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CHEMICAL TECHNOLOGY DIVISION
UNIT OPERATIONS SECTION
MONTHLY PROGRESS REPORT
AUGUST 1959

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ORNL CF 59-8-76

UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT

August 1959

CHEMICAL TECHNOLOGY DIVISION

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Date Issued

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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UNION CARBIDE CORPORATION
for the
U. S. Atomic Energy Commission

ABSTRACT

The concentration gradients of uranyl ion in aqueous and organic solutions were analyzed by taking a macro photograph of the desired gradient by monochromatic (436 mμ) light transmitted by the solution normal to the gradient in an appropriate diffusion cell. Two Druhm runs were terminated due to malfunction of the sodium metering system and the third run was terminated when the UF_6 nozzle ruptured. Calculations of particle temperature versus time relations for the flame denitration-calcination method of preparing metallic oxide from nitrate solutions indicate that the times required for heat transfer are controlled by the rate of radiant heat transfer to particle surfaces instead of by conductive heat transfer within the particles. A completed experimental study indicated that electrolysis in a cell with a mercury cathode and a platinum anode is a practical process for removing nickel from HRT fuel solution. The apparent diffusion coefficient of uranium loading on Dowex 21K was shown to be directly related to the resin size. An explosion of sufficient violent to blow apart the Pyrex pipe dissolver occurred during the fifth Darex dissolution of simulated SRE fuel, probably from a rapid gas phase reaction between hydrogen and oxidizing gases such as NO_2 . Materials handling flowsheets were completed for (A) decladding, washing, recanning and storing spent SRE uranium fuel slugs and (B) the shearing and leaching of stainless steel clad UO_2 and UO_2 - ThO_2 fuels. A literature survey is being conducted dealing with reactor coolant and coolant loop contamination and decontamination. During run R-17 for calcination of evaporated Darex waste, the same as run R-16 which deformed the bottom calcination vessel except that one of the three added pressure probes was vibrated to keep it unplugged, the bottom of the calcination vessel did not deform, and there was no pressure indicated on the pressure probes during the test.

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SUMMARY

1.0 CHEMICAL ENGINEERING RESEARCH

Photographic Analysis of Uranium Concentration Gradients

To elucidate the kinetics and mechanism of solvent extraction processes, the resistance of an aqueous-organic interface to molecular diffusion is being studied. A necessary photographic technique for in situ analysis of micro concentration gradients has been developed.

The concentration gradients of uranyl ion are analyzed by taking a macro photograph of the desired gradient by monochromatic (436 mμ) light transmitted by the solution normal to the gradient in an appropriate diffusion cell. The photographic plate (Kodak type IV spectroscopic) is developed and its density is determined as a function of position by means of a Leeds and Northrup microdensitometer. Due to the complimentary nature of Beer's Law and photographic sensitometric relations, the concentration at any point in the gradient is a linear function of the logarithm of the density of the corresponding position of the plate. The relation is

$$\frac{\rho}{\gamma} = 0.434 \beta x C - \log_{10} I_0 - \log_{10} t$$

where γ = slope of the linear portion of the sensitometric curve.

ρ = density of the plate as read by the densitometer.

β = molar absorbtivity of uranyl ion in the cell (11.3 liter cm⁻¹ for 436 mμ light).

x = optical path length in cell, cm.

C = concentration, moles/liter.

I_0 = incident light intensity on cell, a constant.

t = exposure time, sec.

2.0 DRUHM

Three runs were attempted with 1-in. thick graphite liners and copper, He-cooled UF₆ nozzles. Two of the runs were terminated due to malfunction of the sodium metering system and the third run was terminated when the UF₆ nozzle ruptured. In one run 56.5% of the total uranium introduced as UF₆ was collected as uranium metal with a total reduced uranium recovery of 86.0%.

Nine consolidation runs were made to test magnesia and graphite liners at temperatures of 1100 - 1200°C in the presence of uranium metal and sodium fluoride. Graphite was more resistant than magnesia, but the experimental

technique did not allow a detailed examination of possible cracking. Uranium metal reduced sodium fluoride to produce free sodium and uranium fluorides when sodium vapor was not fed to the reactor.

3.0 HR FUEL PROCESSING AND BLANKET PREPARATION

3.1 Flame Denitration-Calcalcination Calculation

Calculations of particle temperature versus time relations for the flame denitration-calcination method of preparing metallic oxide from nitrate solutions indicate that the times required for heat transfer are controlled by the rate of radiant heat transfer to particle surfaces instead of by conductive heat transfer within the particles. Total times for 0.01 to 0.06 seconds were calculated for heat transfer to raise feed solution solution droplets to the required calcination temperatures. A reflector at the desired calcination temperature is necessary for efficient high temperature flame calcination since the equilibrium particle temperature is close to the reflector temperature.

3.2 Nickel Removal System

A completed experimental study indicated that electrolysis in a cell with a mercury cathode and a platinum anode was a practical process for removing nickel from HRT fuel solution. Nickel was removed with a constant 1% current efficiency requiring about 220 ampere-hr/liter to reduce the nickel concentration from 0.045 M to 0.004 M.

4.0 ION EXCHANGE

The apparent diffusion coefficient of uranium loading on Dowex 21K was shown to be directly related to the resin size. The measured coefficients were as follows: for 1200 μ resin, 1.3×10^{-7} sq cm/sec; for 960 μ resin, 9.6×10^{-8} sq cm/sec; and for 820 μ resin, 4.85×10^{-8} sq cm/sec. Nonuniformity of the resin may account for this variation. Applying equations for the counter diffusion of ions with like charges did not result in a significantly better fit of the experimental data than the simpler equation for diffusion into a sphere with a constant surface concentration.

5.0 POWER REACTOR FUEL REPROCESSING

5.1 Darex

Five Darex (2 M HCl-5 HNO₃) dissolutions were made with simulated SRE fuel, each dissolution consisting of a single stainless tube (304 L, 1/2-in. o.d., 20 mil wall thickness, 12-in. long) containing 5 cc of NaK (78% K, 22% Na). The reaction of NaK with the acid during the first four dissolutions was accompanied by flashes of light and pressure surges. An explosion of sufficient violence to blow apart the Pyrex pipe dissolver occurred during the fifth dissolution, probably from a rapid gas phase reaction between hydrogen and oxidizing gases such as NO₂.

5.2 Sulfex

A trial Sulfex run was successfully made in which nearly all of a dummy eleven plate stainless steel fuel assembly weighing 7.75 kg was dissolved in boiling 6 M H_2SO_4 at an approximate rate of 83 g of stainless steel/min. Hydrogen was evolved into the nitrogen gas blanketing the system at about 1.28 cu ft/min (STP). Foaming in the 10-in. (i.d.) dissolver reached a height of 15 ft.

5.3 Feed Clarification

A preliminary filtration flowsheet for removal of siliceous material from Darex (APPR) solvent extraction feed using porous metal element was tested successfully on a laboratory scale (0.18 sq ft filter element).

5.4 Mechanical Processing

Materials handling flowsheets were completed for (A) decladding, washing, recanning and storing spent SRE uranium fuel slugs and (B) the shearing and leaching of stainless steel clad UO_2 and UO_2-ThO_2 fuels.

Shearing of Mark I prototype fuel (stainless clad-porcelain) with eight different blades in combination with three different anvils showed that:

1. Two shear blades (Rockwell C56) were cracked when cutting through the solid stainless steel end caps. One other blade was cracked shearing through stainless steel tubes filled with porcelain.
2. The best punch (blade) anvil combination to give minimum tonnage and produce individual sheared tubes (i.e., break through tubes apart at the structural ferrules) had a stepped blade shape and an anvil with a concave curved edge.
3. Microbraz 50, the bonding agent used in the assembly of some fuel assemblies with a Rockwell C51 hardness, causing galling between blades and breakage of the cutting edges.
4. Rounding the cutting edge of a shear blade to $1/32 - 3/64$ radius prevents chipping of the cutting edge without altering efficiency of cutting.
5. Clearance between blades should be 1 to 3 mils.

6.0 REACTOR COOLANT DECONTAMINATION - A LITERATURE SURVEY

A literature survey is being conducted dealing with reactor coolant and coolant loop contamination and decontamination. The two types of contamination considered are fission products and activated corrosion products. Chemical methods of decontamination are discussed. Data included in the report are listed under reactor coolant type headings (water, organic, gas, and liquid-metal cooled reactors). All reference numbers are to the bibliography at the end of the main body of the report (pg 77).

6.1 Pressurized Water Reactors

Studies have indicated that the corrosion product activity from Inconel loops is at least a factor of two less than activities resulting from stainless steel reactor loops.⁽²³⁾

Analyses of crud deposits on coolant loops when ruptured fuel elements are present give Mo, Te, and Ru as the major deposited fission products and Mn and Co as the major activated corrosion products. These five species contribute between 50 and 90% of the total gamma activity.⁽²¹⁾ Van de Graaff studies have shown that crud deposition rates are much greater under irradiation than in cold coolant loop experiments.⁽¹⁹⁾

Corrosion rates of carbon steel in high temperature, high purity water in dynamic systems have little dependence upon any experimental conditions except pH. High pH (10 to 12) results in lower corrosion rates than lower pH (7 to 10).⁽¹⁸⁾ Release rates of corrosion products are considerably lower than corrosion rates in steel systems and do not decrease as rapidly with increasing time.^(19,25)

With organic ion-exchange resins radiation causes decreases in capacity with different types of resins showing differing resistance to degradation. In order of decreasing resistance the resins are: (1) sulfonic polystyrene and sulfonic phenolic, (2) weakly basic anion exchange resins, and (3) quaternary amine anion exchange resins.⁽⁸⁾ There has been effort made to develop inorganic exchange materials such as zirconium phosphate which actually gain capacity under irradiation.^(1,5)

Work with hot bed filters (that is, filters operating at reactor temperature and pressure) has shown that the axial filter is superior to the radial filter for crud removal since it loses less in efficiency with time of operation.⁽²⁶⁾

Averaging of numerous values of the escape rate coefficient for krypton and cesium from damaged ceramic fuel gives 2.3×10^{-8} and 3.7×10^{-8} sec⁻¹, respectively.^(19,24) All the values were determined for clad UO₂ elements with 0.005-in. dia holes in the clad. Escape rate coefficients for iodine isotopes determined before and after reactor shutdown indicate that iodine will continue to escape at about the same rate during shutdown as during operation. The escape rate coefficients for iodine are about an order of magnitude less than those for krypton and cesium.⁽¹⁸⁾

For decontamination of the Yankee reactor a two solution decontamination has been recommended with the first solution being basic permanganate and the second an ammonium citrate complexing solution. This treatment is said to give overall decontamination factors of at least 10 with low corrosion rates.⁽²⁸⁾

6.2 Organic Cooled Reactors

Diphenyl is the most stable organic coolant tested for thermal and radiation damage and may be useful as a coolant up to about 700°F with a continuous purifying system.⁽¹¹⁾ Although mild local boiling on fuel elements causes little carbon formation, heavy local boiling leads to vapor and liquid phase cracking of the organic coolant.⁽²⁾

6.3 Gas-cooled Reactors

Of the most mentioned reactor coolant gases (helium, carbon dioxide, and nitrogen) helium is best for limiting corrosion. Nitrogen, although it reacts with most metals at high temperature, would be satisfactory at temperatures of 500°C or less. Carbon dioxide can be used at temperatures below 500°C with aluminum, magnesium, iron, and steel.⁽¹⁰⁾ It also reacts with graphite which may be protected by cladding or a protective coating.⁽⁷⁾ The Calder reactor uses CO₂ as a coolant and purifies it by use of filters and cyclones to remove dust and alumina packed towers to dry the gas.⁽⁴⁾

6.4 Liquid-Metal Cooled Reactors

Corrosion of metals by liquid sodium is inhibited by barium with maximum inhibition between 0.1 and 1 wt % barium.⁽¹⁴⁾

Decontamination of easily contacted surfaces contaminated with radioactive sodium and associated impurities may be accomplished with a solution of detergent with scrubbing recommended. When surfaces cannot be easily reached a Versene soak or an acid etch may be necessary.⁽⁹⁾

7.0 VOLATILITY

Fused Salt Dissolution Equipment

The pumping rate of a gas lift pump using nitrogen gas to pump a fused salt at 700°C has been determined for seven gas rates ranging from 190 to 1900 standard cc/min. The rate was slightly less with fused salt than for water at 26°C.

8.0 WASTE PROCESSING

8.1 Calcination

Run (R-17) calcination of evaporated Darex waste, was the same as run R-16 which deformed the bottom calcination vessel, except that one of the three added pressure probes was vibrated to keep it unplugged. The calcination vessel was filled within 4 in. of the top with 80 liters of Darex waste. The density of the calcined solid was 0.80 g/cc. The bottom of the calcination vessel did not deform, and there was no pressure indicated on the pressure probes during the test.

