluid bed above the hole was no longer fluidized and it loosely sintered into an easily broken-up cake while the bottom part of the bed remained fluidized. A large amount of scale and sintered bed material up to 1/4 in. thick accumulated on the reactor wall and partially plugged the solids overflow.

3.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

P. A. Haas

Methods are being developed for preparation and processing of solutions and slurries used for aqueous homogeneous reactor fuels and blankets. Direct denitration of thorium nitrate and/or uranium nitrate is being studied for the production of 1-10 micron oxide particles by flame denitration and 50-500 micron particles by agitated trough denitration. A multiple hydroclone and an electrolytic process for removal of nickel are being tested for application to HRT fuel processing.

3.1 Nickel Removal System - E. L. Youngblood, D. H. Newman

Construction of the system for electrolytic removal of nickel from simulated HRT fuel solution was completed^a. Preliminary runs using a uranium-free feed solution containing nickel, copper and manganese sulfate were made to check the performance of the equipment.

Twenty-five gallons of a light water solution of approximately the concentration given below was prepared for run No. 1.

0.24 <u>M</u>	H ₂ SO ₄
0.045 <u>M</u>	NiSO ₄
0.27 <u>M</u>	CuSO ₄
0.03 <u>M</u>	MnSO ₄

The system operated satisfactorily using the above solution for 771 ampere hours. The run was terminated because of an electrical short circuit in the cell due to a solid amalgam formation which grew from the mercury cathode to the anode located about 2-1/2 in. above the cathode.

Figure 3.1 is a photograph of the platinum anode used in the cell. The cathode is a pool of 0.63 gal of mercury at the bottom of a 6-in. diameter horizontal glass-lined tank. Analysis of the amalgam formation which caused the short circuit showed that it contained 2.1 wt per cent Cu and 0.19 wt per cent Ni while the average amalgam concentration was 0.92 wt per cent Cu and 0.18 wt per cent Ni. When the amalgam in the cell was mixed, a single phase was formed indicating that the amalgam formation which caused the short circuit might be eliminated by agitation of the mercury during operation.

^aFlow diagram in UNOP March monthly report, ORNL CF 59-3-61.

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Fig. 3.1 Head for Electrolytic Nickel Removal System.

A second run was made using the fuel solution left from run No. 1 with a fresh mercury cathode and an air sparger beneath the mercury to provide agitation during cell operation. Run No. 2 was satisfactory for 1236 ampere hours but was terminated because of an electrical short circuit similar to that in run No. 1. Additional tests will be made to determine the degree to which the mercury cathode can be loaded and the type of agitation necessary to avoid short circuits. The analysis of the fuel solution used in runs 1 and 2 and a list of the operating conditions of the cell are listed in Table 3.1. The nickel analyses in the first run are erratic, but the analyses in the second run indicate approximately an 80% removal of nickel and a 75% removal of copper.

Table 3.1. Conditions and Analyses
Electrolytic Nickel Removal Tests

Cathode current density:		0.15 amperes/sq cm		
Cell temperature:		20°C		
Cell voltage:		~ 10 V		
Cell current:		~ 200 amperes		
Cell efficiency (for runs 1 and 2):		64%		
U concentration:		None		
Run No.	Ampere-Hours	Fuel Solution Concentration (g/liter)		
		Cu	Ni	Mn
1	0	14.6	3.16	1.55
	310	10.9	1.82	1.43
	771	7.88	2.25	1.43
2	0	7.88	2.25	1.43
	203	6.05	1.33	1.37
	748	3.30	1.00	1.03
	1236	2.03	0.486	0.89

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

A run was made in the agitated trough calciner (UNOP monthly report for February 1959, ORNL CF 59-2-45) feeding an Al and Th nitrate aqueous solution to give an oxide product containing 5 wt per cent Al_2O_3 . The initial agitated bed was a mixture of Al_2O_3 and sand from previous operation of the trough. The trough temperature was maintained between 425 and 450°C, and the aqueous feed rate was 30 ml/min. Very little product was collected in the product receiver, and the packed glass column in the off-gas system was white with ThO_2 fines throughout the run.

From the results of this run and previously reported runs, the use of an agitated trough denitrator is not considered feasible for producing dense 50-500 micron diameter ThO_2 particles. There was a high yield of oxide fines in all of the Th runs with essentially no ThO_2 growth on the agitated bed particles. There are no future runs planned for denitrating Th in the agitated trough calciner.

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

Slurry properties of flame-fired thoria-urania are markedly affected by the presence of alumina. Surface areas may be lowered from 6-8 sq m/g without alumina to 2.0-3.0 sq m/g. Similarly, yield stresses may be decreased from 0.5-1.0 lb/sq ft range to values near zero.

Spherical particulates were obtained from a 1500°C firing of a system consisting of thorium-uranium-aluminum nitrates dissolved in CH_3OH (see Figure 3.2). The thorium and uranium nitrates were combined to give a U/Th ratio of 0.08, while sufficient aluminum nitrate was added to give concentrations between 1.0 to 10 wt per cent alumina in the product oxides.

Marked changes in the slurry properties of the particulates have been obtained as a result of the alumina addition (see Table 3.2). Compare the results of runs 52-4 and 63 with those of run 55, typical of a nonalumina bearing product. Yield stresses and surface areas were considerably lowered by the presence of the alumina. The particles shown in Figure 3.2 were obtained during run 63.

Two tests were made to increase production rate and to decrease the operating periods required for sample collection. A crude aspirating type torch was built based upon a commercial spray nozzle. The yield within the usable particle size range (< 5 micron) was trebled. Design of an improved torch of this type was completed and a model is being fabricated. Another alteration tested was to increase the diameter of the feed capillary from 0.016 in. to 0.032 in. and increase the feed rate. However, only one-half as much product within the usable size range was obtained.

A series of tests was made with water based feeds (ThNT solutions and thoria sols) to explore the possibilities of this type firing. The particles produced were rounded and had a "blackberry" surface under an optical microscope. The mechanical strength of the particles was poor, probably because of the low operating temperatures (maximum 1000°C). Water feed solutions or slurries produce much lower flame temperatures compared with methanol. However, the use of water feeds offers an advantage in that considerably higher salt concentrations can be used than are possible with methanol. A water solution above 1.5 M in thorium can be fed, while a 0.3 M thorium nitrate-methanol solution may be the maximum that can be used.

Two runs with a uranyl nitrate-methanol feed yielded samples for analysis of the U to O ratio of the product. One sample was contaminated with ThO_2 but the second attempt was successful. Two samples obtained in different locations within the equipment analyzed $\text{UO}_{2.88}$ and $\text{UO}_{2.88}$ indicating the formation of U_3O_8 .

CONDITIONS

U/Th MASS RATIO = 0.08
OUTSIDE REFLECTOR TEMP. = 1500°C
CLASSIFICATION = 95% < 5μ

OXIDE PROPERTIES

SURFACE AREA = 2.4 sq m/g
YIELD STRESS = 0.02 lb/sq ft
MEAN PARTICLE SIZE = 1.7μ

Fig. 3.2 Flame Calcined Thorium/Uranium Oxide Containing 2.5% Al_2O_3 .

Table 3.2. Flame Calcination Experiments
Effect of Alumina Addition on Slurry Properties
 Compositions: Th:U = 1.0:0.08 plus added oxides

Run No.	Reflector Temp., ^a °C	Nominal Alumina Conc., wt %	Particle Size Mass Average, micron	Yield Stress, lb/sq ft	Surface Area, sq m/g
52	1425	5	1.5	-	2.0
53	1400	10	1.8	0.2	5.7
54	1400	2.6 ^b	1.6	-	3.0
55	900	0	2.0	0.8	8.3
63	1530	2.5	1.7	0.02	2.4

^aFiring temperatures may be considered equal for all runs except run 55. Thermocouple location was changed for run 63.

^bThis product also contained 5.6 wt per cent SiO₂ and 1.1 wt per cent Na₂O.

4.0 ION EXCHANGE

M. E. Whatley

Exchange Mechanism and Kinetics Studies - J. S. Watson

Rational predictions of the operating characteristics of uranium anion exchange contactors require an understanding of the mechanism and kinetics of the exchange. In this study the equilibrium sorption isotherms and rates of sorption of uranium from sulfate solutions onto Dowex 21K anion exchange resin are being determined.

Kinetic studies were made of the rate of sorption of uranium on Dowex 21K from sulfate solutions by contacting a few resin beads with an enriched uranium solution in a stirred bath. Beads were removed from the bath at various times after the start of contact, and the uranium loading on each bead was determined by counting in a gamma spectrometer.

The results of the first three runs are shown in Figures 4.1, 4.2 and 4.3. The data were correlated with the simple model of single ion diffusion into a sphere with constant surface concentration. The solution used in all of these runs was approximately 0.005 M in uranium, 0.020 M in sulfuric acid, and 0.2 M in total sulfate. Evaporation of the solution caused some variation in the concentration during each run and introduced some uncertainty in the equilibrium loadings, but these effects were considered where possible in the calculations.

The correlating equation was:

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

where

M = loading

M_∞ = equilibrium loading

a = bead radius

t = time

D = diffusion coefficient

The first two runs were made with sulfate loaded beads of different average diameters, 1.161 mm ± 3.7% and 0.795 mm ± 3.9%. The mixer speed was also different in the two runs, 1650 rpm and approximately 1000 rpm. The few points available in the first run makes the exact shape of the curve uncertain. However, the curves for runs 1 and 2 are quite similar.

