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UNIT OPERATIONS
MONTHLY PROGRESS REPORT
MARCH 1958

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Report No. CF-58-3-71

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UNIT OPERATIONS MONTHLY PROGRESS REPORT

MARCH 1958

Chemical Technology Division

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Date Issued

AUG 12 1958

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ABSTRACT

The alpha activity for scintillation area measurement was estimated to be 10^{-6} of that for the (α, n) method. The UF_6 recovery during Run FBR-16 was 67.3% of the theoretical recovery for the Fluorox reaction. Hydroclones were used for collection of thorium slurries with recoveries exceeding 99%. Flame calcination studies were continued with thorium dispersed in methanol by oxalic acid, using graphite and zirconia reflected burners and acetylene-oxygen flame. Equations for complex ion formation in $UO_2SO_4-H_2SO_4-Na_2SO_4-H_2O$ systems were solved for a few hypothetical solution compositions. A continuous Darex dissolution and stripping run was carried out for 32 hours with chloride removal in the product to 100 ppm. A nine pound section of a fuel element was completely hydrochlorinated in 24 hours with an HCl utilization of 70 percent and uranium losses to the $ZrCl_4$ sublimate of 0.07%. The specific dissolution rate for the fused salt dissolution of zircalloy-3 was proportional to the logarithm of the HF feed rate. One percent of the initial β activity and fourteen percent of the initial γ activity was leached by distilled water from a $900^\circ C$ fired sinter of concentrated fission products in a mix of shale and limestone (Mix 15).

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SUMMARY

1.0 Chemical Engineering Research

Methods of measuring liquid-liquid interfacial areas are being developed for application to evaluating solvent extraction contactors. Alternate methods are being examined from the viewpoint of avoiding limitations of the presently developed procedure using an (α, n) reaction. The use of a photomultiplier tube with a liquid scintillator organic phase in contact with an alpha-emitting aqueous phase may have many attractive features. The alpha activity required was estimated to be 10^{-6} of that necessary for the (α, n) reaction.

2.0 Fluorox

Run FBR-17 was made and the overall operation of the fluid bed reactor was satisfactory. Further evaluation of Run FBR-16 has been made. The UF_6 recovery during the run was 67.3%. A four-inch reactor system is being installed in place of the three-inch reactor which was damaged by overheating.

3.0 HRP Fuel and Blanket Processing Studies

Hydroclones have been used for over 99% collection of a loop slurry charge into an underflow receiver and are being tested for production of clarified purge and/or rinse streams from a circulating slurry. Tests of heat removal from a mock-up of a ORR slurry bomb have indicated that modifications of the initial design will be necessary.

Results for flame calcination of ThO_2 showed that oxalic acid gave an improved feed dispersion of ThO_2 in CH_3OH and that graphite or ZrO_2 reflected burners resulted in higher flame and calcination temperatures. Product surface areas were 2.3 and 2.7 sq m/g starting with 22.3 sq m/g feed ThO_2 . Results have shown that hydroclones can classify ThO_2 without use of a dispersing agent.

Tests were made of the continuous operation of a TM-3 cascade with ThO_2 in water. A Sharples "Super-D-Canter" effectively clarified 1.2 to 1.3 micron ThO_2 and continuously discharged 84% solids cake.

4.0 ION EXCHANGE

Equations for complex-ion formation in $\text{UO}_2\text{SO}_4\text{-H}_2\text{O-Na}_2\text{SO}_4\text{-H}_2\text{O}$ solutions previously presented (UNOP Monthly Report February 1958, CF-58-2-139) were solved for a few hypothetical solution compositions. Comparisons with actual solution compositions were hindered by lack of a suitable relation between ion activity as determined on solutions by pH measurement and hydrogen ion concentration as assumed in the calculations.

5.0 POWER REACTOR FUEL REPROCESSING

Darex

A continuous self-sustaining run, in which 304-L stainless steel was dissolved in 5-2 aqua regia and chloride stripped from the dissolved product with 15.8 N strip vapor at an average V/L of 0.98, was maintained for 32 hr before mechanical trouble terminated the run. Based on average analytical values, chloride was reduced to 100 ppm in the strip column. An overall material balance (out/in) was 100, 100 and 94.5% for HNO_3 , HCl and H_2O , respectively. Approximately 1.5 moles of HNO_3 and 0.25 moles of HCl was lost to the off-gas per mole of stainless steel dissolved.