8.2 Particulate Attenuation in a Packed Distillation Tower

An apparatus was constructed containing an aerosol generator of the type developed by the Chemical Warfare Service and an isokinetic sampler leading to particle collection devices. A Casella cascade impactor will be used for particle size determination and a millipore filter for particle loading determination. A thermal precipitator may be used for small particle collection if the need arises. After sampling, the aerosol stream will be fed to a 3-in. dia 10 ft. tall distillation column packed with 1/4-in. Raschig rings to determine the off-gas clean-up efficiency.

1.0 CHEMICAL ENGINEERING RESEARCH

M. E. Whatley

Photographic Photometric Analysis of Uranium Concentration Gradients - C. V. Chester

To elucidate the kinetics and mechanism of solvent extraction processes, the resistance of an aqueous-organic interface to molecular diffusion is being studied. An essential technique has been developed which employs photographic photometry for analysis of micro concentration gradients in situ.

The concentration gradients of uranyl ion are analyzed by taking a macrophotograph of the desired gradient by monochromatic (436 mμ) light transmitted by the solution normal to the gradient in an appropriate diffusion cell. The photographic plate (Kodak type IV spectroscopic) is subjected to a standard development (3 min in D-19) and its density determined as a function of position by means of a Leeds and Northrup microdensitometer. Due to the complimentary nature of Beer's Law and photographic sensitometric relations, the concentration at any point in the gradient is a linear function of the density of the corresponding position of the plate. The relation is:

$$\frac{\rho}{\gamma} = .434 \beta x C - \log_{10} I_0 - \log_{10} t \quad (1)$$

where

γ = slope of linear portion of sensitometric curve

ρ = density of the plate (equal to $-\log_{10}$ transmittance)

β = molar absorbtivity of uranyl ion in the cell (11.3 liter/mole cm for 436 mμ light)

x = optical path length in cell, cm

C = uranyl ion concentration, mole/liter

I_0 = incident light intensity on cell, meter candles

t = exposure time, sec

Figure 1.1 is a densitometer trace of a type IV plate (Figure 1.2) exposed in the equipment for 90 sec. The ordinate of the trace is plate transmittance, from zero per cent for opaque plate to 100% for clear plate. (The plate density is the negative logarithm of the transmittance.) Of interest in this figure are the traces of the aqueous standard solutions. From the known solution concentrations, cell thickness (0.080-in.) and equation (1) above, it is possible to calculate exposure using the observed transmittance and the estimated value (4.5) of γ for the plate. The plate density is plotted against exposure along with the published sensitometric curves on Figure 1.3. The points fall close to the curve, indicating the internal consistency of the data and procedures.

Fig.1.1. Densitometer Trace of Plate 82 (See Fig.1.2.).

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Fig.1.2. Photograph of Diffusion Cell.

Fig.1.3. Sensitometric Curves for Kodak Type III-O and Type IV-O Plates (3-min Development IN D-A).

It may be noted that the linear portion of the sensitometric curve for type IV plate begins at an optical density of about 0.8, corresponding to a transmittance of 16%, and extends well beyond a density of 2.0, corresponding to a transmittance of 1%. On the present traces, this range is a limited portion of the scale. Fortunately the densitometer has provision for changing the range and spreading the densities of the linear portion of the sensitometric curve over the entire available scale of the trace. Quantitative treatment of subsequent plates will make use of this factor, after the instrument has received such adjustment as necessary to make the electronics adequately stable in the more sensitive range.

Revised Cell Construction

A modification of the diffusion cell has been put into operation. The revised cell overcomes the shortcomings of the compression seal cell and its successors by having a stainless steel body and a rubber cushion in the compression train (see Figure 1.4). The compression seal cell had a Teflon body (reported in February 1959 Unit Operations monthly report) which leaked badly. Teflon is extremely oleophilic and will creep under a compressive load, resulting in severe capillary leakage of the organic phase and loss of the compression seal after a few hours. Attempt to take up the slack with the frame bolts invariably resulted in fracture of the cover glasses, since the Teflon crept from the edge, leaving the edge of the cover glasses unsupported. The glass failed from first order membrane flexure as it attempted to conform to the resulting lens-shaped cell.

The return to stainless steel as a cell body material avoids the severe creep problem. Creep of the 0.002-in. polyethylene gasket used to obtain a seal between the glass and steel does not distort the glass enough to threaten it. However, the seal may be weakened, so a resilient cushion is included between the rear cover glass and rear cover plate. The cushion is a piece of 1/2-in. o.d. x 1/8-in. wall surgical rubber tubing flattened by the seal. The relatively low spring constant of the cushion and its extreme compression assures that the compressive load on the cell remains constant over the small displacement permitted by creep in the gasket. In previous modifications, most of the elasticity in the system was in the six 3/8-in. bolts holding the cell assembly together.

The polyethylene gaskets are permitted to creep for 24 hrs prior to a run, in order to conform to scratches and other possible irregularities in the surface of the cell. In operations thus far, the cell has not been absolutely leak tight, since wetting of the gasket between chambers has been observed. However, there has been no observable accumulation of solution in any empty chamber even after several hours standing. By immersing the assembly in the water of the thermostat bath and selecting the elevation of the discharge lines to be close to the thermostat water level, there is very little head to cause flow through any potential leaks. Common discharge of all the chambers insures that they are at nearly equal hydrostatic pressures.

Fig.1.4. Revised Cell Assembly.

2.0 DRUHM

P. A. Haas

A process is being developed for the direct reduction of uranium hexafluoride by use of sodium metal. The present studies are of the reactor conditions, materials, and procedures which would permit continuous feed of UF_6 and Na with consolidation of the molten U product.

2.1 Reactor Development - C. D. Scott, W. G. Sisson

Three semi-continuous reduction runs were made in the DRUHM experimental facility. The reduction was carried out continuously with product collection on a batch basis. Current work was with a 6-in. Inconel reactor, a 1-in. thick graphite liner which was thermally insulated from the top of the reactor, and a copper UF_6 nozzle which was internally cooled with chilled helium.

The three semi-continuous reductions runs (D-35, D-36 and D-37) were made with 1-in. graphite liners and copper UF_6 nozzles. In each run an attempt was made to use a sodium boiler to vaporize the metered, liquid sodium stream prior to its entry to the reactor. Although two different designs for the sodium boiler were used, the boiler was not run successfully during any of the three runs. Failure of the boiler caused termination of two runs.

Run D-35 lasted for 10 minutes with feed rates of 33.2 g UF_6 /min and sodium at 82% excess. The run was terminated when the sodium boiler burned out and wide fluctuations of sodium flow occurred. The reaction zone temperatures during the period were between 1100 - 1200°C. A total of 159 g of metal was recovered in the bottom of the liner with 189 g of slag in a single mass and 89 g of mixed metal and slag was recovered as an "icicle" on the nozzle. This recovery resulted in the following material balance:

Table 2.1.

Material Balance for DRUHM Run D-35

Reactants:	UF_6	332 g
	Stoichiometric Na	<u>130 g</u>
	Total	462 g
Products:	Metal	159 g
	Slag	189 g
	Nozzle "icicle"	<u>89 g</u>
	Total	437 g

Total product recovery was 94.6% of the reactants. The recovery of uranium based on the amount introduced was 127 g or 56.5% as uranium metal and 192.7 g or 86.0% total recovery.

There was no damage to the graphite liner and the UF_6 nozzle was apparently not damaged during the actual run. Several minutes after the run was ended and the reactor was still above the melting point of copper, the nozzle helium cooling gas was accidentally introduced at room temperature instead of $-60^\circ C$ and the nozzle ruptured. Some contamination of the uranium metal by copper resulted.

Runs D-36 and D-37 were terminated shortly after they were started. In run D-36 the sodium system failed after three attempts to begin the run and after three thermal cycles of the system to $> 1100^\circ C$. Run D-37 was terminated because of nozzle rupture. In this run the nozzle was withdrawn 1/2-in. from the proposed reaction zone, and the actual reaction occurred at the nozzle tip due to a changed flow pattern. In both runs there was a single crack down the length of the graphite liner.

2.2 Materials and Consolidation - D. R. Edwards, C. D. Scott

Reactor liner materials and metal consolidation for the DRUHM process were studied in a laboratory induction heated reactor. Graphite and magnesia crucibles were selected for test after a literature survey of possible liner materials.

A total of nine consolidation runs were made, four using 1/8-in. wall thickness magnesia liners and five using 1/8-in. wall thickness graphite liners. The graphite was superior to the magnesia. Both were weakened by contact with sodium liquid and vapor at $1100-1200^\circ C$, but the weakening of the magnesia was more pronounced.

Melting of the Inconel reactors occurred during several runs due to either (1) molten uranium coming in contact with the Inconel and forming a low melting alloy or (2) thermal hot spots on the exterior of the reactor caused by the reactor coming in contact with the graphite susceptor sleeve. The last hypothesis seems to be the most probable as there was evidence that the reactor had started to melt in runs when uranium was not present.

Runs C-2, C-3 and C-4 were practically identical in results (Table 2.2). Run C-4 was to have been made with a sodium atmosphere in the crucible but the sodium line clogged. All three runs contained an initial charge of 47.6 g of uranium and 50.4 g of sodium fluoride. In all three the outer reactor wall melted and the graphite liner had to be chipped out, so it could not be determined if the liner cracked or not. With the exception of possible cracking, the graphite held up very well since analytical results showed very little penetration by either uranium or sodium fluoride. No metal consolidation was noted with interior temperatures up to $1210^\circ C$ due to the reaction of uranium with sodium fluoride to liberate sodium metal and one of the uranium fluorides.

Table 2.2. DRUHM Liner Materials Tests

Run	Crucible Material	Charge Material		Atmosphere	Run Time*	Comments
		g NaF	g U			
C-2	graphite	50.4	47.6	Helium	1 hour	Reactor melted, U reacted to give free Na.
C-3	graphite	50.4	47.6	Helium	1 hour	Reactor melted, U reacted to give free Na.
C-4	graphite	50.4	47.6	Helium	15 min	Reactor melted, U reacted to give free Na.
C-5	graphite	-	50.9	Helium	1 hour	No attack in graphite.
C-6	graphite	53.3	-	Helium	1 hour	No attack in graphite.
C-7	magnesia	56.8	-	Helium	1 hour	MgO porous to liquid NaF.
C-8	magnesia	-	47.1	Helium	1 hour	MgO discolored by U.
C-9	magnesia	50.4	47.6	Helium	2 hour	MgO discolored, metal consolidation at 1180°C.
C-10	magnesia	50.4	47.6	Sodium	-	MgO discolored and weakened.

* Run time was considered as the time at which the interior temperature was $\geq 1150^{\circ}\text{C}$.

Runs C-5 through C-8 were made to determine the compatibility of MgO or graphite liners with NaF or uranium alone. For Run C-5, the uranium was not completely melted at an interior temperature of about 1160°C and the graphite crucible held up quite well. There was some penetration of graphite by sodium fluoride in Run C-6 but it was not serious. There was no reaction between the graphite and the sodium fluoride. A magnesia liner was not attacked by sodium fluoride in Run C-7 but was extremely porous. Magnesia was discolored by uranium in Run C-8, but no chemical reaction was noted.

Runs C-9 and C-10 were made with uranium and sodium fluoride in magnesia liners. During Run C-9 with a helium atmosphere, the magnesia was discolored but no reaction was noted. The uranium was completely melted and consolidated with a maximum interior temperature of 1180°C. Free sodium was present denoting reaction between the two components. Run C-10 with a sodium atmosphere ended before the desired temperature could be attained due to a hole melted in the reactor side. The magnesia was discolored and weakened. The bottom of the liner crumbled while the contents were being removed. There was no significant consolidation of the metal and fluoride salt.

It was concluded from these tests that reaction between U and NaF to produce uranium fluoride and free sodium will occur at temperatures above 1000°C due to the relatively high volatility of the two products compared with the reactants. The reverse reaction can be minimized by an overpressure of sodium, a condition present in the DRUHM reactor. The consolidation of uranium depends upon the attaining of a reactor temperature in excess of 1180°C. Graphite may be a satisfactory reactor liner for semi-continuous reduction of UF_6 in which a batch of uranium metal is collected in a crucible and the crucible is sacrificed for removal of the casting.

3.0 HR FUEL PROCESSING AND BLANKET PREPARATION

P. A. Haas

Methods are being developed for fuel processing and slurry preparation as required for the aqueous homogeneous reactor program. The present emphasis is on the preparation of improved slurry materials, particularly spherical thorium particles for blanket slurries by flame denitration procedures.

3.1 Flame Denitration-Calcination Calculations - P. A. Haas

Calculations were made to indicate the relative importance of heat-transfer operations in flame calcination of thorium nitrate solutions to thorium dioxide and equipment design parameters dependent on heat-transfer data. The preparation of high-temperature calcined metal oxides for use in homogeneous reactor fuel and blanket slurries is basically a heat-transfer operation. While introducing and dispersing the feed and collecting the product may be difficult engineering problems, the performance to be expected from flame-calcination operations can be calculated from heat-transfer theory.