Fig. 4.1. Uranium Loading Curve from Run 1.

Fig. 4.2. Uranium Loading Curve from Run 2.

Fig. 4.3. Uranium Loading Curve from Run 3.

If the two curves were the same, the sorption rate would be independent of the stirrer speed and the apparent diffusion coefficient would be independent of the bead size. However, the two effects may be partially compensating.

If the sorption rate were independent of the stirrer speed, particle diffusion would be the controlling transport mechanism. In cation exchange resins, concentrations of several cations less than 0.1 M resulted in significant effects from film diffusion, but the studies generally involved much smaller beads and different resins and ions.¹ The only indication that film resistance may be contributing to the diffusion in the present system is a slight depression in the loading curve from the predicted curve for particle diffusion at low values of time.

The third run was made with resin beads initially loaded with chloride ions. The apparent diffusion coefficient for this run was slightly higher than in the previous run when sulfate loaded beads were employed. This result might be expected if the chloride diffusion coefficient was notably greater than that of the sulfate ion.

¹G. E. Boyd, A. W. Adamson, and L. S. Myers, Jr., J. Am. Chem. Soc., 69, 2836 (1947).

5.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

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

The purpose of the Darex process is to convert SS-U and SS- UO_2 fuels into chloride-free nitrate solutions suitable for processing in existing stainless steel solvent extraction equipment. Chloride is necessary for dissolution of stainless steel in HNO_3 but it must be removed to avoid corrosion of process equipment. In the present investigation, a batch flowsheet (Reference flowsheet - see UNOP March 1959 monthly report, ORNL CF 59-3-61) is being developed in which the dissolution product is treated with 61 wt per cent HNO_3 to produce solvent extraction feed solution which contains 2-3 M HNO_3 and less than 350 ppm chloride.

Chloride Removal and Feed Adjustment. A Reference flowsheet run (APPR-56) was made in the 4-in. I.D. pyrex feed adjustment tank using a dissolver product to which 80 cc of sodium silicate solution had been added (equivalent to 5 g/liter SiO_2 in the solvent extraction feed). The sodium silicate was added as a nucleus for precipitation of all soluble silica as SiO_2 in the dissolver product which should aid the subsequent removal of silica in a feed clarification step. However, the addition of soluble silica was not beneficial.

When the sodium silicate was added to the dissolver product prior to charging the feed adjustment tank, SiO_2 crystals formed almost immediately making the transfer of solution to the feed adjustment tank more difficult than usual. In normal operation, SiO_2 is precipitated in the feed adjustment tank without the addition of sodium silicate. The run was similar in all respects to runs APPR-52 -55 reported in the UNOP monthly report for March 1959 and chloride was removed to 39 ppm in the solvent extraction feed.

Titanium Feed Adjustment Tank. A titanium feed adjustment tank (see Figure 5.1) with 2 sq ft heat transfer area and a capacity approximately 4% of the proposed Power Reactor Fuel Reprocessing Pilot Plant tank was fabricated and installed in cell 1B of Building 4505 for evaluation testing. Figure 5.2 is a schematic diagram of the tank including the necessary auxiliary equipment. The tank was operated to determine: (1) characteristics of convective circulating and heating including over-all heat transfer coefficients, (2) operability with regards to foaming and bumping, and (3) chloride removal efficiency.

A series of tests was made to determine the over-all heat transfer coefficients for boiling water. The over-all heat transfer coefficients based on the overhead condensate and steam condensate are presented in Figure 5.3. Steady state values of 450-500 Btu/hr-ft²-°F were attained.

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Fig. 5.1 Prototype Titanium Feed Adjustment Tank.

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Fig. 5.2 Schematic Diagram of Titanium Feed Adjustment Tank.

Fig.5.3. Over-all Heat Transfer Coefficient as a Function of Temperature Difference for a Titanium Feed Adjustment Tank.

The over-all heat transfer coefficient increased with temperature difference resulting from an increase in the convection velocity of the water being heated.

Two Reference flowsheet runs were made using an initial DP charge of 10.8 liters. Chloride removal in the resulting solvent extraction feed to 423 and 206 ppm was achieved. There was some bumping of the tank solution particularly in the second run. Additional runs will be required to establish whether or not the bumping will be a serious problem.

Laboratory Scale Chloride Removal Studies. Five laboratory scale chloride removal runs were made to determine the effect of air sparging on chloride removal. With the exception of the air sparge, these runs were similar to the runs reported in the UNOP March 1959 monthly report, ORNL CF 59-3-61. The results of the five runs are presented in Figure 5.4 and a comparison of the runs made with and without air sparging are presented in Table 5.1. Air sparging produced a definite beneficial effect on chloride removal. The effect of the air sparge was approximately equivalent to refluxing for the same time without an air sparge with an acid solution 2 moles higher in nitric acid. For example, the chloride concentration in the DP with an initial 8 M HNO_3 concentration with air sparge was 0.034 M after 6 hr reflux as compared to the 0.064 M chloride in the 10 M HNO_3 DP after 6 hr reflux without air sparge.

Fig. 5.4. Darex Dissolver Product Chloride Concentration as a Function of Reflux Time for Various Initial Nitric Acid Concentrations Using an Air Sparge.

Table 5.1. Comparison of Chloride Concentration in Darex Dissolver Product
as a Function of Reflux Time and Various HNO₃ Concentrations

With and Without Air Sparging

Dissolver Product: 100 g/liter APPR metal loading, 0.58 M initial chloride concentration, and 8-14 M HNO₃

Condenser: Updraft with total reflux

Boil-up Rate: $\frac{1}{150}$ per min
 Liquid Volume:

Air Sparge Rate: $\frac{8.5}{1}$ per hr
 Liquid Volume

Initial HNO ₃ Conc., <u>M</u>	8		9		10		12		14	
	<u>Cl Content, <u>M</u></u>		<u>Cl Content, <u>M</u></u>		<u>Cl Content, <u>M</u></u>		<u>Cl Content, <u>M</u></u>		<u>Cl Content, <u>M</u></u>	
	No		No		No		No		No	
Reflux Time, hr	Sparge	Sparge	Sparge	Sparge	Sparge	Sparge	Sparge	Sparge	Sparge	Sparge
1	0.15	0.57	0.062	0.50	0.215	0.31	0.003	0.14	0.0005	0.022
2	0.08	0.54	0.03	0.42	0.0093	0.20	0.0007	0.04	0.00035	0.012
3	0.062	0.54	0.0176	0.38	0.0047	0.15	0.00051	0.0146	<0.00028	0.0037
4	0.048	0.54	0.0124	0.34	0.0024	0.11	0.00037	0.006	<0.00014	0.0018
5	0.0415	0.53	0.0095	0.31	0.0018	0.092	0.00034	0.006	<0.00014	0.0012
6	0.034	0.50	0.0072	0.30	0.0013	0.064	0.00028	0.0025	<0.00014	0.0007

5.2 Sulfex - J. B. Adams, F. L. Rogers, Jr.

Stainless steel clad $\text{ThO}_2\text{-UO}_2$ and UO_2 power reactor fuel may be reprocessed by the Sulfex process. The clad metal is dissolved in boiling 4-6 M H_2SO_4 ; the core is dissolved in nitric acid (for UO_2) or fluoride catalyzed nitric acid (for $\text{ThO}_2\text{-UO}_2$ mixtures). The application of the Sulfex process to Consolidated Edison fuel is being investigated.

Results of a total of 15 batch and semi-continuous decladding runs showed soluble uranium losses from 0.02-0.24%. The average loss was 0.08% with 80% of the samples 0.10% loss or less.

No consistent correlation of uranium loss figures with operating conditions could be made. It can be noted (Table 5.2) that in semi-continuous runs, longer decladding times with 3 and 4 M H_2SO_4 and resultant lower stainless steel loadings led to higher uranium losses (runs 15 and 16). However, other data (run 14) are contradictory. The same type of contradiction can be found in the batch data (runs 1-3) which were essentially identical tests, but produced widely varying uranium losses. In semi-continuous runs (runs 13-20) the small heel of liquid in the dissolver had approximately twice the uranium concentration of the composite sample for the complete run. This was true even in runs where extra pellet fragments were present during the entire decladding operation (runs 17-20).

The validity of the uranium loss data is dependent upon the properties of the pellets. Recent estimates* indicate the contained uranium oxide corresponds to approximately $\text{UO}_{2.75}$. Under the circumstances it is surprising that the uranium losses were not higher.

The prototype pins had been welded closed in air. The amount of oxygen contained within the jacket was estimated to be sufficient to cause a soluble uranium loss of approximately 0.06%, assuming an acid soluble coating of UO_3 formed on the pellet surface during thermal cycling.

More valid results should be obtained with a new batch of prototype pins now being made. Specifications call for approximately $\text{UO}_{2.01}$ based on total excess oxygen in both the ThO_2 and UO_2 powders used to make the pellets. In addition the pins will be sealed in a helium atmosphere to eliminate possible air oxidation.

The unirradiated prototype pins used in these tests were thermal cycled (heat soaked at 1100°F , then quenched in cold water for 5 cycles) to simulate pellet breakage due to thermal gradients and to develop an oxide coating on the cladding under simulated reactor exposure conditions. Disassembly and direct examination of a pin showed that little breakage resulted from this treatment. The same observation was made with pins that had been declad with sulfuric acid. A dense black coat of oxide was formed on the stainless steel clad. The unidentified black oxide was

*Verbal communication, L. M. Ferris, ORNL.