A continuous run at 125°C, 22 hr duration, and a residence time of 1.5 hr was made in the newly installed feed adjustment tank with stainless steel dissolver product stripped to a chloride content of 114 to 170 ppm. At these conditions, the feed stream was concentrated by an approximate factor of 4 with about 85% of the free HNO_3 reporting to the overhead as 15.0 N HNO_3 . Approximately 50% of the chloride reported to the overhead and 50% to the concentrate. The concentrate which contained 155 to 167 g SS/liter and 6 to 6.5 N free HNO_3 , solidified after setting at room temperature for 24 to 36 hr. Dilution of the concentrate with an equal volume of water gave a feed approximating the desired composition for solvent extraction.

Zircex

A 4.24 kg section of a fuel element was completely hydrochlorinated at an average rate of 177 g/hr in 24 hr at a constant HCl gas (cylinder quality) rate of 10 g moles/hr. The utilization of HCl was approximately 70%. Uranium lost to the ZrCl_4 sublimate was 0.07% and 1.67% was trapped in the off-gas line in a fiberglass filter at 375 to 400°C. Approximately 6.3% of the hydrochlorinated uranium remaining in the hydrochlorinator was insoluble in 10 M HNO_3 .

Mechanical Processing

Crushing the oxide cores of stainless steel clad Consolidated Edison and Yankee type fuels by rolling in a Mackintosh-Hemphill derodder was suffi-

ciently effective to permit the cores to be "poured out" when an end cap was removed by shearing.

6.0 VOLATILITY

HF-Fused Salt Dissolution of Zirconium

Three complete dissolutions of zircalloy-3 dummy fuel elements in a fused, sodium fluoride-zirconium tetrafluoride mixture using anhydrous hydrogen fluoride, resulted in specific dissolution rates of 0.122, 0.143, and 0.156 lb zirconium/hr/sq ft of metal surface. The HF flow rates were 11.3, 27.0, and 44.9 lb HF/hr/sq ft of dissolver cross sectional area, respectively, and the corresponding utilization rates of acid were 5.9%, 2.6%, and 1.7%. The specific dissolution rate was proportional to the logarithm of the HF feed rate, and the proportionality constant was approximately that determined in previous tests.

The dissolution rate relation may be expressed as:

$$\text{Spec. Rate} = R = K \log \left(\frac{G}{G_0} \right)$$

where R = Specific dissolution rate

G = lb HF per unit of time per unit of dissolver cross sectional area

G_0 and K = constants

The data from fourteen runs made at 650°C follow this relationship. It was found the geometry of the fuel element and the dissolver are important in determining effect of the flow rate.

7.0 WASTE PROCESSING

Fixation of Waste Activity by Sintering

The field construction of the adiabatic self-sintering experimental pilot plant is 75% complete.

In small scale experiments to fix fission product activity from concentrated Savannah River waste (converted to Hope type waste) in a mix of shale and limestone (Mix 15), 0.004-0.09% of the β activity and 0.02-0.16% of the γ activity were trapped in the offgas scrubbers during a 900°C sintering operation. Activity was evolved throughout the sintering cycle. In one experiment the evolution of activity appeared to be linear from 0-1500 min. and leveling off after 2250 min. One percent of the β activity and fourteen percent of the γ activity in a sinter was soluble in distilled water. Analysis of the gas scrubber solution and leach liquor for nuclides, Sr, Cr, Cs, Ru, and Zr-Nb showed all to be present. Analyses for other nuclides were not made.

1.0 CHEMICAL ENGINEERING RESEARCH

Interfacial Area Measurement by Liquid Scintillators - C. V. Chester, S. G. Kent

The use of liquid scintillators in an organic phase in contact with an alpha-emitting aqueous phase offers a method of measuring interfacial area which requires only 10^{-6} of the activity used in α, n reaction.

In the α, n reaction the yield of neutrons is only about 1 per 10^5 α crossing the interface. In addition, it is very difficult to arrange a counter assembly which will detect more than a few percent of the neutrons; therefore the overall efficiency is about 1 detectable event (1 neutron count) for every 10^6 α crossing the interface. This efficiency is much better than the chemical radiolysis method, where 10^5 radiolyzed molecules are produced per α particle or 10^{11} molecules per 10^6 α . If one can analyze a 1 milliliter sample, 10^{-7} moles for chloride might be detectable. Thus 10^{-6} chemically detectable events occur per 10^{-6} α 's crossing the interface.