The three factors governing the degree of calcination were examined separately: (1) the rate of heat transfer to the particle or drop surface, radiation being the controlling means at flame temperatures above 1000°C but convection becoming significant at lower temperatures; (2) the rate of heat transfer inside the particle, which is assumed to be by conduction although convection may contribute in larger fluid drops; and (3) the equilibrium temperature of the particle under the conditions used. The unsteady-state heat-transfer rates controlled by the first two factors determine how rapidly the equilibrium temperature is approached. The exactness of the calculated results is limited chiefly by uncertainties in operating conditions and in the preferred product characteristics, although the incomplete knowledge of the thermal properties of thorium dioxide at high temperatures contributes to the inexactness.

Although developed primarily for flame calcination, the methods and conclusions are in many respects applicable to spray drying. Convective heat transfer is significant, and often controlling for spray drying operations because of the countercurrent particle-gas flow and the below 1000°C temperatures. Also spray drying usually is for particles larger than 100μ ; therefore, heat transfer and diffusion within the particle are important.

Calculations of particle temperature vs. time relations for the flame denitration-calcination method of preparing thorium dioxide from thorium nitrate solutions indicated that the times required for heat transfer are controlled by the rate of radiant heat transfer to particle surfaces instead of by conductive heat transfer within particles. The times required for heat conduction within the particles are 0.1 to 100 microseconds as shown by calculated T/T_s values (Figure 3.1). T is the particle center temperature while T_s is a constant surface temperature. The times required for radiant heat transfer to the particle surface are 10^3 to 10^5 microseconds (Figure 3.2)

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Fig. 3.1. Center Temperatures of ThO_2 Particles vs Time for a Constant Surface Temperature, T_S . $T_0 = 0$; $\alpha \pi^2 = 5 \times 10^6 \mu^2/\text{sec}$.

Fig. 3.2. ThO_2 Particle Temperatures vs Time; Rate of Heat Transfer to Particle Surface Controlling. $C = 75 \text{ ft}^{-1}$; $\alpha = 0.5 \times 10^{-6} \mu^2/\text{sec}$.

as shown by $(T-T_0)/(T_R-T_0)$ values. T_R is the reflector temperature, T_0 is the initial particle temperature, α is the thermal diffusivity, and C is h/k or apparent radiant heat transfer coefficient/thermal conductivity.

Most of the heat added is necessary to evaporate the water or methyl alcohol feed solvent. Since the larger volume (and larger surface) and the high absorptivity of the solutions as compared to the thorium dioxide particles result in high heat transfer rates in terms of unit amounts of thorium dioxide produced, the times for solvent evaporation and calcination are of about the same magnitude. Total times of 0.01 to 0.06 sec were calculated for heat transfer to raise feed solution droplets to the required calcination temperatures.

A reflector at the desired calcination temperature is necessary for efficient high-temperature flame calcination. With a high reflector temperature the equilibrium particle temperature is close to the reflector temperature. Without a reflector the particles reach maximum temperatures of only 40-60% of the absolute flame temperature because of the low emissivity of gases compared to that of thorium dioxide at temperatures above 1500°C (Figure 3.3).

Combinations of acceptable gas velocities, acceptable dust loadings, and times required for heat transfer indicate minimum reflector lengths of 1-6 ft and capacities of 5-20 kg of thorium per hour per sq ft of cross-sectional area. For pilot plant production of thorium or mixed thorium-uranium oxides the dimensions would be 4 ft length and 6-in. i.d., giving a capacity of about 2 kg of thorium per hour.

With 2-in. dia reflectors used in development studies, the major heat losses are through the reflector walls. For 6-in. dia reflectors 4 ft long, the major heat losses are radiation to the water-cooled burner and exit tube and the latent heat of the feed solvent (Figure 3.4).

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

The results of runs made in a full scale electrolytic cell containing a mercury cathode and a platinum screen anode indicated that electrolytic nickel removal from a concentrated HRT type fuel solution is feasible. The system was designed to process 30 gallon batches of fuel solution* of approximately the following compositions:

0.045 M NiSO_4

0.27 M CuSO_4

0.03 M MnSO_4

0.34 M UO_2SO_4

0.24 M H_2SO_4

*See March Unit Operations Monthly Report, CF 59-3-61 for flow diagram.

Fig. 3.3. Equilibrium Temperature for ThO_2 Particles in a Flame. "Gray" ThO_2 Particles and Reflector. For a Hydrocarbon Fuel Gas, $\epsilon_g = 0.02$ is a Practical Minimum and 0.2 is a Practical Maximum.

Fig. 3.4. Typical Reflector Temperature Distributions.

The nickel removal rate from a heavy water fuel solution was approximately a linear function of the quantity of electricity passed through the solution (see Figure 3.5). The current efficiency based on the quantity of nickel removal was approximately 1%, requiring about 220 ampere hrs/liter to remove 90% of the nickel from the concentrated fuel solution.

Copper was removed from the fuel solution at a rate proportional to the quantity of copper present (see Figure 3.6). The copper removal rate was considerably higher than that for nickel so copper was almost completely removed during the nickel removal step.

The removal of manganese occurred only after a considerable part of the copper and nickel had been removed from the fuel solution (see Figure 3.7). Approximately 60% of the uranium was reduced from the +6 to the +4 valence state during removal of 90% of the nickel.

Electric short circuits in the cell due to amalgam growth from the cathode to the anode were largely eliminated by agitation of the mercury with a stream of fuel solution from the circulating pump discharge and stable amalgam loading up to 4.7 weight per cent deposited metal were obtained. However, there were some indications that an excessive mercury loading may hinder nickel removal.

Anodic corrosion of the stainless steel components near the anode was severe for unprotected surfaces. In the last cell design, anodes corrosion was controlled by covering the stainless steel components near the anode with plastic; however, because of the instability of plastics in a high radiation field other means of protection would be required for reactor service.

Preliminary testing indicates that a 1 M HNO_3 and 1.5% H_2O_2 solution can be used to regenerate the mercury in the electrolytic cell at copper and nickel removal rates up to 30 g/hr (requiring 80 hr to regeneration amalgam from a 30 gallon batch of fuel solution). This method resulted in the dissolution of some of the mercury cathode (up to 10% per run). Additional testing would be required to determine if difficulties develop in successive regenerations of the cathode.

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Fig. 3.5. Rate of Nickel Removal from Heavy Water Fuel Solution in Electrolytic Cell.

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Fig. 3.6. Rate of Copper Removal from a Heavy Water Solution in Electrolytic Cell.

Fig. 3.7 Rate of Manganese Removal from a Heavy Water Fuel Solution in Electrolytic Cell.

4.0 ION EXCHANGE

M. E. Whatley

To make rational predictions of the operating characteristics of uranium anion exchange contactors, an understanding of the mechanism and kinetics of the exchange is necessary. Toward this objective the equilibrium sorption isotherms and rates of sorption of uranium on Dowex 2LK are being determined.

4.1 Experimental Kinetics Studies - J. S. Watson, D. A. McWhirter

The kinetics of uranyl sulfate anion exchange is being studied by measuring the uranium loading on Dowex 2LK after various contactor times in a stirred uranyl sulfate bath. Enriched uranium is used in the bath, and the beads are analyzed by counting their gamma emissions in a gamma spectrometer. The most recent efforts have been aimed at studying the effects of resin size and understanding the shape of the loading curve.

In earlier progress reports ⁽¹⁾ the loading of Dowex 2LK as a function of time was shown to be approximated by the equation for simple diffusion into a sphere with a constant surface concentration. Using 1200 μ resin beads an apparent uranium diffusion coefficient of 1.3×10^{-7} sq cm/sec (independent of sulfate concentration) was measured. The loading solution concentrations could be varied between 0.026 M and 0.201 M in sulfate and 0.0029 M and 0.0058 M in uranium without changing the apparent diffusion coefficient.

A run made with 960 μ resin and a loading solution containing 0.0058 M uranium and 0.201 M sulfate gave a diffusion coefficient of 9.6×10^{-8} sq cm/sec. An identical run was made with the same loading solution but 1200 μ beads and the coefficient was 1.3×10^{-7} sq cm/sec. It thus became necessary to discover if there was an error in the experiment in which the low coefficient was measured.

Two runs have been completed which indicate that this lower diffusivity is truly a property of the system. One run was made with 960 μ resin but with a loading solution 0.0029 M in uranium and 0.201 M in sulfate. The apparent coefficient measured was 7.6×10^{-8} sq cm/sec, identical to that found in the previous run using this resin (see Figure 4.1). The other run was made with an even smaller resin size, 820 μ , and the same loading solution. The apparent coefficient for this run was 4.85×10^{-8} sq cm/sec (see Figure 4.2). The 1200 μ resin under these conditions continued to give an apparent diffusion coefficient of 1.3×10^{-7} sq cm/sec (see Figure 4.3). This result shows conclusively that there is a variation in the apparent uranium diffusion coefficient with resin size; the smaller resin particles show lower diffusion coefficients. The only explanation proposed thus far for this property is nonuniformity of different size fractions of the resin. The smaller resin particles are known to have slightly higher capacities,

(1) Unit Operations July 1959 monthly report, ORNL CF 59-7-58.

Fig.4.1. The Rate of Uranium Loading on 960μ Dowex 21 K Resin.

Fig. 4.2. The Rate of Uranium Loading on 820 μ Dowex 21 K Resin.

Fig. 4.3. Composition of Aqueous Uranyl Sulfate Solutions.

and it is possible that the resin differs also in cross-linkage.

Studies of this phenomenon will be continued. The self-diffusion of sulfate ions in these smaller resin size fractions will be studied to see if the sulfate diffusion coefficient varies with resin size. If it does, there would be more support to the idea of nonuniform beads.

The shape of the loading curve is also of particular interest. The approximate equation for simple diffusion into a sphere with a constant surface concentration does not fit the data for low values of the fractional loading. The data fall below the loadings predicted by the simple model in this region. Both experimental errors and the diffusion model are being investigated to explain the discrepancy. Changing the stirrer speed in the bath did not change the loading curve, so it was concluded that the loading curve shape was probably not due to film resistance to diffusion.⁽²⁾

The experimental procedure was reviewed to determine if any other steps were likely to introduce erroneous results. The pre-run equilibrium of the resin was the most questionable step, so a run was made with very carefully equilibrated resin to see if the shape of the curve would change. The resin was equilibrated for one week with a solution having the same total sulfate and sulfuric acid concentration as the bath, but with no uranium present. The beads were not rinsed with water as they had been in previous runs before going into the bath. However, there was no observable difference in the results from this run and a previous run under the same conditions. The data still fell below the curve for the simple diffusion equation at low bead loadings.

Refinements and changes in the diffusion model are also being investigated to determine the cause for the poor fit of the data at low loadings. However, before describing any refinements, a review of what is known of the sorption kinetics is necessary.

4.2 Theoretical Study of the Sorption Kinetics - J. S. Watson

In the loading solutions, the uranium exists as the UO_2^{++} ion (when the pH is 2.0 or less) and its sulfate complexes, UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^-$, and $\text{UO}_2(\text{SO}_4)_3^{--}$. The constants of formation for these species have been determined by Arhland⁽³⁾ and Allen.⁽⁴⁾ Using these constants and the best activity data available, the concentration of these species through the sulfate concentrations studied were calculated. The results are shown in Figure 4.4. Note that the concentrations of the species go through considerable change in the region shown in the figure. There is disagreement between Arhland and Allen's constant for the third complex formation, and there is even some doubt of its existence. The diffusion coefficients for these complexes should be quite different because both the masses and charges (or valences) result in greater hydration and ordering of water molecules around the ion.

(2) Unit Operations June 1959 monthly report, ORNL CF 59-6-63.

(3) "Acta. Chemia Scandinavica," 5, 1151-67 (1951).

(4) Allen, ORNL - 2709.

Fig. 4.4. The Rate of Uranium Loading on 1200 μ Dowex 21 K Resin.

A series of runs gave identical loading curves while the uranium concentration was held constant at 0.0059 M and the sulfate concentration was varied between 0.026 M and 0.201 M⁽²⁾. At a first glance this result appears surprising because of the information shown in Figure 4.4. However, the Donnon membrane concept of ion exchange resins shows that this result should be expected. The ion exchanger is pictured as a concentrated sulfate solution in which the positive ions (quaternary ammonium) are refrained from movement. This picture is equivalent to considering the resin to be a solution surrounded by a membrane which will not allow the positive resin ions to pass. Several properties of ion exchange resins such as selectivity and osmotic swelling have been discussed and explained by Gregor⁽⁵⁾ using this concept. The important property of the Donnon ion exchanger is that the resin sulfate concentration is essentially equal to the resin capacity and increasing the bulk solution concentration affects the total concentration only slightly. Also at high sulfate concentrations such as those found within the resin, the distribution of the uranium between the various complexes is not changed greatly by small changes in the resin sulfate concentration.

One can then visualize the uranium loading taking place in the following manner. The uranium in all of its complexed forms first diffuses through a thin liquid film and the solution-resin interface. It has been assumed that the effective diffusion resistance in this step is negligible. However, if more elaborate checks than simply changing the stirrer speed in the bath show that this step is important it will be considered.