Table 5.2. Sulfex Decladding
of Consolidated Edison Unirradiated Prototype Fuel
Summary of Uranium Loss Data

Run No.	Run Type	H ₂ SO ₄ , M	Contact Time, min	Uranium Concentration (Composite Sample) in Decladding Solution, g/liter	Loss of Uranium to Decladding Solution, %	SS Concentration in Decladding Solution, g/liter
1	Batch	6	80	0.013	0.17	72
2	"	6	80	0.009	0.13	69
3	"	6	85	0.0052	0.07	65
4	"	5.1 ^a	90	0.007	0.08	89
5	"	5.1 ^a	90	0.005	0.05	105
11	Semi-Continuous	6	145	0.0014	0.05	50
12	"	6	100	0.0012	0.02	30
13	"	6	160	0.0015 ^c	0.03	53
14	"	3 ^a	180	0.0022 ^c	0.05	36
15	"	4 ^a	200	0.004 ^c	0.10	38
16	"	3 ^a	310	0.006 ^c	0.24	26
17	"	6	180 ^b	0.0017 ^c	0.04	35
18	"	6	140 ^b	0.002 ^c	0.04	50
19	"	6	170 ^b	0.003 ^c	0.06	46
20	"	6	160 ^b	0.003 ^c	0.06	48

^aReaction initiated by a small amount of 6 M H₂SO₄.

^bDissolver contained approximately 10 small fragments (0.35 g) of ThO₂-UO₂ pellets from a previous incomplete core dissolution.

^cUranium in the beel in the dissolver was approximately twice the concentration of the composite solution.

apparently insoluble in boiling sulfuric acid as it survived as an insoluble dispersion of fines in the decladding solutions.

The procedures for the decladding runs with Con Ed prototype pins* in boiling 3-6 M H_2SO_4 were as follows: the five batch runs were made by charging the pin to boiling H_2SO_4 in the 1" I.D. x 8" long dissolver and measuring the dissolution rate by the hydrogen evolution rate. In semi-continuous runs, the reaction was initiated in a small charge of 6 M H_2SO_4 and completed while feeding the desired strength of H_2SO_4 (3, 4 or 6 M) into the bottom of the reaction vessel at a rate of approximately 2.5 cc/min. The product solution overflowed through a side arm and seal leg. Hydrogen evolution rates were measured with a wet test meter.

A solution loading of stainless steel from 65-105 g/liter was obtained in batch runs and 26-53 g SS/liter in semi-continuous runs. Solutions of stainless steel in sulfuric acid precipitate on standing above approximately 70 g/liter (depending somewhat on the free acid concentration).

*0.31" dia x 7-3/8" long; ~ 44 g ThO_2 - 5% UO_2 pellets with 25 g of 304L SS.

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

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

Dissolver solutions resulting from the chemical dejacketing and/or core dissolution of spent power reactor fuels require clarification before they are discarded or reprocessed. Filtration of deacid solution and subsequent wash solutions is necessary to recover undissolved particles of fissile and fertile core material dislodged during the deacid step. Likewise, dissolved core solutions or solutions resulting from the total dissolution of spent fuel are filtered to recover undissolved particles of fissile and fertile material and to remove emulsion formers.

Renewable sand filters have been investigated for this purpose previously and were shown to be promising. However, criticality considerations (i.e., obtaining a large filtration area in a 5-in. diameter cylindrical vessel) prompted an investigation of micrometallic filters.

Cleaning tests using boiling caustic were made with a porous stainless steel filter, type F (20 micron), fouled with siliceous sludge from batch filtrations of 700 ml quantities of Darex solvent extraction feed solution. Results (Table 5.3) show that a 10-min submergence in a boiling 25% caustic (NaOH) solution restored the throughput of filtrate to that measured prior to the fouling step. If a used filter which has not been backwashed with water is allowed to dry, significant fouling results. Backwashing with water or steam and water is effective in removing filter cake but it does not significantly reduce fouling.

In these tests an uncoated 20 micron Grade F micrometallic filter was tested. The filter had previously been partially fouled from filtering siliceous bearing Darex solutions. Filtration times for plain water and silica-free Darex solutions were not measured prior to this partial fouling.

Filtration measurements were made with this used filter over several progressive steps of filtration, backwashing, and cleaning (see Table 5.3). Water backwashes of short duration (1-2 min) to remove filter cake was made after each filtration. A 700 ml quantity of silica-bearing Darex solution was filtered in each test.

Table 5.3. Stepwise Fouling and Cleaning Testing
of a Grade F (20 μ) Micrometallic Filter

Conditions:

Fouling medium - precipitated silica (~20 g wet solids/liter)
 to give a cake thickness of ~ 1/16".

Filter Average:^a 0.18 sq ft

Solution: Darex solvent extraction feed solution - 40 g
 SS/liter, 5 g U/liter, 2.5 N H⁺ at 25°C;
 ρ = 1.21 g/cc μ = 1.9 cp.

Volume of solution filtered each filtration: 700 ml

Pressure difference across filter: 5 in. Hg

Progressive Step Filtration, Cleaning or Fouling	Number of Filtrations	Average Filtra- tion Time, sec ^b
1. Filtration of Darex solution Filter backwashed to remove cake with steam and water.	6	187
2. Filtration of Darex solution Filter backwashed with water to remove cake and dried at 25°C in air for 48 hr.	1	186
3. Filtration of Darex solution Filter backwashed with water and steam to remove filter cake.	4	225
4. Filtration of Darex solution Filter cleaned by immersion for 15 min in boiling 25% NaOH.	2	233
5. Filtration of Darex solution Filter backwashed with water to remove cake and submerged in water 48 hr	3	153
6. Filtration of Darex solution Filter backwashed with water to remove filter cake and dried in air at 25°C for 11 days.	1	147
7. Filtration of Darex solution Filter backwashed with water to re- move filter cake and cleaned by immersion for 10 min in 25% boiling NaOH.	2	161
8. Filtration of Darex solution Filter backwashed with water to re- move filter cake and cleaned by immersion for 10 min in 25% boil- ing NaOH.	3	150

Table 5.3. Stepwise Fouling and Cleaning Testing
of a Grade F (20 μ) Micrometallic Filter (Contd)

Progressive Step Filtration, Cleaning or Fouling	Number of Filtrations	Average Filtra- tion Time, sec ^b
9. Filtration of Darex solution Excess cake scraped from ele- ment (not backwashed); element allowed to air dry.	3	149 sec
10. Filtration of Darex solution Filter backwashed with water to remove filter cake and cleaned by immersion for 10 min in 25% boiling caustic.	1	265 sec
11. Filtration of Darex solution	6	138 sec

^aMicrometallic Corp.; cylindrical element No. C-14-6, 316 SS, Grade F porosity, 20 micron mean pore opening.

^bTime required to filter a 700 cc batch of Darex solvent extraction feed solution (H8-5-A) under 5 in. Hg vacuum; no filter aid addition or pre-coat used.

5.4 Solvent Extraction Studies (Hanford Assistance Studies) - R. J. McNamee, F. L. Rogers, K. Ladd, R. O. Payne

The purpose of these solvent extraction studies is to obtain performance data from a packed solvent extraction column to assist in the adaptation of the Redox process to the reprocessing of SS-U power reactor fuels.

Two flooding studies were made during the current Hanford Assistance Program. The purpose of the studies was to define the effect of soluble silicon in dissolved stainless steel-uranium extraction feed (Darex) on column capacity, and to determine the effect on column capacity of adding Mistron, an insoluble calcium-magnesium silicate (approximately 25 micron) powder to the feed. As had been stated previously, column capacity decreased with increasing soluble silicon content. The addition of Mistron greatly increased column capacity (by a factor of approximately 2.5).

The feed for run 3h-6 contained 0.004 M soluble silicon. The column flooded at a feed rate between 160 and 167 ml/min (see Figure 5.5)* corresponding to an average total throughput of 484 GSFH. An earlier comparable run with feed containing 0.016 M silica resulted in flooding at an average throughput of 333 GSFH.

*For a discussion of the method of flooding rate determination, see ORNL CF 56-4-210. Criteria used are deviation from linear steady state solvent hold-up, and unsteady state hold-up behavior.

Fig.5.5. Flooding Rate Determination: Solvent Hold-Up vs Column Throughput.

The run 3h-5 feed contained 0.015 M soluble silicon to which was added 100 ppm Mistron. Flooding occurred at a feed rate between 250 and 300 ml/min (see Figure 5.5), corresponding to an average total throughput of 815 GSFH, the highest throughput of any previous test. The Mistron treatment appears to be very effective in reducing the effect of dissolved silicon on the capacity of a packed column.

5.5 Mechanical Processing - J. B. Adams, G. K. Ellis, G. A. West, D. E. Willis

Mechanical processing of power reactor fuel may reduce the quantity of inert structural material processed chemically in a fuel recovery plant, increasing plant capacity and reducing the volume of waste streams to be stored. The purpose of this program is to evaluate various mechanical methods of fuel processing and to demonstrate selected methods with irradiated fuel for: (1) removal of inert end adapters and other structural material; (2) the disassembly of fuel assemblies into appropriately sized subassemblies; (3) the shearing and leaching of assemblies or subassemblies; (4) the dejacketing of individual fuel elements; and (5) the disposal of jackets freed from fissile and fertile material.