In scintillation counting, there is a distinct flash for essentially every α particle crossing the interface, an improvement of 10^6 over α, n and 10^{12} over chemical analysis.

If the range of α particles is assumed to be about 27μ in water, theoretically, one-fourth of the α particles in a 27μ layer arrive at the interface. Thus only a small fraction of the α particles formed a significant distance from the interface actually cross the interface. The rate of crossing in counts per square centimeter per minute is only 0.07% of the rate of formation, in counts per cubic centimeter per minute. If an α activity level of 10^3 Cpm/ml were used, a scintillation rate of 0.7 Cpm/square centimeter would be detected, a rate currently attained with the α, n technique using an α activity level of 10^9 Cpm/ml from polonium-210. Assuming 0.36×10^{-6} curies/g of uranium, or $2.22 \times 0.36 \times 10^{-6} \times 10^{12} = 0.8 \times 10^6$ disintegrations/min., g uranium, the same count rate could be obtained with a loading of about 2 g of uranium per liter. For optical reasons, a loading of from 10 to 100 g per liter will probably be used.

There is a problem using visible light production that is not encountered in neutron production; i.e., the attenuation of the light by scattering at the randomly oriented interfaces in the volume of the dispersion. This results in the light intensity being independent of the interfacial area if a sufficient depth of solution is observed. The requirement is that a relatively thin section of the liquid be observed if the light intensity is to be proportional to the interfacial area.

1.1 Theoretical Aspects of the Use of Liquid Scintillators

By the Beer-Lambert Law, the expression for attenuation of light by scattering in a two-phase polydisperse medium is:

$$\ln \frac{I}{I_0} = \alpha A L$$

where I_0 = incident light intensity (1)

I = transmittal light intensity

α = light loss by scattering per unit interfacial area

A = interfacial area per unit volume

L = optical path length

This expression is valid providing that light once scattered is lost from the system. This condition is met by either a sufficiently dilute dispersion or a sufficiently narrow columnated beam. In most systems used for interfacial area measurement by light transmission, the expression is not valid due to "build up" from multiple scattering, and empirical relations must be used. For mathematical simplicity a system where the expression is valid will be assumed.

Consider a photocell which can only "see" a narrow column of a dispersion of cross sectional area, W . The rate of light production dU_0 in an increment of the column dL is given by:

$$dU_0 = KWdL \quad (2)$$

where K is the light produced per square centimeter of interface. However, in travelling L centimeters to the photocell, the light will be attenuated by scattering. So the light arriving at the photocell dU will be given by:

$$dU = e^{-\alpha A L} dU_0 \quad (3)$$

$$\text{or } dU = KWA e^{-\alpha A L} dL \quad (4)$$

The total light reaching the photocell from a column of length L extending into the medium is obtained by integrating the above expression from 0 to L :

$$U(L) = \frac{KW}{\alpha} (1 - e^{-\alpha A L}) \quad (5)$$

If L is so large that light generated some distance into the volume is essentially all scattered before reaching the photocell, the exponential term approaches zero, and the light intensity at the photocell is independent of interfacial area.

The exponential can be expanded in MacLaurin's series, and if L is sufficiently small, the higher terms can be disregarded:

$$U(L) = \frac{KW}{\alpha} \left[\alpha A L - \frac{(\alpha A L)^2}{2!} + \frac{(\alpha A L)^3}{3!} - \dots \right] \quad (6)$$

or for small L

$$U = KWAL \quad (7)$$

This last approximation introduces an error of less than 1% if $\alpha AL < 0.10$; i.e., light generated at L is 90% transmitted.

The effect of multiple scattering may be reintroduced at this point by noting that its effect is to increase the value of L which equation (7) is valid. Multiple scattering effectively increases transmittance, and may be enhanced by making the diameter of W large compared with L.