Once within the resin the uranium immediately saturates the outer differential shell of the resin and forms a new distribution of complexes because of the new sulfate environment. The distribution shifts toward the higher complexes because of the high sulfate concentration in the resin. Diffusion in the bead will then proceed much as predicted by the simple diffusion equation; however, three conditions will cause the diffusion process to be different.

1. Counterdiffusion of sulfate ions with a larger diffusion coefficient than uranium introduces electric as well as chemical potential fields.
2. The distribution of uranium between the different complexes is not constant along the diffusion path.
3. The bead contracts as it is loaded with uranium.

The refinements necessary to correct for the first condition has been discussed by Helfferick and Plesset.^(6,7) They numerically solved the Nernst-Planck equations for diffusion of an ion A into an exchanger loaded with ion B.

- (5) Gregor, H. P. J. A. Chem. Soc., 73, 642-50 (1951).
- (6) J. Chem. Phys., 28, 418-424 (1958).
- (7) J. Chem. Phys., 28, 1064-1069 (1958).

$$\bar{\phi}_A = -D_A \left[\text{grad } C_A + Z_A C_A (F/RT) \text{ grad } \phi \right]$$

$$\bar{\phi}_B = -D_B \left[\text{grad } C_B + Z_B C_B (F/RT) \text{ grad } \phi \right]$$

where $\bar{\phi}$ = flux of the specified ion

D = diffusion coefficient of the ion

Z = the ion valence

F = Faraday's constant

R = gas constant

T = absolute temperature

ϕ = electric field potential

For electric neutrality the condition for no electric current was applied:

$$Z_A C_A + Z_B C_B = \text{constant}$$

$$Z_A \bar{\phi}_A + Z_B \bar{\phi}_B = 0$$

Solving for $\bar{\phi}_A$ gives:

$$\bar{\phi}_A = - \left[\frac{D_A D_B (Z_A^2 C_A + Z_B^2 C_B)}{D_A Z_A^2 C_A + D_B Z_B^2 C_B} \right] \text{grad } C_A$$

The terms in brackets may be termed the interdiffusion coefficient. The expression reduces to the simple particle diffusion equation when the two ions have the same charge and diffusion coefficient. This condition is met in self-diffusion or isotopic exchange.

The two cases of interest in the uranyl sulfate case are when $Z_A = Z_B = 2$ and when $Z_A = 4$ and $Z_B = 2$. One of these conditions would apply if the uranium in the resin phase was converted to the highest sulfate complexes. The first case would apply if the highest complex were $\text{UO}_2(\text{SO}_4)_2^{2-}$, and the second case would apply if the highest complex were $\text{UO}_2(\text{SO}_4)_3^{3-}$. The first case has been solved by Helfferick and Plesset, but their data must be extrapolated to a larger ratio of the diffusion coefficients than they tabulated.

The sulfate diffusion coefficient, D_B , was assumed to be 1.27×10^{-6} sq cm/sec; this value had been measured from a previous self-diffusion run.⁽¹⁾ A uranium diffusion coefficient of 8.64×10^{-8} sq cm/sec was assumed to make the results fall near the calculated values. The apparent diffusion coefficients calculated from the simple model were not applicable to this treatment. The resulting curve is shown in Figure 4.3. A slightly lower assumed value for the uranium diffusion coefficient would have given a slightly better fit of the data but the important thing to note is that the data still falls below the curve predicted by this more refined treatment at low loading.

The other two conditions for deviations of the data from the simple diffusion model must also be studied before a complete understanding of uranyl sulfate anion exchange is possible.

5.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

5.1 Darex - F. G. Kitts

The purpose of the Darex process is to convert SS-U and SS-UO₂ fuels into chloride-free nitrate solutions suitable for processing in existing stainless steel solvent extraction equipment. Chloride is necessary to effect dissolution of stainless steel in HNO₃ but it must be removed to avoid corrosion of process equipment. The ORNL reference flowsheet, which employs 13.3 M HNO₃ to produce SX feed containing <350 ppm chloride, is being applied to additional fuels such as Nuclear Ship Savannah (SS-clad UO₂), SS-clad UO₂-ThO₂, and NaK or Na bonded U metal or alloy.

The Explosive Reaction of NaK and Dilute Aqua Regia. The purpose of the present study was to determine the effect of NaK reacting with aqua regia while the aqua regia was simultaneously reacting with stainless steel. This situation would exist in the Darex processing of SRE fuel (SS-clad, NaK bonded uranium metal). In the final test of five experiments a detonation occurred which shattered the glass dissolver.

Prototype fuel pins consisting of 12-in. lengths of 0.4-in. o.d. (0.010-in. wall) 304 L tubing, 5 cc of NaK (eutectic), and 10-1/4-in. lengths of glass rod (see Figure 5.1) were made up for the experiments. This design gave a NaK annulus of 8 to 12 mils. Closure was made by a cap-type fitting on a piece of 1/2-in. tubing welded to the thin-walled 0.4-in. tubing.

Five dissolutions using one pin as described were made with 1.5 liter of 5 M HNO₃ - 2 M HCl as dissolvent. During the first four dissolutions yellow flashes and streaks of flame were visible with only one audible explosion which did no damage. During the fifth dissolution a violent explosion occurred which shattered the 1 ft length of 3-in. Pyrex pipe at the bottom of the dissolver.

Figure 5.1 shows the fragments of the lower section of the dissolver with only the upper flange intact. On the right the pin may be seen with penetration extending only about 1-in. above the severed end cap; the glass rod was not etched or crazed as had been observed in several of the earlier experiments. This explosion and the previous uneventful dissolution were recorded photographically at 32 frames/sec. These sequences along with scenes showing prototype assembly and procedure were combined into a movie entitled "Darex Dissolution of NaK-Bonded Prototype Fuel" and designated RE-163-64-65-R-B. This movie is available for loan to anyone interested.

Since the chemical system involved is so complex no detailed discussion of possible reaction mechanisms will be presented. However, it should be noted that in addition to the violent reaction of NaK with acid solutions there is a possibility of further reaction between the various gases produced. Flammability limits for hydrogen in nitrous and nitric oxide (produced in the aqua regia dissolution of stainless steel) are 5.2 - 80 and 13.5 - 49%, respectively⁽¹⁾

(1) Coward, J. F. and Jones, G. W., "Limits of Flammability of Gases and Vapors," Bureau of Mines Bulletin 503, p. 134, 1952.

Fig.5.1. Prototype Fuel Pin before and after Dissolver Explosion.

Figure 5.2 shows the experimental equipment inside the enclosure with an element in the dissolver. Two 6-in. reducers provided a disengaging space, and the condenser, with water inside the coils, was a vent with a large free area. Heat was supplied by a hot plate placed beneath the titanium bottom flange plate. The element was suspended on a tantalum wire extending outside the enclosure so it could be lifted from the solution remotely for examination. Figure 5.3 shows the construction of the enclosure with the dissolver positioned before the two 6-in. thick lead glass viewing windows.

5.2 Sulfex - B. C. Finney, R. C. Early

The Sulfex equipment (1/25 pilot plant scale, see Unit Operations May monthly report ORNL CF 59-5-47) was leak tested, and the operational procedure was checked using boiling water and air to simulate dissolution with gas evolution. A scouting run (SX-1) of 1.68 hrs duration was then made, dissolving a stainless steel plate-type fuel element.

Dissolution started immediately upon contacting the prototype fuel with hot H_2SO_4 ($\sim 115^\circ C$) indicating no passivation. The flow rate of H_2SO_4 for the first hour was approximately 2 liter/min and for last 0.68 hrs approximately 1 liter/min. The hydrogen off-gas flow rate leveled off at approximately 1.28 cfm (STP) which is equivalent to a dissolution rate of approximately 83 g stainless steel/min. At shutdown, approximately 1/10 of the fuel element remained and the volume of product was 163 liters. It was observed that there were black particles dispersed throughout the dissolver. Some of the dekad solution will be centrifuged to determine the relative amount and composition of the particles.

Foam and liquid reached a height of 15 ft in the dissolver, approximately 11 ft above the bottom of the fuel element. This foam resulted in the de-entrainer becoming full of dissolver solution, and the solution entered the off-gas line. This entrainment caused erratic operation of the off-gas system; otherwise, the equipment operated satisfactorily.

The dummy fuel element consisted of 11 - 304 L stainless steel plates 4.5 ft x 3-in. x 0.038-in. bolted together with 1/4-in. plate spacing and weighing 7.75 kg. The dissolvent was boiling 6 M H_2SO_4 . Prior to starting the run, the system was purged with approximately 30 cu ft (15 volumes) of N_2 . An Orsat analysis of the off-gas indicated 2.2% oxygen after the purging was completed.

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

The purpose of the feed clarification studies is to obtain data for the design of solid-liquid separators for treatment of solvent extraction feed streams and spent dejacketing solutions.

Filtration Flowsheet - Small Scale Demonstration. A preliminary filtration flowsheet (Figure 5.4) for removing siliceous material from Darex (APPR)

Fig.5.2. Dissolution Equipment Inside Enclosure.

Fig. 5.3. Exterior of Enclosure

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Fig. 5.4 Flow Sheet of Small Scale Feed Clarification of Darex (APPR) SX Feed Solution.

solvent extraction feed using a porous metal element was tested successfully on a laboratory scale. Reagent makeup and addition (filter aid, gelatin, soluble silica), the silica-gelatin precipitation, gravity settling, and split feed filtration were satisfactory. Washing efficiency was less satisfactory due to unsuitable experimental equipment rather than being an inherent difficulty.

Following the proposed flowsheet (Figure 5.4) reagents were premixed to form a 10% slurry of Celite 545 filter aid in water (486 cc) containing 1.40 g of soluble silica and 0.72 g of gelatin. This mixture can be prepared and handled easily. Darex liquor (5.4 liter) was preheated to 80°C, the reagent slurry was added, and the mixture was heated to 85°C for 1/2 hour. Most particles settled in 5 min; settling was essentially completed after 1/2 hour cooling (to 75°C). A few fine flocs floating on convection currents remained. No further settling occurred up to 1-1/2 hours, and 4 liters out of 5.9 liters total of clear liquor were removed for filtration. A larger fraction of clear liquor could have been separated without disturbing the sludge by using a properly designed withdrawal line. The 4 liter of clear liquor with 1 g of Celite 545 filter aid added was filtered on a 0.18 sq ft porous stainless steel filter element⁽²⁾ followed by the sludge. Filtration was completed in 40 min (Figure 5.5) duplicating filtration cycles times previously reported⁽³⁾. Two hundred eighty grams of damp filter cake was recovered after four 1.5 liter washes with 0.01 M HNO_3 .

Washing efficiency was poor (Table 5.1). Only 98.6% uranium recovery was achieved after two washes, while close to 99.9% would have been expected from previous data. Through washing, needed for high washing efficiency, was not attained because of equipment limitations (see Note 1, Table 5.1). A recheck of the filtration rate after water backwashing for cleaning the filter element showed no fouling had occurred.

The following additional observations were made during the tests:

a. The salt, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, was readily soluble in water. It was a convenient source of soluble silica when required. b. Gelatin solutions up to at least 20 g/liter of water can be conveniently prepared. c. The bulk density of the filter cake, drained of fluid, was ~0.9 g/cc.

The feasibility was investigated of using a single filter aid addition after the gelatin-silica precipitation. The filter aid-water slurry (540 g; 10% Celite 545) was added to 5.4 liters of Darex (APPR) solution. Settling was complete in 7 min. In use, filtration of clear liquor would be started after approximately 2 min. Operating in this manner would allow most of the filter aid to settle with the sludge but would leave a small portion with the clear liquor. The small amount of filter aid with the clear liquor (essentially as a precoat) protects porous metal elements from premature blinding and reduces the frequency of caustic cleaning. Water and steam cleaning keep the element clean for several cycles.

(2) Micrometallic Co., 20 μ mean pore size.

(3) Unit Operations monthly report, July 1959, CF 59-7-58.

Fig.5.5. Feed Clarification Filtration of Darex (APPR) Solvent Extraction Feed Solution.

Table 5.1. Uranium Recovery in the Filtration Cycle⁽¹⁾

Sample	Volume (liter)	Weight (g)	Uranium			Uranium Recovery (%)	Cumulative Uranium Recovery (%)
			(g/liter)	(%)	(g)		
Filtrate	5.15	-	4.89	-	25.18	95.27	95.27
1st Wash	1.5	-	0.41	-	0.69	2.61	97.88
2nd Wash	1.5	-	0.135	-	0.20	0.76	98.64
3rd Wash	1.5	-	0.078	-	0.12	0.45	99.09
4th Wash ⁽²⁾	1.5	-	0.135	-	0.20	0.76	99.85
Cake (wet)	-	280	-	0.014	0.04	0.15	100.00

- (1) Washing was poor since the desired through washing at the cake was only partially attained; the cylindrical element and cake volume occupied almost the whole volume of a cylindrical container so that wash water could not freely reach most of the cake surface.
- (2) The 4th wash was by repulping to facilitate cake recovery; the increase in uranium analysis in this wash indicates poor washing.