Shearing Thrust Calculations. A minimum thrust of 270 tons is required to shear the seven assemblies considered in this program (Table 5.4) if the Nuclear Ship Savannah is reduced to subassemblies. This thrust was calculated from an experimental thrust measurement of 80 tons required to shear a Mark I prototype fuel assembly. The separate contributions of metal and porcelain to the total thrust requirement for shearing were calculated using the revised Hanford shear data in which S_c for porcelain (or UO_2) was 9000 psi and S_c for 304L stainless steel was 57,000 psi. The calculated total thrust checked the experimentally determined 80 tons within the limits of experimental accuracy. A thrust of 367 tons required for the Nuclear Ship Savannah assembly is the maximum thrust requirement if no disassembly is made.

A Mark I prototype was sheared at blade velocities of about 3 in./sec with a 125-ton Manco shear. This higher velocity closed the tube ends less than previously experienced, but it may increase blade wear by increasing wiping damage to the blades. At this velocity, there was an impact sufficient to cold weld the wiped pieces in place on the blade surface. A bin was designed to enclose the shear during cutting with either the batch or continuous leachers to evaluate shearing in a dry isolated atmosphere and under a water spray. A fuel assembly pressing and holding device to operate with the shear was designed and fabrication is 30% complete. Initial fabrication of two "plane of contact" blades was completed for use in the 125-ton Manco shear but because of a design error, reworking in the shops was required which is 50% completed.

Shear Blade Evaluation. The feasibility of "chopping and leaching" spent power reactor fuel depends largely upon an experimental demonstration of an acceptable shear blade life. An experimental program has been initiated primarily to measure the shear blade life on the Mark I prototype,

Table 5.4. Thrust Requirements for Shearing Fuel Assemblies
of Interest in the Mechanical Processing Program

Basis: One Fuel Assembly	Basis for Thrust Calculations				Total Shearing Thrust	
	Stainless Steel (304)		Ceramic			
		(a) Shearing Thrust Requirement		(b) Shearing Thrust Requirement		
	Fuel Type	Cross-Section	S _c = 57,000 psi	Cross-Section	S _c = 9,000 psi	(a) + (b) ₁ Calculated ¹
	sq in.	tons	sq in.	tons	tons	tons
Mark I Prototype	1.835	52.3	5.22	23.5	76	80 ²
Nuclear Ship Savannah	9.27	264	22.9	103	367	-
Yankee	6.27	179	20.25	91	270	-
FWR Blanket I	3.86	110	12.05	54.2	164	-
Consolidated Edison	3.72	106	11.28	50.8	157	-
Commonwealth Edison	2.01	57.2	7.07	31.8	89	-
Rural Co-op	0.675	19.25	3.25	14.62	34	-

¹Considering only the metal in tube walls and the ceramic, and neglecting cross section of ferrules and straps.

²The same total shearing thrust was required within the limits of experimental error at a ferrule as a nonferrule cross section.

but also to study the effect of blade shape and velocity on blade life, tube end closure, and material transfer of the assembly through the shear. Fabrication of eight pairs of different shaped blades (consisting of a punch and anvil each) and 2 die sets, with provision for interchange of most punches and anvils, is approximately 50% completed. Research contracts to supplement the ORNL program have been let to Birdsboro and Clearing Machine Company for shear blade studies. These studies will start as soon as prototype fuel assemblies are available from Continental Technical Services of Cleveland, Ohio. The Birdsboro development proposal and the design of three sets of experimental blade designs has been approved. Consideration is now being given the Clearing proposal.

Procurement of a 200-ton surplus press was cancelled because of excessive delay in obtaining it. Studies requiring this size press have been included in the Clearing and Birdsboro programs.

Collection and Transfer of Sheared Fuel. One of the most difficult problems associated with chopping and leaching is a means of remotely transferring and collecting sheared solids. Clad rod fuel enters the process as the complete fuel assembly and leaves as sheared disposable empty cylinders and metal fines from which the fissile material has been leached. The most difficult intermediate problems are:

1. Holding the end of the fuel assembly for the last shear cut.
2. Collecting the chopped pieces from the shear in a bucket and transferring the container to the leacher without spread of radioactive contamination from either the shear enclosure or the bucket.
3. Decontamination of the inside enclosure around shear and fuel assembly feeding box for either maintenance or insertion of additional fuel assemblies.
4. Providing access of acid to the fuel in the leach bucket.
5. Transfer of leached cylinders from the leacher to disposal.
6. Transfer of stainless steel or zirconium fines from the leacher.

The simplest experimental approach is shown in schematic form in Figure 5.6. It is proposed to use the 125-ton Manco shear previously described, shearing in a dry isolated atmosphere into a wire mesh bucket (1000 micron openings in the wire mesh) around which there has previously been inserted an aluminum foil preformed bucket. A slide valve would be closed after the bucket is filled, isolating the container from the shear. Then a water spray from nozzles under the valve would wash off all surfaces around the underside of the valve and wet the fuel in the bucket to minimize air contamination.

Access of acid to the fuel in the dissolver would be obtained by dissolving the aluminum foil in the nitric acid containing 0.005 M HgNO_3 to

Fig 56 An Experimental Approach for Shearing in a Dry Isolated Atmosphere

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catalyze the aluminum-nitric acid reaction. Stainless steel or zirconium fines which pass through the 1000 micron holes would be jetted from the dissolver with the uranyl nitrate dissolver product solution and removed in a feed clarification step.

Tests were conducted to determine the extent to which UO_2 pellets would be crushed to form a fine powder when sheared inside stainless steel tubes (Yankee Atomic-type fuel).

Thirty per cent of the separated UO_2 in Table 5.5 or approximately 10% of the total available UO_2 was less than 44 micron size in 150 cuts at 0.5-in. lengths of 0.5-in. dia single UO_2 filled stainless steel tubes. Fines resulting from shearing are probably best handled by shearing in a dry atmosphere and dropping the product directly into a bucket below. Caking of powdered fuel throughout the shear enclosure might result from shearing under water, and the use of additional water to wash out the cake at frequent intervals would complicate the filtration step which may not be necessary in a dry environment.

Filtration would be required if large volumes of water were added to the enclosure around the shear head as the fuel shearing progressed. For example, water might be sprayed on the cutting surfaces and drained together with wetted powder through a porous collection bucket.

Two preliminary tests were carried out with 10 sq in. Poromesh filters of nominal 150 and 5 micron pore size using water at a 7-in. head. The initial flow rate through both filters was in excess of 1 liter/min·sq in. The nonmagnetic stainless steel fines from 2 Mark I prototype fuel elements (see Table 5.3, UNOP monthly report for March 1959, ORNL CF 59-3-61, for distribution of particle size for magnetic and nonmagnetic fines) were added evenly over the 150 micron filter surface and the flow measurements were repeated. The flow rate was reduced to 0.2 liters/min·sq in.

The experiment was repeated with the nonmagnetic fines from 1.4 Mark I prototypes distributed on the 5 micron filter. The flow rate was again reduced to approximately 0.2 liters/min·sq in. After backwashing with water, the initial pressure drop-flow rate relationship was restored.

Prototype Fuel Procurement. Porcelain-filled and UO_2 -filled prototype fuel assemblies are required in the shear program primarily for determining the effect of shear blade shape and velocity on blade life, and to furnish feed for evaluation of the performance of specific batch and continuous solids prototype discharging leachers. One hundred prototype fuel assemblies are being fabricated by contract with Continental Technical Services of Dayton, Ohio who sub-contracted the assembly and brazing to the Ferrotherm Company of Cleveland, Ohio.

The first of 50 Mark I porcelain-filled prototype fuel assemblies was assembled and microbrazed by the Ferrotherm Company for the purpose of developing a suitable brazing procedure. The proper brazing atmosphere

Table 5.5. Size Distribution of UO₂
Separated from 0.5-in. Sheared Lengths
of Single 0.5-in. Dia Stainless Steel Tubes
Filled with UO₂ Pellets

Conditions: (a) Shear - 1-1/2" Manco
 (b) Blade type - "line of contact"
 (c) 150 cuts

Tensile strength of UO₂ 5-10,000 psi
 Compressive strength of UO₂ 90,000 psi
 Flexural strength of UO₂ 10-20,000 psi
 Hardness strength of UO₂ 7-9 moh scale

Particle Size, microns		Wt, g	Per Cent
Over	Under		
2000		0	0
840	2000	15.6	5.1
590	840	22.7	7.43
420	590	23.0	7.53
250	420	31.7	10.37
177	250	25.3	8.28
149	177	12.6	4.12
125	149	15.1	4.94
105	125	18.4	6.02
88	105	10.6	3.47
74	88	14.1	4.61
62	74	16.2	5.30
53	62	0	0
44	53	8.8	2.88
-	44	<u>91.5</u>	<u>29.94</u>
		305.6	100.0

was not maintained since the braze alloy did not flow into the brazing joints at 4 or 5 ferrule locations and end pins. The procedure was modified to correct this problem.

Starting April 27th, when the completed tool jigs are available, the production rate will be about 10 assemblies per week. Porcelain rods through the 1/8 in. thick stainless steel end plates at either end of the Mark I assembly will be replaced by iron pins to eliminate the problem of simultaneously sawing through porcelain and metal, a condition which is not representative of any real fuel assemblies of concern in this program.