The major problem then is to observe a thin section of the liquid in a mixer. An opaque baffle in front of the window would provide such a section, except there would be doubt that the liquid between the baffle and the window was representative of the bulk in the mixer. If uranium were used as an α source, and stilbene in phenylcyclohexane as the scintillant, a very fortuitous solution to the problem would be available. Stilbene scintillates at 4200 Å. At this wave length the uranyl ion has a molar extinction coefficient of about 6; i.e.,

$$E_o = 6 = \frac{\log_{10} \frac{I_o}{I}}{C_o L}$$

where E_o = molar extinction coefficient

C_o = moles UO_2^{++} per liter

L = optical light path length in solution, centimeters

Thus, if 50% absorbtion is to be obtained in 2 millimeters of light path, C_o would be 0.4 M or about 100 g uranium/liter.

Using pulse circuitry with the photomultiplier, it is possible to set the pulse height selector on the amplifier so that only pulses above a certain height are counted. If 100 g uranium/liter is used and the pulse height selector (PHS) is set to omit all pulses less than 50% of maximum, only interfacial area within 2 millimeters of the window would be measured.

If the organic-to-aqueous ratio, $\frac{O}{A}$, in a mixer is m, the pulses counted per unit time would be:

$U = K\omega A (1 + m)$ assuming the organic is transparent to 4200 Å light.

where K is the rate of scintillation at the interface, modified to take into account attenuation by the light absorption of uranium and the PHS setting, determined experimentally. The variable of interest is A , sq cm of interface per cubic centimeter of liquid.

1.2 Experimental Equipment for Area Measurement

The required equipment for the experiment is listed below:

- (1) Photomultiplier tube and associated voltage divider resistors and capacitors.
- (2) Preamplifier.
- (3) Linear amplifier.
- (4) Scaler and counter.
- (5) Count rate meter.

The photomultiplier and its associated electronic instrumentation (Figs. 1.1, 1.2) are on hand from the neutron experiments. The photomultiplier will be mounted against the flat bottom of a vessel suspended from a torque measuring device (Fig. 1.3). The connection to the tube is also shown in this figure.

1.3 Proposed Experimental Procedure

To evaluate K and E_o , a series of static experiments will be carried out with thin layers of aqueous uranium solutions of varying strengths. For a given solution strength, a plot of log count rate vs. solution thickness will give a line of slope $(K W E_o C_o)$ and intercept K_w . Since W and C_o can be accurately measured, the other parameters can be determined.

During the experiments, effect of pulse height selection can be determined. The count rate should be very nearly a step function of pulse height.

Once the parameters of the method have been determined, the method will become an absolute measure of interfacial area.

1.4 Conclusions

The proposed method may be more widely applicable than the $Po (\alpha, n)$ method. The use of uranium permits the use of stainless steel for material

Fig. 1.1 Block Diagram of Scintillation Counting Equipment

$R_{pc} = 140 \text{ K}\Omega$
 $R_1 - R_{10} = 70 \text{ K}\Omega$
 $C_1, C_2, C_3 = 100 \mu\mu\text{f}$
 1000 VSC
 TUBE IS RCA 6199

Fig. 1.2 Proposed Connections to Photomultiplier Tube

Fig. 1.3 Arrangement of Photomultiplier In Interfacial Area Experiments

of construction, and the contamination problem is vastly reduced (i.e., the α hazard is no longer lethal).

Uranium need not be the only α emitter. Extremely small quantities of Po-210 may be used together with a dye of the proper absorptivity to reduce the depth of solution.

In addition, the liquid scintillator may be adjusted to a wide range of properties: density or viscosity adjusted by means of bulk diluents, and surface tension reduced by surfactants.

The major drawback to the proposed method is that by the very nature of the phenomenon being used only interfacial area very near a surface may be observed. Thus the effect of the surface on the phase mixing will always be present.

2.0 FLUOROX

C. D. Scott, D. H. Newman

The Fluorox Program is the engineering development of processes which produce UF_6 from uranium compounds of lesser fluorine content without the use of elemental fluorine. The process under investigation at present is the green salt-oxygen reaction: $2 UF_4 + O_2 \longrightarrow UO_2F_2 + UF_6 \uparrow$.

The UF_4 oxidation process is being carried out in a fluidized bed reactor constructed of Inconel. Sized UF_4 is continuously fed to a UO_2F_2 bed which is fluidized in dry oxygen at temperatures of $800^\circ C$ or greater and the UF_6 is removed from the offgas by a cold trap.