Centrifugation. Unwashed cake centrifuged from Darex SX feed (APPR) at 1200 gees had a density of 1.35 g/ml. Concentration of silica was 27.4 g SiO₂ liter of cake. An order was placed for rental of a Tolhurst 12-in. laboratory centrifuge.

Centrifugation - Problem Statement. The purpose of the centrifugation program is to devise and evaluate methods of separating and recovering fissile and fertile matter from particulates (silica, carbides, UO₂, and UO₂-ThO₂ fines) contained in process and decladding solutions and to dispose of the undesired particles as waste.

The removal of precipitated silica from solvent extraction feed solutions resulting from the dissolution of stainless steel alloy and stainless steel clad UO₂ fuels is desirable to prevent possible misoperation of the solvent columns. Aqueous reprocessing of stainless steel or zirconium-clad UO₂ or UO₂-ThO₂ fuels require separation of fine particles of core material from the decladding solution.

The removal of silica allows solvent extraction columns to be operated with a reduced amount of interfacial crud formation. Recovery of fine particles of UO₂ and UO₂-ThO₂ is necessary for economic reprocessing. The separation equipment must be simple, reliable, remotely operated and decontaminable.

Silica removal by centrifugation will be studied in 5-in. and 12-in. batch-type centrifuges to determine residence time and cake washing efficiencies. Methods of slurring the cake will be studied, and a suitable procedure for skimming the supernate and removing the washed cake will be determined. The objective of the tests will be to develop data for the design and operation of pilot plant equipment.

Similar studies will be made on separation of UO₂ fines and siliceous material from declad and product solutions. In later operation, the 12-in. centrifuge will be used in conjunction with the existing Sulfex facility, providing continuous clarification of declad and product streams.

Centrifugation - Cake Removal. Solids collected on the walls of a solid centrifuge bowl must be dislodged and slurried in order that the cake may be washed and jetted from the bowl. In preliminary tests, an H₂O wash volume equal to twice the cake volume was effective in dislodging siliceous Darex APPR cake from the wall of a 5-in. dia centrifuge bowl, when distributed through a spray nozzle at 30-40 psi pressure. Acquisition of a 12-in. dia laboratory centrifuge will permit the extension of cake removal tests to a cake thickness approaching that expected in the production centrifuge. Attempts will be made to achieve cake dislodgment and pulping with a wash/cake volume ratio of unity.

5.4 Mechanical Processing - J. B. Adams, G. K. Ellis, G. A. West, C. J. Claffey
F. L. Rogers, D. E. Willis

Materials handling flowsheets were prepared for (a) decladding, washing, recanning and storing spent SRE uranium fuel slugs and (b) the shearing and leaching of stainless steel-clad UO₂ and UO₂-ThO₂ fuels.

SRE Decladding

Equipment for decladding, washing, recanning and storing spent SRE uranium fuel slugs has been designed and arranged in the High Level Segmenting Facility in a stepwise materials handling flowsheet (Figures 5.6 and 5.7). Spent fuel clusters (7 NaK-bonded SS tubes containing 84 uranium slugs) will arrive at the Segmenting Facility in a special fuel cask (Figure 5.8) with a rotating rack (Figure 5.9) for positioning individual assemblies for discharge through the 5 ft thick concrete walls onto a traversing table inside the hot cell. Equipment in the Segmenting Facility consists of the following:

- (1) A traversing table with vise clamps to constrain each assembly and position it under an abrasion disc saw.
- (2) A multipurpose abrasive disc disassembly saw for the removal of inert end assemblies.
- (3) A SRE hydraulic decladding device.
- (4) Slug baskets to receive decladded slugs.
- (5) A slug washer to remove oil and NaK by steam cleansing.
- (6) A slug washer filter to reclaim particulate uranium dislodged during the washing operation.
- (7) NaK disposal equipment for the safe reaction of NaK with steam.
- (8) Finger washers to remove oil from manipulator fingers.
- (9) A slug recanning machine to recan the 12 slugs from a SRE element in an aluminum can for transfer and safe storage.
- (10) A slug canning table.
- (11) An auxiliary clad-slitting tool to declad deformed rods that can not be decladded by normal hydraulic means with the regular decladding equipment.
- (12) Scrap containers to receive inert materials.
- (13) Tool rack.
- (14) Model E-3 manipulator.
- (15) Model 7 manipulators.
- (16) A 3 ton crane hoist.

Fig.5.6. Proposed Installation Of SRE Fuel Element Reprocessing Equipment - Bldg. 3048
Plan View - Cell "A"

Fig. 5.7. Proposed Installation of SRE Fuel Element Reprocessing Equipment - Bldg. 3048
Front Elevation - Cell "A"

FIG.5.8 SRE FUEL ELEMENT CARRIER

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FIG. 5.9 SECTION OF SRE FUEL ELEMENT CARRIER

All the equipment for decladding the SRE fuel elements is scheduled to be fabricated and ready for evaluation tests by September 30, 1959.

SRE Decladder. The SRE decladding equipment which was fabricated by the Southern Machine Co., Chattanooga, Tennessee is being reworked. Refabrication of forty-three parts is necessary. Improved design requires the fabrication of an additional fifteen parts which are also being made simultaneously with the "off specification" parts.

Disassembly. The design of hydraulically powered multipurpose saw for the disassembly of loops and the removal of inert end adapters, etc., from spent fuel was completed and fabrication of the support pedestal was started by Ty-Sa-Man Machine Co., Knoxville, Tennessee, the designer and fabricator.

Shearing and Leaching

A layout of the shearing and leaching equipment in the High Level Segmenting Facility for shearing metal-clad UO_2 tubular bundles and leaching the UO_2 from sheared pieces is shown in Figure 5.10. Shearing is done in Cell A, the sheared product transferred into Cell B via a vibrating tray and, in the concept shown, there is continuous leaching in an inclined drum leacher (see Figure 5.11, Unit Operations June 1959 monthly report, CF 59-6-63 for a description of the inclined drum leacher). Other concepts not shown include leaching in a spiral vibrating leacher (see Figure 5.10, Unit Operations January 1959 monthly report, CF 59-1-74), either batchwise or continuously, or batchwise in a vibrating tray. The vibrating transfer tray which also functions as a sheared product surge volume may be eliminated and leaching done in a similar vibrating tray leacher into which the shear feeds directly. This technique would be a final recourse if the sheared product is of a size too large to be compatible with feeding the spiral vibrating and inclined drum leachers.

Also shown in Figure 5.10 is the layout of chemical equipment in Cell B, the saw table for cutting off inert end hardware, and the method of feeding the shear through an adjacent enclosed feed trough into which the fuel bundle is inserted.

Shear Blade Evaluation. Feasibility testing of Clearing Machine Company and Birdsboro Machine and Foundry Company, Inc. has shown that shearing of spent fuel elements with reasonable blade wear is possible (Unit Operations July 1959 monthly progress report, CF 59-7-58). Additional information is needed, however, for final criteria for the production prototype shear which Birdsboro will design and fabricate for use in the ORNL Mechanical Processing program. Some of this information is now being obtained in shearing tests at ORNL using ORNL blades and die sets.

Several preliminary observations were made from this series of tests.

1. The hardness (Rockwell C51 or greater) and physical characteristics of Microbraz 50 contribute significantly to shear blade damage, shortening blade life by galling of these brazed pieces between

LAYOUT

ELEVATION

Fig. 5.10. Equipment Elevation and Layout in Building 3048 for Remote Shearing and Leaching of Irradiated Stainless Clad Ceramic Fuels:

the blades (Rockwell C56). In this manner during a single cut, a piece of metal approximately 10 mils thick was broken from the punch and the anvil was noticeably abraded.

2. Chipping of the blade edge usually occurs during the first 50-75 cuts. By grinding a 1/32-in. radius on the blade edges, the initial blade wear and chipping of the cutting edge was eliminated.
3. A significant and difficult problem is the shearing of bundle end pieces to a size which can be passed through continuous solids discharging leachers without jamming. The existing die set is being altered to shear at shorter lengths by supporting the tube bundle along its axial length between a double anvil while constraining it with a gag.
4. A spring-loaded metallic envelope through which a fuel assembly is fed successfully retains the prototype bundle for shearing and facilitates material transfer of the bundle into the shear throat for any of the blade combinations tried. This method appears to be readily adapted to remote operation.
5. The best punch and anvil shape combination tested was a stepped and circular pair.

The ORNL tests were made at a blade velocity of 2 in./sec, 2 to 3 mils clearance between blades, and a blade hardness of Rockwell C56 (Carpenter Vega tool steel). A total of eight punch blades used with each of three different anvil shapes (24 blade combinations) were evaluated by making 10 cuts with each blade combination. (Most blade shapes are shown in the March Unit Operations monthly progress report, CF 59-3-61). The shearing characteristics of each blade combination were analyzed qualitatively by reference to two high speed (2000 frames per second) movies made of each blade combination while shearing Mark I porcelain filled bundles.

Tentative Shear Criteria for the Prototype Shear Design by Birdsboro

The criteria presented to Birdsboro are intended to supplement, in a more detailed manner, those of specification PRFR-1a dated March 26, 1959. In general, these criteria do not supersede or negate the requirements of specification PRFR-1a. However, the size of fuel elements to be sheared as shown in Table 5.2 are revised and thus supersede those of specification PRFR-1a.

Location and Layout. The shear shall be located in Cell A, Bldg. 3048, near the northeast corner of the cell and at the highest practical elevation to allow maximum clearance beneath the shear for flexibility of conveyor installation and for possible future installation of a leacher under the shear. The shear shall be arranged for horizontal cutting stroke and horizontal feed. Insofar as practical, all hydraulic components shall be located outside the cell. The cell equipment shall be approximately as shown in Figure 5.10.

Table 5.2. Fuel Element Shearing Data⁽³⁾

Subassembly	Length L (in.)	Width W (in.)	Height H (in.)	Minimum Stroke ⁽¹⁾ (in.)	Minimum No. of Cuts/min ⁽²⁾	Tube o.d. (in.)	Tube Wall Thickness (in.)	No. Rods per Subassembly
1	99	2.54	2.54	3.6	4.0	0.340	0.021	34
2	108	2.54	2.54	3.6	3.8	0.305	0.019	43
3	71	4.53	3.87	6.0	1.6	0.500	0.035	41
4		3.42	3.42	4.9	1.3	0.57	0.033	36
5	10.25	4.52	4.52	6.4	0.78	0.411	0.027	120
6	102.25	5.20	5.20	7.4	0.94	0.304	0.020	196
7	63	3.52	3.52	5.0	3.3	0.450	0.020	25

(1) Min. stroke = Diagonal Dim. = $\sqrt{(W)^2 + (H)^2}$

(2) Required No. of 1-in. cuts/min. based on production rate of 300 Kg U or U + Th per day, allowing 4 hrs per day actual shearing time.

(3) This table superseded page 7 of spec. PRFR-1a dated 3/26/59.

Dated 8/21/59

Design of Shear. The shear shall be designed so that the blades and blade holders may be removed and replaced as a unit by remote means. The discharge chute at the bottom of the shear shall have a sufficiently steep pitch to ensure against accumulation of solids. The discharge chute shall be designed to accommodate a discharge valve which will be selected by ORNL.

Dimensional Criteria. The dimensions of fuel elements to be sheared are shown in attached Table 5.2. The length of shear stroke shall be variable up to 12-in. maximum. The clearance between moving and stationary blades in the closed positions shall be 0.002-in. $\pm$ 0.001-in. The shear discharge chute shall not exceed 9-in. dia.

Preparation of Fuel Elements. In general, as much as possible of the inert metal hardware will be removed from each fuel element assembly by remote sawing prior to shearing. These sawing operations will result in subassemblies of the sizes indicated in Table 5.2. The shear shall be designed to accommodate the fuel element bundle dimensions shown therein. Figure 5.11 shows fuel element subassemblies as prepared for shearing.

Feeder. The shear feeder shall feed, constrain, and guide the fuel elements. Reliability of the mechanism ease of maintenance and decontamination shall be given prime consideration in design of the feeder mechanism. The least possible number of working parts shall be exposed to abrasive particles. As much of the mechanism as practical shall be external to the enclosure specified below.

Feeding action shall be synchronized with action of the shear and with the fuel bundle clamp and/or compactor. The mechanism shall have the ability to sense an incomplete cut and to permit additional cutting strokes as required to complete the cut before the feed mechanism advances the bundle for the next cut. The mechanism shall have overload protection. Provision shall be made for holding and shearing end pieces of fuel elements so as to prevent large end pieces from passing through the shear without being cut. Design of the shear feeder shall be compatible with the design, by ORNL, of the mechanism which will elevate each fuel bundle from the sawing table into the shear feeder.

Position Indicators. Provision shall be made for remote indication of position of shear cutting ram so that the operator is informed of the length of the remaining uncut portion of the element.

Enclosure. Shearing and feeding of the fuel element shall be performed inside an air-tight enclosure. Windows shall be provided in the enclosure to permit remote observation, with the aid of a closed-circuit T.V. camera, of (a) the end of the fuel bundle following the cut and (b) the appearance of the sheared product. The window glass shall have provision for heating to prevent browning of the glass. A quick-operating air-tight closure shall be provided for entry of the fuel element into the feeder.