Solids Discharging Leachers: Batch Leaching. Three batch dissolving runs, each with 0.5 kg UO_2 , were made using lengths of 0.5-in., 1.0-in. and 2.75-in. sheared pieces of 0.5-in. dia stainless steel tubing filled with UO_2 pellets. One 0.5-in. long end cap section with the "open" end a slit 1/32 in. wide was leached free of UO_2 after 2 hr in boiling 13 M HNO_3 (reduced to 11.1 M after 2 hr) and one additional hour at boiling in a new 13 M rinse solution. No foaming was observed when the UO_2 dissolution was started at room temperature. Analytical results from these runs are not yet available.

A preliminary experiment was performed to determine if insoluble stainless steel fines of 1000 micron size or smaller (the size range expected to result from a shearing operation) could be vacuum jetted from the bottom of a 10-in. dia round bottom glass tank simulating the 100 kg batch dissolver geometry. One hundred ninety-two grams of fines equivalent to the stainless steel fines from 8 Mark I assemblies were removed through a centrally located vacuum line in the tank bottom by propelling the fines to the center with directed streams of water from a header around the perimeter of the tank bottom. The addition of 13 liters of water was required to remove the fines.

The free settling velocity of 1000 micron size particles is 0.035 ft/sec from the Stokes Law equation assuming a spherical shaped particle. This velocity requires a minimum mass flow rate through a 0.5-in. schedule 40 pipe, such as exists in the batch dissolver, of 0.33 gal/min.

Solids Discharging Leachers: Continuous Leachers. The basic installation was completed for the spiral vibrating leacher and the auxiliaries which will be used for either batch or continuous leachers. A concept for feeding a continuous leacher at a uniform rate was completed and detailed drawings are being made. Sheared solids will be transferred by gravity from the shear to an enclosed vibrating conveyor and drop at a measured rate into the dissolver. The shear enclosure is vented through the dissolver.

Construction of the rotating drum leacher is scheduled to start on May 7. Detailed and assembly drawings have been completed for the American Machine and Foundry type turning screw dissolver, but there are no plans to fabricate it at this time.

Fuel Disassembly. The primary approach to Mechanical Processing includes shearing the full assembly with end caps removed except the Nuclear Ship Savannah which will be quartered. However, disassembly into slabs and individual elements is being considered as a possible alternate approach.

- (a) Slabbing of Assemblies. An interesting conceptional design has been completed of a production model machine for disassembly of fuels into slabs of elements and then into individual elements by the impact wedge technique. This machine will not be designed and fabricated unless disassembly into slabs or individual elements prior to shearing becomes a necessity. The existing portable impact wedge described in the March UNOP monthly report will probably be sufficient for use in the present program.
- (b) Mechanical Equipment for the Interim Plant Canal. A design study is being made of methods for the removal of end boxes from the Yankee and Commonwealth Edison fuel assemblies by an underwater saw. These assemblies could then be quartered by sawing or an impact wedge to a size which would fit into the 5-in. dia APPR dissolver for complete dissolution.
- (c) Multipurpose Saw. A contract has been let to the Ty-Sa-Man Co. for the design and construction of a variable speed multipurpose saw for use in the segmenting cell to remove nonfuel bearing inert hardware such as end boxes, banding straps and end plates. This radial type saw will operate either as an abrasive or friction tool at speeds varying from 500-3600 rpm at the saw arbor.

High Level Segmenting Facility. Irradiated fuel assemblies of interest to the Mechanical Processing program will be sheared in cell A and leached in cell B of Building 3048. A revised specification has been issued for the production prototype shear to be installed in cell A.

Process equipment for cell B including a batch leacher, caustic scrubber, recycle tanks, acid, caustic and rinse solution mixing tanks, and an 8 station sampler system have been designed. The reflux condenser design is being completed. Piping and final layout and unitization of the equipment components for easy removal will be started upon completion of the condenser design.

A tentative layout has been selected for location of the dissolver, caustic scrubber and recycle tanks in cell B-1. The mixing tanks will be placed on the roof of the cell for gravity flow to the equipment in the cell. The product storage carrier will be located in the discharge room behind lead shielding. The leaching flowsheet has been revised to add acid to the leacher through the recycle tank using a steam jet. A chemical procedure has been established using Turco decontamination on the inside and outside of equipment. Design of the equipment for decontamina-

tion has been begun.

Abrasive Sawing. The cost of blades consumed and the amount of waste produced in removing inert end adapters from typical reactor fuel assemblies was computed for Ty-Sa-Man abrasive saw with a 16 in. diameter Manhattan No. 239 blade. Calculations based on previous cutting rates show that cost of the abrasive blades consumed would range from \$0.12 to \$1.19 per assembly and the volume of waste produced will be from 16.3 to 184 c.c. or 123 to 1252 g/assembly (Table 5.6). The actual cutting time (not including set-up time) would vary from 0.1 to 1.0 min based on a feed rate of 30 in./min. A feed rate of 30 in./min produced satisfactory cutting at a wear ratio, by volume, of 1 to 3.5 parts blade consumed per parts metal removed.

The high cost value obtained for cutting a Consolidated Edison assembly is the result of a large cross section and the number of cuts required which necessitates frequent blade changes if the cross section is to be completely severed in two cuts. Actually, the replaced blades are only slightly consumed and if salvaged and used for cutting fuels of smaller cross section would result in a marked decrease in cutting cost. Approximately 52 gas-cooled reactor assemblies can be cut with one blade as compared to only five Consolidated Edison assemblies (see Table 5.6).

Leaching Studies. The rate at which unirradiated UO_2 is leached from selected lengths of sheared stainless steel-clad UO_2 pellets in boiling 10 M HNO_3 (150% excess) was measured in bench scale studies to obtain data for the design and operation of experimental leachers. Instantaneous and average leach rates were measured for four different sheared lengths, 1/2 in., 1 in., 2 in., 2-3/4 in., with the fines dislodged from the shearing operation included in each batch. These measurements were similar to those reported in the March report except that larger quantities of sheared pieces were used in the experiments.

The 10 M HNO_3 dissolvent was reduced to 6 M after complete reaction of each batch of the 1/2 in., 1 in., 2 in. and 2-3/4 in. sheared lengths in 30, 42, 55 and approximately 75 min, respectively. Seventy per cent of the core material was dissolved in 5, 23, 30 and 37 min (Figure 5.7 and Table 5.7). The average leaching rate was 0.033, 0.023, 0.017 and 0.0133 g/min/g of original U (Figure 5.8, Table 5.7).

The amount of core material dissolved during the first 10-min period, when the solution temperature was increased from 25-105°C, was 26, 8.5, 6.5 and 4.0 g/min on the 1/2 in. to 2-3/4 in. lengths, respectively (Table 5.7). The fast initial rate on the 1/2 in. sheared lengths resulted from the higher percentage of UO_2 (25%) dislodged during shearing of which approximately 55% was less than 149 microns in size. The UO_2 dislodged in shearing the 1 in., 2 in. and 2-3/4 in. lengths was 16, 6 and 5%, respectively. The effect of sheared length on leaching rates appears to be small over the lengths tested. However, in Figure 5.8 the correlation indicated that there may be excessive leach time for lengths much greater than 2-3/4 in.

Table 5.6. Disassembly of Stainless SteelFuel Assemblies by Abrasive Sawing

1. Abrasive - Manhattan No. 239 blade, 16 in. dia x 1/8 in. thick - cost \$5.98 each
2. Operating Speed - 10,450 SFPM
3. Feed Rate - 30 in./min
4. Wear Ratio - 1 to 3.5 (parts abrasive consumed/metal removed)

	Reactor						
	Consolidated Edison	Nuclear Ship Savannah	Rural Co-op	Yankee Atomic	SRE	Gas- Cooled Reactor	Common- wealth Edison
Assembly cross section, in.	5.755 sq	8.9 sq	3.87 sq	7.66 sq	2.79 dia	3.1875 dia	4.4 sq
Material	S.S.	S.S.	S.S.	S.S.	S.S.	S.S.	Zr-2
Number of rods to cut	824	42	50	50	7	14	144
Rod O.D., in.	0.3	0.6	0.45	0.4	0.375	0.750	0.310 and 0.570
Depth of cut, in.	2.86 ¹	4.5 ¹	3.87 ²	3.83 ¹	2.79 ²	3.1875 ²	2.2 ¹
Usable blade radius, in.	2.26	0.625	1.25	1.3	2.33	1.94	2.9
Metal waste, cc	143	24.4	16.3	12.9	15.8	12.7	48.9
g	1142	196	130.4	107	127	101.6	313
Abrasive waste, cc	41	8.15	4.66	3.7	4.53	3.63	14
g	110	18.9	12.6	11.6	12.2	9.8	37.7
Total waste, cc	184	32.55	20.96	16.6	20.4	16.3	62.9
g	1252	217	143	118.6	139	111.4	357
Number of Assemblies cut/blade consumed	5	5.5	27.2	38.3	46.6	51.7	18.1
Cutting time ³ , min	1.0	0.6	0.26	0.51	0.1	0.21	0.59
Number of cross-sectional cuts	6	2	2	2	1	2	4
Abrasive blade cost, (\$)/assembly	1.19	1.09	0.22	0.16	0.13	0.12	0.33

¹Assembly rotated for 2 cuts.²Cut complete in one pass.³Cutting time only - set-up time not included.