The number of seals through the enclosure shall be kept to a minimum. The inside of the enclosure shall be free of crevices, for ease of decontamination. The enclosure bottom shall be pitched for positive drainage of liquids through the product removal port below the shear blades.

Fig. 5.11. Appearance of PRFR Fuel Assemblies Prepared for Shearing to Expose UO_2 Core Material for Subsequent Nitric Acid Leaching. Preparation Includes the Required Disassembly End Removal and Banding.

Product Properties. The sheared product shall consist of discrete pieces rather than agglomerates.

Blade Development. Blade material, blade velocity configuration, and hardness shall be subject to approval by ORNL.

Wash-Down and Decontamination. Shearing shall be done in the dry state with internal water sprays used before the enclosure is opened. Spray nozzles shall be provided inside the enclosure to permit recovery of fines and decontamination of the enclosure. Water and/or nitric acid will be sprayed.

Special Handling Requirements. Design of the shear feeding mechanism shall be integrated with the design, by ORNL, of the mechanism which will elevate the fuel elements from the sawing table into the shear feeder. Special handling external devices will be provided by ORNL as required for remote changing of shear blades and blade holders. Consideration shall be given by Birdsboro as integral in design of the shear to facilitate changing of blades and holders. Consideration shall be given to accommodation of the various fuel subassemblies as shown in Table 5.2 and in Figure 5.11.

Criticality. Geometry of the interior of the shear enclosure shall be subject to review and approval by ORNL to ensure against accumulation of a critical mass.

Materials of Construction. All exposed internal and external surfaces used inside the cell shall be fabricated of materials which are resistant to corrosion by water and nitric acid. Stabilized or low-carbon grades of austenitic (300 series) stainless steels are the recommended construction materials. Such materials shall conform to the applicable ASTM specification. Materials shall be approved by ORNL. The use of exposed castings shall be avoided unless such castings can be guaranteed free of surface porosity. The surface of castings which do not meet these porosity requirements may be covered with sheet metal which meets the above requirements.

Welding. All welding shall be performed in accordance with the requirements of Section VIII of the ASME Boiler and Pressure Vessel Code. Welders shall be currently qualified in accordance with the requirements of Section IX of the ASME Boiler and Pressure Vessel Code. All exposed inside or outside welds shall be inspected using a commercial liquid dye penetrant. No indications of porosity will be permitted. As a minimum requirement, all other welds shall be visually inspected.

Surface Finish. The finish of all exposed internal and external surfaces inside the cell shall be 125 RMS micro-inches or better.

Leaching - G. K. Ellis

Considerable time has been lost preparing the vibrating spiral leacher for leaching of UO_2 because of weld and electrical failures. Each failure caused detuning of the conveyor and required approximately a week's delay in conveyor disassembly, removal from the cell, location of the trouble, and

reassembly. The vagaries of the machine have usually required the visit of a Syntron representative for maintenance. At this time several alternatives are being considered because of generally inadequate welding in the unit. The unit will either be discarded and emphasis placed on other types of leacher, the spiral will be rebuilt by grinding out all existing welds and rewelding, or a new spiral will be built.

6.0. REACTOR COOLANT DECONTAMINATION - A LITERATURE SURVEY

J. C. Mailen

6.1 Pressurized Water Reactors

Comparisons of corrosion product activities as given in Tables 6.1 and 6.2⁽²³⁾ indicate that the use of Inconel in the coolant piping of a pressurized water reactor may reduce the deposited activity by a factor of two or greater. Table 6.2 indicates that the bulk of the gamma contribution (about 67%) comes from zirconium and antimony deposits. These two elements originate not in the Inconel piping, but from fuel cladding and other alloys.

When cladding ruptures are present, considerable amounts of deposited activity will be due to escaping fission products. Pipe wall analyses for the first and second X-1-L pipe studies are given in Table 6.3.⁽²¹⁾ In the first test the three fission products Mo, Te, Ru and the two activation products Mn and Co contributed between 80 and 90% of the total gamma counts. In the second test these five contributed between 50 and 67%. It may be seen from the percentage totals that in the second case there was more activity unaccounted for. This result indicates that greater amounts of unidentified fission products escaped during the second test. In this second test Mo⁹⁹ was the major contributor identified (~50% of total).

The ORR reactor⁽¹²⁾ at ORNL is an example of a low pressure light water cooled reactor using aluminum piping. This reactor has had little difficulty with internal corrosion and crud, probably because of the low operating temperatures. Purification is by separate ion exchangers and filters with 80 gpm through the resin beds and 100 gpm through the clarification filters. The internal flow rate is about 16,000 gpm and the total coolant volume 59,000 gallons. The reactor is of the pool type and has a separate purification system for the pool. The power level is about 20 megawatts in the summer and 30 megawatts in the winter. Water pH is kept between 5.5 and 6.5 and the specific resistivity averages about 800,000 ohms. In Table 6.4⁽¹⁵⁾ are given typical water conditions after operation for nine days at 20 megawatts.

Data presented in reports WAPD-MRH-10⁽²¹⁾ and WAPD-MRH-13⁽²³⁾ support the general conclusion that the thickness of the crud deposit in a pressurized water system is dependent upon the amount of ionizing radiation. Data in WAPD-MRH-8⁽¹⁹⁾ from the Van de Graaff program give proof that deposition is much greater under irradiation than with no radiation present. A portion of this data is presented in Table 6.5. Some data⁽²⁰⁾ indicates that when a portion of the fuel elements undergoes local boiling the crud deposit on this area will be thicker than on non-boiling elements.

In WAPD-LSR(C)-134⁽¹⁸⁾ the data from numerous experimental measurements of corrosion rates of carbon steel in high-temperature, high-purity water in dynamic systems has been correlated. The data fell fairly well on two curves, one for pH 7 to 10 and one for pH 10 to 12, regardless of other variables such as:

Table 6.1. CR-V Water Borne Crud Data⁽²³⁾

Nuclide Activity, $\mu\text{c}/\text{mg}$				
Nuclide	Stainless Steel	Inconel	1st Monel*	2nd Monel
Co ⁵⁸⁺	0.014	0.031	0.068	0.054
Co ⁶⁰⁺	0.091	0.112	0.135	0.14
Fe ⁵⁹⁺	0.155	0.157	0.445	0.42
Cr ⁵¹⁺	-	-	7.0	11.7
Ni ^{65†}	0.045	0.22	0.67	0.36
Mn ^{56†}	7.2	8.9	33.8	19.0
Cu ^{64†}	-	19.0	13.5	9.5
crud conc. ppb	2.8	3.1	3.2	4.5

* Does not include samples taken early in cycle.

+ Seven days after sampling.

† Corrected for decay during sampling.

Table 6.2. CR-V Inconel Pipe Test⁽²³⁾

Nuclide	Stainless Steel Pre-Inconel	% Gamma Energy Contribution	Inconel Pipe Avg. $\mu\text{c}/\text{sq dm}$	% Gamma Energy Contribution
	$\mu\text{c}/\text{sq dm}$			
65d Zr ⁹⁵	1.65	2.4	4.5	37.7
310d Mn ⁵⁴	3.15	5.35	0.06	0.6
28d Cr ⁵¹	9.5	0.5	4.5	1.4
45d Fe ⁵⁹	1.5	3.65	0.6	8.5
60d Sb ¹²⁴	0.27	1.0	1.2	29.7
5.2 yr Co ⁶⁰	16.5	83.5	0.63	19.3
72d Co ⁵⁸	<u>1.8</u>	<u>3.5</u>	<u>0.24</u>	<u>2.8</u>
	24.45	99.9	11.73	100.0

Table 6.3. Comparison of First and Second X-1-L Pipe Studies ⁽²¹⁾

Per cent contribution, at various hours after shutdown*

Nuclide	First Test			Second Test		
	3 hr	8 hr	96 hr	3 hr	8 hr	96 hr
Mo ⁹⁹	54.6	63.3	46.3	41.4	47.3	53.4
Mn ⁵⁶	5.7	1.5	-	8.0	2.5	-
Te ¹²⁹ + Te ¹³²	9.5	11.6	19.3	-	-	-
Te ¹³²	-	-	-	0.28	0.31	0.39
Te ¹²⁹	-	-	-	0.36	0.43	1.1
Co ⁶⁰	4.9	6.0	10.74	2.7	3.2	9.1
Co ⁵⁸	~0.4	~0.5	~0.94	0.09	0.11	0.29
Ru ¹⁰⁶	4.2	5.1	9.13	ND**	ND	ND
Ru ¹⁰³	ND	ND	ND	0.76	0.91	2.33
Ba ¹⁴⁰	2.0	2.4	3.51	0.23	0.27	0.62
Sb ¹²⁴	1.1	1.4	2.42	2.96	3.52	9.5
Ta ¹⁸²	<1.1	<1.4	2.50	ND	ND	ND
Zr ⁹⁵	1.1	1.4	2.36	0.25	0.30	0.81
Fe ⁵⁹	0.11	0.13	0.22	1.11	1.33	3.53
Ce ¹⁴⁴	0.8	1.0	1.75	ND	ND	ND
Cr ⁵¹	<u>0.08</u>	<u>0.11</u>	<u>0.15</u>	<u>0.25</u>	<u>0.30</u>	<u>0.72</u>
	85.6	95.8	97.3	58.4	60.5	81.8

* Ratio = $\frac{\text{Total Gamma counts above 30 kev from isotope}}{\text{Total Gamma counts above 30 kev, all activity}} \times 100$

** ND = Not Detectable.

Table 6.4. Water Analysis of ORR Water (15)

Pool Flow = 730 gpm

Reactor Flow = 15,600 gpm

Pool Demineralizer = 75 gpm

Reactor Demineralizer = 67 gpm

<u>Impurities</u>	<u>Quantity, ppm</u>	
	<u>Reactor</u>	<u>Pool</u>
Al	<0.05	<0.05
Fe	<0.05	<0.05
Ni	<0.05	<0.05
Co	<0.05	<0.05
Pb	<0.05	<0.05
Si	2	<0.1
OH ⁻ as CaCO ₃	3	3
pH	5.65	5.75
Specific Resistance	8.94×10^5 ohm-cm	1.07×10^6 ohm-cm
T.S.	4.4	2.1
Cr	<10	<10
Ca	<0.05	<0.07
Cl ⁻	<1	<1
Cu	<0.05	<0.05
Na	<0.1	<0.1

Table 6.5. Van de Graaff Generator Irradiation Study

With Carbon Steel Crud Source⁽¹⁹⁾

Temperature = 450°F

Conductivity = 1.0 μ mho

Pressure = 2000 psi

Loop pH = 6.5 to 7.0

Run No.	26	27	28	29	30	31	32	33	34	35	36	37	38
Time, hr	46	48	48	48	48	50	47	48	48	48	48	48.8	48.5
Beam current, μ amps	-	-	-	-	125	125	126	128	-	125	-	125	-
Fluid velocity, fps	4.4	4.4	2.2	2.2	4.4	4.4	2.2	2.2	4.4	4.3	2.2	2.2	4.4
O ₂ Conc., ppm	0.53	0.47	0.54	0.61	0.51	0.61	0.32	0.51	0.62	0.47	0.63	0.55	0.37
% Dis- position	0.13	0.28	0.51	0.34	3.24	4.81	4.25	5.14	0.32	6.72	0.53	5.78	0.25

- a. Variations in the alkalinity in the range of pH 10.5 - 11.5,
- b. Variations in the alkalinity in the range of pH 7 - 9.5,
- c. Differences in the material tested over the range of carbon steels investigated,
- d. Differences in surface finish over the range of surface preparations used,
- e. Variations in the hydrogen concentration in high alkalinity water (pH 10.5 - 11.5), at least when oxygen concentrations were low,
- f. Variations in the resistivity in the range of 10^4 - 10^6 ohm-centimeters,
- g. Variations in velocity of the water across the surface in the range of 15 fps to 35 fps,
- h. Variations in testing temperature in the range of 500 to 600°F, at pressures well above saturation pressure,
- i. Thermal cycling between 200 and 600°F at the rate of one cycle per day (8 hours at 200°F and 16 hours at 600°F),
- j. Whether the test facility is constructed of stainless steel or carbon steel,
- k. Whether the alkalinity is obtained with lithium or ammonia, as long as the alkalinity is in the range of pH 10.5 - 11.5,
- l. Differences in specimen size and shape over the range used,
- m. The type and operation of the demineralizer over the range of variables considered.

The most significant effect was in the change of pH from 7 - 10 to 10 - 12. At the high pH the corrosion rate is reduced as is shown by the curves (18) reproduced in Figures 6.1, 6.2 and 6.3 (pages 11, 12 and 13, respectively, of the original report).

Numerous pretreatments have been considered, but only a run at high alkalinity with lithium shows promise for reduction in the corrosion rate.

Release rates are usually lower than corrosion rates by a large factor as is demonstrated by comparison of the data in Table 6.6(19) with the pH 7 - 9.5 curve in Figure 6.3. These data if plotted on Figure 6.3 would fall considerably below the corrosion rate lines and would not show as great a slope. That is, the release rate does not decrease as rapidly with time as does the corrosion rate. The data of Table 6.7(25) also bears out the conclusion that release rates remain fairly constant with time.