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CONDITIONS

VOLUME TO MASS RATIO: 2.5 ml/g UO_2
CLAD: 304-L SS, 0.40-in. O.D. WITH 0.010-in. WALL
PELLETS: $\sim$ 0.370-in. O.D., SINTERED, UNIRRADIATED

Fig. 5.7. HNO_3 Leaching of Sheared SS Clad UO_2 vs Time.

Table 5.7. Leaching Rate of Various Sheared Lengths
of Stainless Steel Clad UO₂ in Nitric Acid

Conditions: (1) Volume to mass ratio: 2.5 ml/g
(2) Clad: 304-L SS, 0.400 in. O.D., 10 mil wall
(3) UO₂ Pellets: 0.370 in. O.D.
(4) Dislodged UO₂ particles from shearing were included

Sheared Length, in.	% of UO ₂ Dislodged	Initial Mass, g	Mass Dissolved, g	Temp., °C	Time, min	Reaction Rate		H ⁺ , N
						Instantaneous, g/min	Over-all Average, g/min/g	
0.5	25	355	-	25	0	-	-	10.0
			143	68	5	28.6		7.2
			197	80	7	28.2		6.7
			255	105	10	25.5		6.2
			337	111	20	16.8		6.0
			355	111	30	11.8	0.033	6.0
1.0	16	236	-	25	0	-	-	10.0
			37.4	68	5	7.5		9.5
			61.2	80	7	8.75		9.2
			85	105	10	8.5		8.5
			183.5	111	20	9.2		7.0
			217	111	30	7.2	0.0225	6.2
			236	111	42	5.6		5.9
2.0	6	220	-	25	0	-	-	10.0
			22.6	68	5	4.5		9.7
			36.7	80	7	5.25		9.5
			60	105	10	6.0		9.0
			141	111	20	7.0		7.7
			194	111	30	6.5		6.7
			221	111	40	5.5	0.0166	6.0
			220	111	55	4.0		6.0
2.75	5	222	-	25	0	1	-	10.0
			13	68	5	2.6		9.9
			24.7	80	7	3.5		9.75
			39	105	10	3.9		9.5
			104	111	20	5.2		8.2
			156	111	30	5.2		7.2
			190	111	40	4.8		6.7
			204	111	50	4.1		6.3
			207	111	60	3.5		6.2
			222	111	75	3.0	0.0133	6.0

Fig.5.8. Effect of Sheared Length on Time of Leaching and Average Leach Rate.

Each batch leaching was made with the leach acid initially at room temperature. The acid temperature increased to the boiling temperature, 111°C , in approximately 12 min. The gradual temperature rise prevented the violent reaction and the resultant sudden release of off-gas due to adding powdered fuel to boiling acid. Rates were obtained by sampling the solution when the temperature reached 80°C and at 2-min intervals over a period of 30 min followed by samples collected every 10 min, thereafter, until the dissolution was complete.

SRE Decanner. A unit for decanning the SRE elements (NaK bonded, stainless steel-clad uranium rods) is being fabricated by the Southern Machine Company at Chattanooga, Tennessee. The machine parts are approximately 75% completed and it is estimated that the parts and assembly will be completed by the scheduled date of April 30, 1959.

The auxiliary components for the handling and cleaning of SRE slugs are as follows:

1. A steam cleaning unit and transfer baskets are being fabricated by the Brinkman Tool and Die Co., Inc., Dayton, Ohio. The units are scheduled for final assembly by May 1, 1959.
2. A lifting device for transferring the elements from a table to the SRE decanning unit is being designed.
3. A plow-type cutter and wheel for decanning individual 6-in. long slugs that cannot be decanned normally by the SRE decanning unit is being designed.

Fabrication of aluminum cans for recanning the SRE rods for storage and subsequent dissolution is scheduled for completion by May 1, 1959 by the George D. Ellis and Sons Company in Philadelphia, Pa. The final lid seal is by a home type canning machine, scheduled for delivery by May 1, 1959.

6.0 VOLATILITY

R. W. Horton

6.1 HF-Fused Salt Dissolution of Zirconium - E. C. Moncrief, S. H. Stankner

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 subassemblies. The salt product from these dissolutions will serve as feed material for the fluorination step. Dissolutions have been made using dummy subassemblies fabricated from Zr-2 rolled plate. The present program is directed toward: (1) corrosion studies in an INOR-8 dissolver under dissolution conditions, and (2) the study of the effects of dissolver geometry on dissolution variables.

Three dissolution runs were started using the NaF-LiF system with Zircaloy subassemblies 100% submerged but only two progressed sufficiently to yield useful data. In run D-24 (590-600°C) 5.37 lb of zirconium was dissolved at an HF rate of 2 lb/hr. An average dissolution rate of 0.158 lb/hr-sq ft (original area) was observed with HF utilizations of 71.2 (maximum) and 15.6 (average) per cent. The composition of the NaF-LiF fused salt melt was varied from 23-40 mol per cent ZrF₄. Run INOR-8 -5 (675-700°C) was terminated by stray currents in the auto-resistance heating circuits prior to HF addition to the dissolver. Run INOR-8 -6 (690-700°C) was terminated by operating difficulties after 95 min of dissolution. Prior to shutdown, 2.48 lb of zirconium was dissolved at HF feed rates of 3 lb/hr (during the first 65 min) and 2 lb/hr (during the last 30 min of the run).

Data and Results. The cumulative hydrogen off-gas evolution from runs D-24 and INOR-8 -6 are shown in Figures 6.1 and 6.3. In Figure 6.3 the off-gas rate for the first 65 min applies for the 3 lb/hr HF feed gas rate, and the rate for the last 30 min corresponds to the 2 lb/hr HF rate.

The zirconium dissolution rates and HF utilizations for runs D-24 and INOR-8 -6 are plotted in Figures 6.2 and 6.4. The use of two dissolution rate scales in Figure 6.4 was necessary to accommodate the two HF rates used during the run.

The operating conditions for the two dissolution runs are summarized in Table 6.1.

Alternate Fused Salt Dissolution Cycle. Run D-24 constituted the final run of the alternate fused salt dissolution cycle discussed in a previous report of this series (UNOP March 1959 monthly progress report, ORNL CF 59-3-61).

Run D-23 was performed to increase the composition of the NaF-LiF fused salt to 20 mol per cent ZrF₄ (chemical analysis later established

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Fig 6 1 Cumulative Hydrogen Evolution During Run D-24

Fig. 6.2. Dissolution Rate and HF Utilization During Run D-24.

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Fig. 6.3. Cumulative Hydrogen Evolution During Run INOR-8-6

Fig. 6.4 Dissolution Rate and HF Utilization During Run IMOR-B-6

Table 6.1. Operating Conditions
for Dissolution Runs

Operating Condition	Run	
	D-24 ^a	INOR-8 -6
Dissolver temperature, °C	590-600	690-700
HF rate, lb/hr	2	3, 2 ^b
Zirconium dissolved, lb	5.37	2.48
Subassembly dissolution, %	100	19.5
Run time, hr	15.0	1.6 ^c
Fused salt recovered, lb	24.2	24.5
Cooling air required, ft ³ /min	-	2
Total height subassembly, in.	5.5	12
Mol % ZrF ₄ in NaF-LiF salt	23	15

^aRun made in copper-lined dissolver.

^bHF flow rate decreased from 3 to 2 lb/hr at 65 min.

^cRun terminated by operating difficulties.

Subassembly Description:

- (1) Run D-24; ten 1/8"x2-1/2"x5-1/2" Zr-2 plates with 1/8"x1/4"x5-1/2" Zr-2 spacers.
- (2) Run INOR-8 -6; ten 1/8"x2-1/2"x12" Zr-2 plates with 1/8"x1/4"x12" Zr-2 spacers.

the ZrF_4 content as 23 mol per cent). Run D-24 was performed to study the fused salt dissolution rate of zirconium in the range 20-40 mol per cent ZrF_4 in NaF-LiF at a dissolution temperature of 600°C.

Although comparative data for the NaF-LiF system are not available for dissolutions in the copper-lined dissolver geometry, some dissolution data under similar conditions using the NaF- ZrF_4 system are available.

Dissolutions of completely submerged Zr-3 subassemblies at 650°C with a starting salt composition of 38 mol per cent ZrF_4 in NaF gave dissolution rates of 0.122 to 0.156 lb/hr-sq ft for HF rates of 11.20 to 44.8 lb/hr-sq ft (see UNOP March 1958 monthly report, ORNL CF 58-3-71, for complete description of the NaF- ZrF_4 runs). From these data, an HF rate of 21.4 lb/hr-sq ft (2 lb/hr HF) corresponds to a dissolution rate of 0.138 lb/hr-sq ft.

Under similar conditions of vessel geometry and per cent submergence, the Zr-2 dissolution rate from run D-24 was 0.158 lb/hr-sq ft. Thus, the dissolution rate with the NaF-LiF system in the range 20 to 40 mol per cent ZrF_4 at 600°C was faster by more than 10% than the rates obtained at 650°C with the NaF- ZrF_4 system. It was not felt that the use of different zirconium alloys, and different subassembly height contributed greatly to the variation between the dissolution rates.

Thus fused salt dissolution of Zr-2 subassemblies in the NaF-LiF system can be performed at less than 600°C with dissolution rates comparable to those obtained with the NaF- ZrF_4 system. Both the NaF- ZrF_4 and the NaF-LiF systems can be operated at approximately equal dissolution temperatures and zirconium capacity.

The primary advantage of dissolution at 600°C, or less, would be the much lower INOR-8 corrosion rates at this temperature. By performing the dissolutions in the 20 to 40 mol per cent ZrF_4 range of the NaF-LiF system, initial and final dissolution temperatures of 600 and 480°C, respectively, are possible. With the NaF- ZrF_4 system, the corresponding temperatures would be 575 and 540°C for the 36 to 56 mol per cent ZrF_4 range. A twenty mole per cent zirconium concentration change in each salt would reflect a similar zirconium capacity.

Thus the problem of selecting the best fused salt system for the Volatility Pilot Plant may resolve itself to a comparison of the corrosion rate of INOR-8 in the two systems. Additional comparative corrosion data at 600°C is therefore needed for the appropriate ranges of the two systems in the INOR-8 dissolver.

From an operational standpoint, run D-24 was extremely successful. The 15-hr run was characterized by a steady HF flow rate, minor quantities of off-gas solids, a small dissolver residue after fused salt transfer (less than 300 g), and nearly theoretical salt product recovery. In contrast to run D-24, run INOR-8 -6 was performed under a variety of minor

operating difficulties which eventually forced a shutdown. Since the primary purpose of run INOR-8 -6 was to accumulate corrosion data, the results from the two hours of operation are of value.

A secondary objective of run INOR-8 -6 was the study of factors causing the large quantities of fine, black off-gas solids observed in previous INOR-8 runs. During the analysis of a sample of the black off-gas solids by the Analytical Chemistry Division, it was observed that approximately 70% of the sample was volatilized in 10 min at 300°C. This would indicate that sublimation, and not entrainment, was the primary factor in the production of off-gas solids. Since the amount of volatile material and impurities in the fused salt should be negligible after prolonged operation at high temperatures, the fused salt charge from run INOR-8 -1 (22 hr total molten exposure at 700-820°C) was used as feed for run INOR-8 -6.

Approximately 250 g of the black off-gas solids were produced during the two hours of operation. Thus, it would appear that volatile impurities in the fused salt may not be the main source of the off-gas solids. The possibility of a reaction between the zirconium subassembly and the nitrogen purge gas at elevated (fused salt) temperatures is being explored. Such a reaction might result in a zirconium nitride and ammonia compounds which would be quite volatile. To date, consistent analyses of the composition of the off-gas solids have not been obtained from optical, X-ray diffraction, or wet chemical methods of analysis.

6.2 Dry Hydrofluorination - L. E. McNeese

If the NaF-LiF system is used most efficiently for STR dissolution in the present pilot plant hydrofluorinator design, initial fuel element submergence will be approximately 50%. It is therefore of interest to characterize the behavior of unsubmerged fuel elements in the presence of HF and H₂ produced during the fused salt dissolution reaction.

The three most important points to be determined are:

1. Maximum element temperature to be expected due to a gas-metal reaction.
2. Fraction of reaction products entrained from the element surface.
3. Degree of completion of the gas phase reaction.

Interest in the first item stems from a possibility of an element temperature great enough to damage the hydrofluorinator vessel. The second item is of interest since reaction products leaving the element surface may be entrained in the dissolver off-gas, greatly complicating the existing problem of sublimation and entrainment from the salt phase. The last item, the extent of the reaction, may play an important role in determining the time required for complete dissolution of a hydrofluorinator charge.

A series of three runs (DH-5, DH-6, DH-7) was performed in the temperature range 550-750°C with 66.7 mol per cent HF-33.3 mol per cent H₂, a composition which is expected to be generated by the salt dissolution. An attempt was made (DH-8) to cover an element surface with ZrF₄ reaction product at 300-500°C in order to reduce the reaction rate at 700°C and thereby control the maximum element temperature. All experiments were performed in the dry hydrofluorination reaction system (described in UNWOP December 1958 monthly report, ORNL CF 58-12-35).

Experimental conditions for the first series of three experimental runs are given in Table 6.2. Element temperatures were measured by 40 mil diameter Inconel sheathed thermocouples in the element in the positions shown in Figure 6.5. The Zircaloy-3 element dimensions were identical in each of the tests.

Observed element temperatures are given in Figures 6.6, 6.7 and 6.8. Per cent of element reacted, per cent of solids leaving element surface, and average reaction rate for each of the three tests were calculated from weight of reaction products recovered and are shown in Table 6.2. Average reaction rates were based on original element surface area.

The maximum temperature (925°C) observed in runs DH-5 and DH-6 is an indication of minimum element temperatures which might be produced in the pilot plant dissolver. It should be noted that neither the length nor cross section of the elements used in the tests were as great as actual STR fuel elements. This factor is probably very important in determining maximum element temperature. Temperatures along the center line of full scale elements would probably be higher than those observed in these tests. However, the temperatures may remain in the region of 900°C due to the boiling point of the ZrF₄ reaction product (902°C at 760 mm Hg).

The data on the extent of the reaction probably more nearly represent what might be expected from full size elements; essentially complete hydrofluorination in the gas phase may occur with vessel wall temperatures in the range 550-750°C since the average reaction rates observed are roughly in the same as rates observed for salt phase dissolution and the reactions would occur simultaneously.

The relation between the entrainment of reaction products from the element and the entrainment from the dissolver vessel is a complicated function of geometry as well as off-gas rates. Thus the entrainment results in Table 6.2 are indicative only of the relative quantities of fines produced in the range of dissolver wall temperatures of 550-750°C. Certainly not all of the solids leaving the element surface would leave the vessel with the off-gas; much would fall into the fused salt and dissolve.

In run DH-8, the surfaces of an 807.8 g element were precoated with ZrF₄ reaction product in the temperature range 300-550°C in an attempt to control reaction rate and maximum element temperature when the element was exposed to HF at 700°C. Element dimensions and thermocouple locations

Table 6.2. Summary of Data from Runs DH-5, DH-6 and DH-7

Run	Hydrofluorinator Wall Temperature, °C	Element Wt, g	Maximum Element Temperature, °C	Reaction Time, hr	% Element Reacted	% Solids Leaving Surface	Average Reaction Rate, mg/(min)(cm ²)
DH-5	750	790.6	925	7	91.8	10.0	2.58
DH-6	650	789.0	925	8.5	94.6	3.8	2.19
DH-7	550	787.0	670	10	73.4	< 1.0	1.44

HF rate: 1.0 lb/hr.

HF concentration in feed: 66.7 mol % HF-33.3 mol % H₂.

Equivalent salt phase HF utilization: 50%.

Element material: Zircaloy-3.

- RUN DH-5
- ▲ RUN DH-6
- ◆ RUNS DH-7 AND DH-8

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.6.5. Element Dimensions and Thermocouple Locations for Runs DH-5, DH-6, DH-7, and DH-8.

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Fig. 6.6. Element Surface Temperatures During Dry Hydrofluorination Run DH-5.

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Fig. 6.7. Element Surface Temperatures During Dry Hydrofluorination Run DH-6.

Fig. 6.8. Element Surface Temperature During Dry Hydrofluorination Run DH-7.

were identical to those of run DH-7 given in Figure 6.5. Hydrogen produced during the reaction was metered in a wet test meter.

The initial HF rate during the precoating was 0.45 lb/hr with a reactor wall temperature of 300°C. Only a slight reaction occurred when the clean element surface at approximately 225°C was contacted with HF as shown in Figure 6.9. Wall temperature was then increased as shown in Figure 6.9 until a precoating reaction occurred at an element temperature of approximately 400°C as shown in Figure 6.10. Assuming a reaction product density of 2 g/cc, and that all reaction products remained evenly distributed on the element surface, a reaction product thickness of 0.53 mm was calculated from H₂ off-gas data. Reaction rate was calculated from H₂ off-gas data and is based on original element surface.

After the precoating reaction was completed, the HF rate was increased to 1.47 lb/hr. The element temperature was then raised in 50°C increments to 700°C where a second reaction occurred. The temperature in the center of the element (Figure 6.11) slowly increased from 660-740°C and then rapidly increased to approximately 900°C. The temperatures in other sections of the element followed a similar behavior. In a larger fuel element, excessively high centerline temperatures could spread in similar manner to the outer sections of the element.

As shown in Figure 6.9, the reaction rate increased by a factor of ten or more during the second reaction and resulted in a maximum reaction rate of 9.7 mg/(min)(cm²). The average reaction rate during the second reaction was 3.17 mg/(min)(cm²) which may be compared with 2.58 mg/(min)(cm²) from run DH-5. The higher HF concentration and HF rate in DH-8 would account for the difference in reaction rates. At the end of run DH-8, the element was 91.4% reacted.

6.3 Off-Gas Disposal Studies - R. L. Boles, S. H. Stainker

It has been proposed¹ that the off-gas from a volatility hydrofluorinator (fused salt or dry) be passed through a packed column and scrubbed with HF condensed at the top of the column. The packed bed would probably accumulate solids unless the surface of the packing was easily cleaned by the washing action of liquid HF. A plastic such as fluorothene might have the necessary surface properties, and radiation damage to the plastic would be relatively unimportant since the off-gas system would be constructed of halogen-resistant metals.