Fig.6.1. Summary of Carbon Steel Descaled Corrosion in High Temperature Water, pH 10-12.
(Reference 18 , pg 11)

Fig. 6.2. Summary of Carbon Steel Descaled Corrosion in High Temperature Water, pH 7-10.
(Reference 18, pg 12)

Fig.6.3. Instantaneous Descaled Corrosion Rate of Carbon Steel in High Temperature Water.
(Reference 18 , pg 13)

Table 6.6. Release Rate of Carbon Steel
Corrosion Products in a Pressurized Water Reactor (19)

Temperature = 450°F

Loop Pressure = 2000 psi

Conductivity = 1.0 μ mho

O₂ = 0.5 ppm

Loop pH = 6.5 to 7.0

Carbon Steel Area = 33.85 sq dm

<u>Run</u>	<u>Accumulated time, hr</u>	<u>Release rate mg/sq dm month</u>
26	46	10.96
27	94	10.75
28	142	11.14
29	190	9.04
36	238	10.14
34	286	9.75
30	334	8.07
31	384	6.53
32	431	7.86
32	479	6.35
38	527	7.27
35	575.5	6.79
37	624.4	5.87

Table 6.7. Release Rate of Corrosion Products
from Type 304 Stainless Steel⁽²⁵⁾

Specific Area = 0.738 sq dm

Water Velocity = 2 to 3 fps

First period of operation - 0 to 44.5 hrs

O₂ = 0.69 to 1.09 ppm

pH = 10 to 10.4

Temperature = 470 to 500°F

Second period - 44.5 to 65.8 hr

O₂ = 0.29 to 0.80 ppm

pH = 10.0 to 10.4

Temperature = 490 to 500°F

Third period - 65.8 to 93.3 hr

O₂ = 0.40 to 0.87 ppm

pH = 10 to 10.3

Temperature = 405 to 500°F

Release Rate of Element mg/sq dm month

<u>Nuclide</u>	<u>First</u>	<u>Second</u>	<u>Third</u>
Co ⁵⁸ + Co ⁶⁰	1.7 x 10 ⁻⁴	3.24 x 10 ⁻⁵	7.1 x 10 ⁻⁶
Cr ⁵¹	0.169	-	-
Fe ⁵⁹	0.077	0.055	0.114

The desirability of regenerating organic ion exchange resins used in reactor purification systems is largely dependent upon the losses of capacity of the resin under gamma irradiation. A table giving radiation damage as per cent capacity change for most of the important organic ion-exchange resins is given in ORNL-1978(8). From this data the report concludes;

1. Degradation of all types of ion-exchange resins is negligible at a radiation exposure to gamma rays of 10^7 r or less.
2. The sulfonic polystyrene resins are barely affected by a radiation exposure of up to 10^8 r. After an irradiation of 1.7×10^9 r, only about 25% of the total cation-exchange capacity has been lost.
3. The sulfonic phenolic resins are more stable than the sulfonic polystyrene at lower levels of exposure. As the radiation exposure increases to 1.7×10^9 r, the degradation of both types is about 25%.
4. The quaternary amine anion exchange resins are unstable and lose about 40-50% of their capacity after an exposure of 3.8×10^8 r. At the 1.7×10^9 r level, the resin is almost completely degraded.
5. The weakly basic anion exchange resins are more stable than the quaternary amine type, and, in some cases, approach the stability of the strongly acidic resins.

One method of improving radiation and temperature stability of ion exchange materials would be the use of synthetic inorganic exchange substances. Work done with zirconium phosphate has shown that it gains capacity under irradiation at least up to 10^8 r of gamma radiation.(1,5) Inclusion of citrate organic residue in the lattice of zirconium phosphate increased the capacity of the material for monovalent ions.(13)

Performance data given in WAPD-MRL-11(26) indicate that both hot (magnetite) and cold filters perform with high efficiency in removing insoluble crud. The cold filter gave a greater backwash crud recovery with a 35.8% recovery compared with a 23% recovery from the hot filter. In tests of axial and radial magnetite filters it was found that the radial filter had the greatest decrease in efficiency with time of operation.

A cyclone separator system has been designed for removal of crud from a carbon steel system.(16) This system would pass 2800 gpm of a total of 88,000 gpm of water through a scalping set of cyclone (about 50 mm dia) followed by a set of smaller cyclones (about 10 mm dia). The overflow from the cyclones consisting of about 90% of the flow to the cyclones would then be returned to the main loop. The underflow (~10%) would be cooled, depressurized and then sent to another small set of cyclones whose underflow (~15 gpm), containing essentially all the particles above 2 microns, is discarded. The 265 gpm overflow from the last set of cyclones would be processed by a demineralizer system. In removal of all particles above 2 microns the system should remove ~99.3% of all crud, according to the analysis given in Table 6.8.(17)

Table 6.8. Crud Particle Size (% by weight) Used in

Solids Removal Tests ⁽¹⁷⁾

<u>Microscope Method</u>		<u>Settling Rate Method</u>	
1-5 microns	5%	< 2 microns	0.7%
5-10	37	2-4	3.2
10-15	<u>58</u>	4-6	5.5
	100	6-8	16.5
		8-10	18.7
		10-12	13.2
		12-20	19.4
		> 20	<u>22.8</u>
			100.0

The crud analyzed was obtained from the KAPL-30 resin by mechanical separation. This technique may not have removed all the particles of small size.

In Table 6.9 are given additional values of the escape rate coefficients determined in various tests. (18,19,22,24) All the defects were planned except for WAPD-29-10. The planned defects consisted of 0.005-in. dia holes drilled in the cladding. The fuel in all cases was UO₂. The values for Kr⁸⁸ and Cs¹³⁸ are seen to have considerable range, but to be approximately the same. The coefficients for iodine isotopes are about an order of magnitude below those of krypton and cesium and remain approximately the same during shutdown. The data from the WAPD-29-10 test with an accidentally failed platelet fell within the experimental values from purposely defected plates. This result seems to indicate that the experimental values may be used to determine rough values of the fission product leaks from defects in operating reactors. A mathematical treatment designed to determine the fission product activity in pressurized water reactors is found in WAPD-TM-83. (6) The equations developed take into account purification treatment, deposition on system surfaces, and system leaks. Some constants used in the equations are determined from the escape coefficient data from the defected element tests.

In connection with the Yankee Reactor program the solution and procedure given in Table 6.10 have been recommended for decontamination. (28) This solution is said to give an overall decontamination factor of at least ten with corrosion rates as given in the second part of Table 6.10. On the basis of results from fatigue tests, cold bend test, and metallographic examinations

Table 6.9. Escape Coefficients λ , sec⁻¹
For Various Radioisotopes from Irradiated UO₂ Fuel

<u>Test</u>	<u>Kr⁸⁸</u>	<u>Cs¹³⁸</u>
X-1-0	1.2 x 10 ⁻⁸	2.3 x 10 ⁻⁸
	2.3 x 10 ⁻⁸	4.2 x 10 ⁻⁸
	2.2 x 10 ⁻⁸	5.5 x 10 ⁻⁸
WAPD-29-15	9.4 x 10 ⁻⁹	8.7 x 10 ⁻⁸
	2.4 x 10 ⁻⁸	4.2 x 10 ⁻⁸
X-1-L	2.2 x 10 ⁻⁸	1.6 x 10 ⁻⁸
	2.0 x 10 ⁻⁸	3.5 x 10 ⁻⁸
	2.6 x 10 ⁻⁸	4.6 x 10 ⁻⁸
	4.8 x 10 ⁻⁸	4.5 x 10 ⁻⁸
	3.6 x 10 ⁻⁸	2.9 x 10 ⁻⁸
	2.9 x 10 ⁻⁸	1.3 x 10 ⁻⁸
	1.8 x 10 ⁻⁸	1.8 x 10 ⁻⁸
WAPD-29-13	4.3 x 10 ⁻⁹	2.6 x 10 ⁻⁸
Average	2.3 x 10 ⁻⁸	3.7 x 10 ⁻⁸

Escape Rate Coefficients for Iodine Isotopes in X-1-L Test ⁽¹⁹⁾

<u>Isotope</u>	<u>Before Shutdown</u>	<u>During Shutdown</u>
I ¹³¹	2.6 x 10 ⁻⁹	2.3 x 10 ⁻⁹
I ¹³³	3.8 x 10 ⁻⁹	2.0 x 10 ⁻⁹

Calculated Values of λ for WAPD-29-10 Test with Accidentally Failed Platelet ⁽²²⁾

<u>Nuclide</u>	<u>Minimum*</u>	<u>Maximum**</u>
Kr ⁸⁸	2.0 x 10 ⁻⁸	4.5 x 10 ⁻⁸
Cs ¹³⁸	1.3 x 10 ⁻⁸	2.9 x 10 ⁻⁸

* Assuming maximum power platelet defected.

** Assuming minimum power platelet defected.

Table 6.10. Recommended Solutions and Procedure for Decontamination of
Yankee Reactor Primary Coolant Loop (28)

<u>Chemical Ingredients of Cleanup Solutions</u>	<u>Contact Time Minutes</u>	<u>Temperature °C</u>
1. 18% NaOH	30	105
3% KMnO ₄		
Hot Water Rinse (65-95°C)		

then

2. 10% Ammonium Citrate	15	100
-------------------------	----	-----

Corrosion of Yankee Reactor Primary Coolant System Materials of Construction

During Basic Permanganate-Citrate Decontamination

<u>Material</u>	<u>Wt. Loss mg/sq cm/30 min</u>	<u>Average Penetration mils</u>
AISI 304 SS	0.035	0.0017
AISI 316 SS	0.033	0.0016
AISI 347 SS	0.032	0.0016
AISI 410 SS	0.34	0.018
Microbrazed-50	0.56	0.032
Inconel	0.02	0.001
80% Ag-15% In-5% Cd)	2.28	0.090
Control Rod Alloy)		
Graphitar-14	0.67	0.132

it was concluded that no caustic embrittlement problem exists as a result of the use of the basic permanganate solution.

A solution for the decontamination of carbon steel loops with the following composition has been recommended; (22)

Sulfamic Acid	53.5 g/liter
2 Mercaptobenzothiazole	0.1 g/liter
Diethylenetriamine	17.5 ml/liter
Hydroxyethylenediaminetriacetic Acid	5 g/liter
pH Initial	1.5

Decontamination factors of 7.3 to 11.5 have been achieved and a pH of 1.5 gives the best results.

The following solution has been reported as best for the removal of radioactivity of sintered irradiated UO_2 . (23)

Sulfamic Acid	40 g/liter
H_2O_2	3.0 g/liter
Acetanilide	1.5 g/liter
Ethylenetriaminetetracetic Acid	3.5 g/liter
Hexamine	1 g/liter

6.2 Organic Cooled Reactors

For use as an organic reactor coolant, diphenyl seems to be the most stable compound when tested for thermal and radiation damage. Diphenyl may be useful as a coolant up to about 700°F with a continuous purifying system to remove polymer. (11) If heavy local boiling is allowed on elements transmitting a high thermal flux it is probable that both vapor phase and liquid phase cracking would occur before burnout of the element. Under mild local boiling little carbon will be formed. (2)

6.3 Gas Cooled Reactors

Of the possible coolant gases, helium, carbon dioxide, and nitrogen are probably being given the most consideration. Helium is the best from the standpoint of corrosion since any corrosion will be due to impurities which should be easily removable. (10)

Nitrogen reacts slowly with most reactor materials as outlined below. (10)

1. Uranium - reacts slowly at 400°C. Rate increases rapidly with temperature.
2. Zirconium - no significant reaction below 600°C.
3. Beryllium - with solid metal, little reaction up to 700°C; probably satisfactory up to 800°C.
4. Aluminum - little significant reaction likely below 600°C.
5. Magnesium - similar to aluminum.
6. Iron and Steel - reaction negligible, less than 400°C. Above this temperature the rate increases relatively slowly.
7. Niobium - reaction negligible less than 500°C.

With carbon dioxide and carbon monoxide (which will be present to some degree in reactor CO₂) the following reactions occur.⁽¹⁰⁾

1. Uranium - with CO₂, reaction becomes appreciable above 200°C. With CO, no significant reaction below 400°C.
2. Zirconium - with both gases the reaction is appreciable at 400°C and the rate increases rapidly with temperature.
3. Beryllium - reacts to form oxide and carbide.
4. Aluminum - a protective oxide forms - should be satisfactory up to 600°C.
5. Magnesium - rate slower than in air - should be satisfactory up to 600°C.
6. Niobium - with both gases the reaction becomes appreciable at 375°C and the rate increases rapidly with temperature.
7. Iron and Steel - carburized by both gases - rates indicate little significant reaction below 500°C.