¹M. E. Whatley and L. E. McNeese, "The Problem of Scrubbing the Hydrofluorination Off-Gas with Liquid HF", ORNL CF 58-7-98, July 11, 1958.

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Fig. 6.9. Reaction Rates During Run DH-8.

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Fig. 6.10. Element Surface Temperatures During Run DH-8.

Fig. 6.11. Temperature Excursion During Dry Hydrofluorination Run DH-8.

A preliminary study was made of the flooding characteristics of 1/4 in. fluorothene Raschig rings at low liquid rates in a 3-in. ID column using an air-water system. Water flow rates were varied from 134-672 lb/(hr)(sq ft column cross section).

The results were compared with an extrapolation of the data on carbon and ceramic rings given by Schoenborn and Dougherty² (Figure 6.12) and it was found that flooding occurred at slightly higher gas rates when the plastic rings were used. The results of the one run made using 1/4 in. steel rings were consistent with an extrapolation of Schoenborn and Dougherty's data.

For fluorothene packing, as the liquid velocity was increased from 134 lb/(hr)(sq ft) to 537 lb/(hr)(sq ft), the gas velocity at flooding decreased from 1152 lb/(hr)(sq ft) to 842 lb/(hr)(sq ft) and the pressure drop $\Delta P/h$ decreased from 4.85 to 3.91 in. of H₂O/ft of packing (Figure 6.13). At a liquid rate of 537 lb/hr-ft² the pressure drop for steel rings was 4.65 in. H₂O/ft at the flooding gas velocity of 716 lb/(hr)(sq ft).³

Pressure drop measurements for dry fluorothene packing showed that as the gas velocity was increased from 325 lb/(hr)(sq ft) to 1222 lb/(hr)(sq ft) the pressure drop increased from 0.58 in. H₂O/ft to 6.72 in./ft and was proportional to the 1.76 power of the gas velocity.³

Visual observation of a dye injected into the liquid stream showed that a large percentage of the water channeled down the sides of the column (Figure 6.14). Photographs taken of the packing as the dye flowed through it at rates slightly below flooding showed that the liquid flowed down one side of the column while the air passed up the other side.³

²Schoenborn, E. M., and Dougherty, W. J., Trans. Am. Inst. Chem. Engrs., 40, 51 (1944).

³Boles, R. L. and Stainker, S. H., "Flooding Characteristics of 1/4" Fluorothene Raschig Rings", ORNL CF 59-4-83, April 27, 1959.

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Fig. 6.12. Correlation of Flooding Rates for $\frac{1}{4}$ -in. Fluorothene Raschig Rings.

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Fig.6.13. Operating Characteristics of $\frac{1}{4}$ -in. Fluorothene Raschig Rings.

Fig. 6.14. Liquid Flow Pattern in 3-in. ID Column Packed with $\frac{1}{4}$ -in. Fluorothene Raschig Rings.

7.0 WASTE PROCESSING

M. E. Whatley

Thermal Conductivity of Calcined Darex Waste - C. W. Hancher and J. J. Perona

In the ultimate disposal of radioactive solid wastes, the size and configuration of the waste containers will be determined primarily by the necessity for the dissipation of the radioactive decay heat without excessive temperature rise. The thermal conductivity and diffusivity of each type of radioactive solid must be determined before temperature rise calculations can be made.

The Darex process, which is being developed for reprocessing power reactor fuels containing stainless-steel, yields a solvent extraction waste stream of iron, chromium, nickel and aluminum nitrates in nitric acid along with the fission products in the original reactor fuel elements. Calcined Darex waste is a cellular material with a density of 0.7 to 0.9 g/cc¹. An unsteady state method for the determination of thermal conductivity was chosen to take advantage of the suspected low thermal conductivity of the cake and to eliminate the necessity of placing thermocouples in the cake.

If an infinite solid, initially at zero temperature, receives a constant heat flux through a cylindrical surface, the temperature for large values of $\alpha t/r^2$ is given by the equation²:

$$T = \frac{QR}{2k} \ln \frac{4\alpha t}{Cr^2} + o\left(\frac{R^2}{\alpha t}\right) \quad (1)$$

where

Q = heat flux, Btu/hr sq ft

R = radius of cavity, ft

k = thermal conductivity, Btu/hr sq ft ($^{\circ}\text{F}/\text{ft}$)

α = thermal diffusivity, sq ft/hr

¹C. W. Hancher, "Reduction of Radioactive Waste to Solids for Ultimate Storage", ORNL CF 59-1-77.

²H. S. Carslow and J. C. Jaeger, "Conduction of Heat in Solids", Oxford Press, 2nd Ed., (1959), p. 339.

t = time, hr

r = radial distance, ft

$C = 1.7811 = \exp(\text{Euler's constant})$

and the Landau O term indicates a remainder of the order of magnitude of $R^2/\alpha t$. In the range of times where equation (1) applies, a plot of T versus $\ln t$ should yield a straight line according to the equation:

$$T_2 - T_1 = \frac{QR}{2k} \ln \frac{t_2}{t_1} \quad (2)$$

If Q and R are known, the thermal conductivity may be obtained from the slope of the plot.

If a thermal resistance exists between the heated tube and the calcined waste, equation (1) is modified to the following equation³:

$$T = \frac{QR}{2k} \left[\frac{2k}{Rh} + \ln \frac{4\alpha t}{Cr^2} \right] + O\left(\frac{R^2}{\alpha t}\right) \quad (3)$$

where

h = heat transfer coefficient, Btu/hr sq ft °F

and equation (2) still represents the slope of a plot of T versus $\ln t$.

In the experimental studies, the effect of an infinite medium was obtained by heating a 0.101 in. diameter tube in an 8-in. diameter cylinder of calcined waste. Thus, values of t/r^2 were less by a factor of 6×10^3 at the boundary of the cylinder than at the surface of the heater. A sketch of the experimental apparatus is shown in Figure 7.1. A thermocouple was inserted into the 0.101-in. diameter tube and the head of the thermocouple was wedged against the tube wall. The ends of the tube were sealed and the tube was held at the axis of a furnace liner while a Darex calcination run was made which brought the final cake temperature to about 900°C. Then the ends of the tube were carefully exposed while thermocouple leads and electrical leads for resistance heating of the tube were attached. The ends of the cylinder were insulated with silocel and epoxy resin was used to maintain structural integrity.

A wiring diagram of the experiment is shown in Figure 7.2. A fixed transformer was used to obtain low voltage power for resistance-heating the stainless steel tube. The heat generation rate was calculated from the ammeter and voltmeter readings. A Rubicon potentiometer accurate to one-hundredth of a millivolt was used to obtain the tube temperature.

³H. S. Carslaw and J. C. Jaeger, op. cit., p. 345.

Fig. 7.1. Sketch of Calcined Waste Cylinder Prepared for Thermal Conductivity Measurement.

Fig. 7.2. Wiring Diagram of Thermal Conductivity Measurement Apparatus.

A series of thermal conductivity measurements was made starting at different uniform initial temperatures. A typical plot of T versus $\log t$ is shown in Figure 7.3. The thermal conductivity obtained from each experiment was assumed to be an average value over the temperature range of the tube from the beginning to the end of the experiment. Thermal conductivities varied from 0.042 Btu/hr sq ft ($^{\circ}\text{F ft}$) over the range of 73.5 to 180 $^{\circ}\text{F}$ to 0.110 over the range of 460-500 $^{\circ}\text{F}$ (Figure 7.4).

Thermal diffusivities may be calculated by substituting experimental data into equation (1) once the thermal conductivity has been determined. Thermal diffusivities obtained in this way varied from 0.0037 sq ft/hr for the temperature range 70-180 $^{\circ}\text{F}$ to 0.0061 sq ft/hr for 460-500 $^{\circ}\text{F}$. However, it must be shown that negligible resistance to heat transfer existed at the outer surface of the heated tube before values calculated from equation (1) can be accepted.

If a significant thermal resistance existed at the tube surface, an expression relating α and h independent of equation (3) must be found for the evaluation of α . For small values of $\alpha t/R^2$, the temperature of the heated tube is given by³:

$$T = \frac{QR C_R}{k} \left[\frac{\alpha t}{R^2} - \frac{R C_R h}{2k} \left(\frac{\alpha t}{R^2} \right)^2 + O \left(\frac{\alpha t}{R^2} \right)^{5/2} \right] \quad (4)$$

where

$$C_R = 2\pi R^2 \rho C / S$$

ρ = density of calcined waste, lb/ft³

C = heat capacity of calcined waste, Btu/lb $^{\circ}\text{F}$

S = thermal capacity of heated tube, Btu/ft $^{\circ}\text{F}$

Using the data in Figure 7.3 between 5 and 10 sec with equation (4) and between 100 and 180 sec with equation (3) attempts were made to solve the two simultaneous equations for α and h . Solutions with positive values of α could not be obtained which showed that h was large. From the right side of equation (4), it was deduced that h was larger than 45 which yields a thermal diffusivity of 0.0024 sq ft/hr (compared with 0.0040 sq ft/hr for $h = \infty$). In order to obtain closer limits on the value for h , data are needed for smaller values of time.

³H. S. Carslaw and J. C. Jaeger, op. cit., p. 345.

Fig. 7.3. Thermal Conductivity Measurements of Calcined Darex Waste: Temperature vs Time with an Initial Uniform Temperature of 73.5°F.

Fig. 7.4. Thermal Conductivity of Calcined Darex Waste as a Function of Temperature.

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