Carbon dioxide also reacts with graphite at elevated temperatures. The reaction rate depends upon both the temperature and neutron flux encountered. Coatings are being tested for usefulness in reducing the reaction of carbon dioxide on graphite, but to present no positive results are available. The most promising at the present time is a silicon-silicon carbide coating developed by Minnesota Mining and Mfg. Co.⁽⁷⁾

At the Calder reactor⁽⁴⁾ only solid particles and moisture are separated from the carbon dioxide coolant. Each dust extraction circuit comprises a pair of ceramic filter units or a pair of cyclones. Approximately 2% of the coolant flow from each blower unit is withdrawn and passed through the circuit. The dust removal units extract all particles above 10 microns.

One coolant drying plant is installed in each blower house. The plant comprises two absorber towers, two gas coolers, a gas heater, a water-gas separator and drain pot. Each tower contains stainless steel wire mesh in mild steel frames in which is placed pelleted activated alumina. Each drying plant can remove 1.25 lbs of water vapor per hr when the gas is at 100 psig and 140°C. The average flow rate under these conditions is 110 cu ft/min. Gas entering the drying tower is at 25°C. To regenerate a tower a portion of the incoming gas is heated to about 315°C, passed through the adsorber, cooled to 25°C, and separated from the condensed water by a cyclone. The gas is then passed to the other adsorber tower and rejoins the rest of the undried gas.

In a system using a nitrogen coolant all reactive impurities can be removed by passing through liquid NaK at room temperature or by passing over heated uranium nitride.⁽¹⁰⁾ Carbon-14 is formed when the nitrogen is irradiated, and its removal is possible by reaction with CuO to give copper carbonate.⁽²⁷⁾

6.4 Liquid-Metal Cooled Reactors

Corrosion by liquid sodium is inhibited by the addition of small amounts of barium. The inhibition appears to be greatest between 0.1 and 1 wt % barium.⁽¹⁴⁾

For the decontamination of surfaces exposed to radioactive sodium and associated impurities, alcohol has been found ineffective. For surfaces easily contacted a solution of detergent such as 5% Alconox has been recommended with scrubbing more beneficial than agitation alone. If the surfaces are not easily reached, a Versene soak may be useful. If neither of the above methods reduces the radiation to acceptable limits an acid etch may be necessary. If acid penetration of equipment must be avoided, 1% nitric acid is probably a safe agent to use, and if gross decontamination of massive parts is required, a 1% chromic acid - 5% nitric acid solution at an elevated temperature will be effective in removal of metal and activity.⁽⁹⁾

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7.0 VOLATILITY

R. W. Horton

Gas Lift Pumping of Fused Salt - E. L. Youngblood

The hydrofluoric acid dissolution of zirconium-uranium alloy fuel elements in a fused salt bath is a method of preparing these fuels for the recovery of uranium by the fluoride volatility process. The fused salt serves to remove reaction products and reaction heat from the reacting metal; to perform this function efficiently it must be circulated past the metal surface. In the dissolver vessels now in use in the Unit Operations Section, this circulation is accomplished by the flow of hydrogen fluoride through the channels of a fuel element. Auxiliary devices such as gas-lift pumps might be used to augment this circulation. The performance of gas-lift pumps has been studied extensively in water systems. This report contains a comparison of the pumping rate of a gas-lift pump in water at 26°C and fused salt at 700°C.

Experimental Results. The pumping rate of a gas-lift pump was measured in water at 26°C and in a fused salt (approximate composition 38 M % NaF, 44 M % LiF, 18 M % ZrF₄) at 700°C under similar operating conditions. The gas-lift pump used was 8-in. long and was constructed of 1/2-in. dia stainless steel tubing. The unit was operated at constant submergence (64%) in both the water and fused salt. The experiments were performed in a 4-in. dia open top pot in which the fused salt was blanketed by the nitrogen used to operate the gas-lift pump.

Liquid flow rates were determined for various gas rates by measuring the time required to collect approximately a 100 ml sample. The liquid flow rate versus gas rate for water and fused salt shown in Figure 7.1 indicate that for the same mass flow rate of gas the pumping rates of water and fused salts in this system were quite similar. While pumping in fused salt the liquid was discharged in spurts. The pumping action in water was smoother, especially at the higher air rates.

A theoretical equation for the pumping rate of an air lift pump has been given by Coulson and Richardson,¹ based on the work done by the expansion of the gas in the pump:

$$\frac{w}{W} = \frac{h_r}{P_a V_a \ln (h_s/h_a + 1)} \quad (1)$$

h_a = atmosphere pressure expressed as feet of liquid.

h_r = height liquid is raised, ft.

h_s = submergence of pump, ft.

P_a = atmospheric pressure, lbs/sq ft.

1. Coulson, J M and Richardson, J. F., Chemical Engineering, Vol. I 126-131, McGraw-Hill Book Company, Inc., New York, 1954.

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Fig. 7.1. A Comparison of the Pumping Rates of a Gas Lift Pump in Water and Fused Salts.

w = weight of air, lbs.

W = weight of liquid, lbs.

V_a = specific volume of gas, cu ft/lb.

Equation (1) assumes isothermal expansion throughout the length of the pump. This assumption would be valid for the fused salt runs only if the gas was heated to the fused salt temperature in the gas inlet line as it passed through the salt before entering the bottom of the pump.

The theoretical curves for water and fused salt based on equation (1) are given in Figure 7.1. These curves indicate that the pumping rate of the fused salt should be considerably higher than that for water for the same mass gas rate due to the expansion of the gas at the higher temperature of the fused salt. Apparently non-isothermal flow and friction losses decreased the salt flow rate.

8.0 WASTE PROCESSING

M. E. Whatley

8.1 Calcination Studies - C. W. Hancher and J. W. Taylor

The purpose of the calcination study is to provide the necessary engineering design data for design of pilot plant calcination equipment. This report will describe calcination experiment R-17, calcination of synthetic Darex waste in an 8-in. dia x 48-in. long pot.

In a previous calcination run, R-16, using a simulated Darex waste feed, there was an unexplained pressure buildup in the calcination vessel which was sufficient to deform the flat bottom into a dish shape and rupture a weld.⁽¹⁾ R-17 was an attempt to duplicate, with adequate instrumentation, the conditions which caused the pressure rise, and to measure the rise during the entire run. In the sense that the run was to duplicate an undesirable effect, it was unsuccessful. The pot was filled over a period of 27 hours and calcined without a feed stream for 7 hours during which time the highest pressure measured was 1.5 psig. The operation was completely trouble-free.

The feeding and off-gas systems used for the test were the same as used for test R-16. The calciner vessel was 8-in. o.d. x 48-in. long, fabricated from 1/8-in. thick 347 SS. The head for the vessel was flat. The vessel welds were X-ray inspected before use.

The bottom flat head had no openings. The top flat head had 9 openings, 4 thermowells, 3 pressure probes, feed inlet and off-gas discharge (Figure 8.1). Six thermocouples were attached to the exterior of the vessel to measure its temperature.

The thermowells extended down to within 12-in. of the bottom of the vessel. The 6 thermocouples in each well were 3-in. apart varying evenly from 12-in. from the bottom to 27-in. from the bottom. Two of the three pressure probes penetrated to 1-in. from the bottom of the vessel, and the other was flush with the inside of the top. One of the deep pressure probes had a vibrated rod inside of the tube to breakup any solid that might form in the tube. All of the pressure probes were purged with nitrogen at a rate of 0.1 to 0.4 cu ft/hr. A cathetometer was used to measure the vertical movement of the top calciner vessel with respect to a fixed point.

Darex feed was prepared from metal salts with the approximate concentration of Darex waste that had been concentrated to 4.2 times its original metal salt weight (Table 8.1).

The calcination vessel (8-in. o.d. x 48-in. long) moved vertically 1.70 cm during preheating at an average skin temperature of 640°C. Thermal

1. July Unit Operations monthly progress report, CF 59-7-58.

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DISTANCE FROM CENTER
FOR THERMOWELLS

- A = 0 in.
- B = 2 in.
- C = $2\frac{3}{4}$ in.
- D = $3\frac{1}{2}$ in.
- E = FEED INLET
- F = OFF-GAS DISCHARGE

Fig. 8.1. Calciner Vessel Layout.

Table 8.1: Conditions and Results for Run R-17

Feed Composition	Component, g/liter				
	Fe	Ni	Cr	Al	NO ₃
	160	15	32	9	860

(Concentrated to ~4.2 times the theoretical original feed concentration by weight.)

Feed Rate - 2.83 liter/hr (80.00 liter in 28 hrs)

Condensate Rate - 1.74 liter/hr (65.7 liter in 38 hrs)

Off-gas - in excess of 200 cu ft

Solid - 35.0 liter)	Bulk density - 0.80 g/cc
28.0 kg)	

Product Composition

	$\frac{\text{Fe}}{\text{wt \%}}$	$\frac{\text{NO}_3}{\text{ppm}}$	$\frac{\text{H}_2\text{O}}{\text{wt \%}}$
Top Sample	50.1	300	0.19
Bottom Sample	49.4	305	0.06

expansion coefficient of stainless steel is approximately $18 \times 10^{-6}/^{\circ}\text{C}$ ⁽²⁾. Therefore, the movement should have been 1.4 cm. The difference probably lies in the range of temperature (300-900°C) included in the average. During the feeding cycle, the maximum verticle movement was 2.07 cm. The average temperature of the vessel was 935°C (920-985°C). The calculated movement should have been 1.99 cm, a good experimental check on the thermal expansion coefficient.

When the vessel was removed from the furnace, the bottom was not deformed. The greatest pressure observed from the vessel probes was 1.0 psig at the lower probes and 1.5 psig at the top probe. A reason why no pressure was observed may be that the vibration of one probe may have caused a gas seal in the off-gas line to break which released the pressure which caused the vessel in the previous test to deform.

The temperature profiles are shown on Figures 8.2 - 8.8. The temperature flux decreased from bottom to top of calciner vessel and from center to edge, possibly due to the thermowell becoming covered with solid that was attached to the pot walls. The solid then allowed a heat leak to the thermowell, which was not completely overcome by liquid surrounding the thermowell.

8.2 Particulate Attenuation in a Packed Distillation Tower - J. J. Perona

In the tentative waste processing flowsheet being studied in Chemical Technology Division, the off-gases from the waste evaporator and pot calciner pass into the bottom of a distillation tower for concentration of the nitric acid and decontamination of the non-condensable off-gases and tower distillate. Since nitric acid is easily concentrated, the operating variables can be adjusted to optimize fission product decontamination of the aqueous effluents from the top of the tower.

The decontamination of the off-gases is primarily a problem in particulate attenuation, since none of the long lived fission products are volatile under flowsheet conditions except ruthenium or cesium. Radioactive aerosols in vapor streams might be transferred very effectively into a liquid phase by the unit operation of distillation. No information regarding particulate removal in distillation columns has been found in the literature. Commercial aerosol separators, such as cyclones and scrubbers, which were known to be inefficient for particles of less than 2 microns, were successfully applied to the separation of particles as small as 0.3 micron by the use of aerosol buildup techniques such as by steam injection.⁽³⁾ It seems reasonable to expect that a distillation column might be effective for the removal of submicron particles by the mechanism of aerosol buildup by the condensing vapors followed by intimate gas-liquid contact.

Because of the chemical complexity of the evaporator and calciner off-gases, a carefully generated and sampled aerosol will be used in initial studies to determine the effects of tower operating variables on particulate

(2) Handbook of Chemistry and Physics, p. 1447.

(3) F. Fahnoe, A. E. Lindroos, and R. J. Abelson, Ind. Eng. Chem., 43, No. 6, 1336 (1951).

Fig. 8.2. Temperature in the Calciner Vessel as a Function of Time for Run (R-17) at 12 inches from the Bottom.

Fig. 8.3. Temperature in the Calciner Vessel as a Function of Time for Run (R-17) at 15 inches from the Bottom.

Fig. 8.4. Temperature in the Calciner Vessel as a Function of Time for Run (R-17) at 18 inches from the Bottom.

Fig. 8.5. Temperature in the Calciner Vessel as a Function of Time for Run (R-17) at 21 inches from the Bottom.

Fig. 8.6. Temperature in the Calciner Vessel as a Function of Time for Run (R-17) at 24 inches from the Bottom.

Fig.8.7. Temperature in the Calclner Vessel as a Function of Time for Run (R-17) at 27 inches from the Bottom.

Fig. 8.8. Calciner Vessel Temperature as a Function of Time for Run (R-17).

attenuation. An apparatus was constructed containing an aerosol generator of the type developed by the Chemical Warfare Service⁽⁴⁾ and an isokinetic sampler leading to particle collection devices (Figure 8.9). A Casella cascade impactor will be used for particle size determination and a Millipore filter for particle loading determination. A thermal precipitator may be used for small particle collection if the need arises. After sampling, the aerosol stream can be fed to a 3-in. dia 10 ft. tall distillation column packed with 1/4-in. Raschig rings. The noncondensable gases emerging from the condenser at the top of the tower will be sampled with an isokinetic sampler and a Millipore filter, permitting the effectiveness of the tower to be evaluated.

(4) Fahnoe et al., loc. cit.

Fig. 8.9 Flow Diagram of Aerosol Generation and Sampling System.

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