2.1 Operation of the Fluidized Bed Reactor

Run FBR-17 was made in which UF_4 , -40 mesh, + 100 mesh, was fed continuously into the fluidized bed at $800^\circ C$. The reactor used was the 3-in. reactor which had been modified since Run FBR-16 (Fig. 2.1). The operating procedure for this run was the same as that used for FBR-16 (Unit Operations February Monthly Report, CF-58-2-139) except that a constant bed level was maintained and continuous bed samples were taken by use of an overflow line. The run was terminated after 5.5 hr of operation when there was a failure in the electrical heating system.

The feed was introduced at an average rate of 710 g/hr. Operation of the unit was generally better than that in any of the previous runs. The bed overflow worked smoothly without plugging and the amount of dusting to the filter assembly was greatly reduced. The system pressure did not exceed 12 psig. Changes which were made in the system and feed material prior to this run probably contributed to the improved operation. These changes included the overflow line, a baffle at the reactor offgas exit, a larger offgas line from the reactor, and the reduction in the amount of fines in the UF_4 feed.

After the run was terminated and before the solids were discharged from the reactor, a reactor heater was accidentally left connected without cooling gas passing through the bed. The reactor wall temperature exceeded $1000^\circ C$ causing fusion of the bed and damage to the reactor components which was irreparable.

Total material balances for Run FBR-17 will be difficult to determine since the sintered mass in the damaged reactor could not be conveniently sampled and weighed. However, with the overflow discharge line in operation, bed samples were taken throughout the run and the last sample before shutdown may be used as a basis for calculation.

The damaged reactor was removed and sectioned for metallurgical examination. Installation was begun on a new 4-in. reactor which had been constructed for a scheduled reactor replacement.

-16-

Fig. 2.1 Revised 3 in Reactor used in Run FBR-17.

2.2 Evaluation of Results from Run FBR-17

Complete analytical data are now available from FBR-16 (reported in Unit Operations Section Monthly Report February CF-58-2-139) and the results of the run have been fully evaluated. The type and amount of uranium compounds and contaminants were determined by use of the available analyses (%U, %U⁴⁺, %U^{water soluble}, %AOI, %F, %H₂O and %Cr). The actual weight material balance showed that very slightly more material was removed from the system than was introduced during the run (material removed/material introduced = 100.8%) probably due to residual material from previous runs.

The material balance on the constituents in each entering and exit stream is shown in Fig. 2.2. This material balance also shows a slight increase in material leaving over that entering; however, as in the case of the weight material balance, it is still complete within the limits of experimental error.

All of the UF₆ that was formed during the run was not collected in the offgas cold traps. Some of the UF₆ was lost or removed by side reactions before reaching the cold traps. This loss can be accounted for by three different side reactions: (1) the reaction of UF₆ with entrained UF₄ to form the intermediate U₄F₁₇ in the filter housing ($7 \text{ UF}_4 + \text{UF}_6 = 2 \text{ U}_4\text{F}_{17}$); (2) the reaction of UF₆ with uranium oxides in the bed to form UO₂F₂ ($2 \text{ U}_3\text{O}_8 + 3 \text{ UF}_6 + \text{O}_2 = 9 \text{ UO}_2\text{F}_2$ and $2 \text{ UO}_2 + \text{UF}_6 + \text{O}_2 = 3 \text{ UO}_2\text{F}_2$); and (3) the corrosion reaction of UF₆ with the metal walls of the reactor system ($\text{metal} + \text{UF}_6 + \text{O}_2 = \text{metal fluoride} + \text{UO}_2\text{F}_2$).

The amount of UF₆ which is lost by each of these routes can be determined if the amounts of uranium oxides, metal fluorides, and U₄F₁₇ in the exit streams are measured, (Table 2.1). Figure 2.3 shows the disposition of the UF₆ which was formed during Run FBR-16. A total of 99.7% of the UF₆ that would have been formed from 100% oxidation of the available UF₄ was accounted for in either the cold traps or by the side reactions. Of the accountable UF₆, 67.3% was recovered in the cold traps.

The disposition of the UF₆ indicates several places where product recovery could be easily increased. It is felt that the majority of the U₄F₁₇ formation was due to UF₆ reacting with fine UF₄ which had been blown into the filter assembly. This loss could probably be decreased by reduction of the amount of fine UF₄ fed to the reactor.

Analysis of the particle size distribution in the bed, feed, and filter solids (Fig. 2.4) showed that the bed maintained essentially the same particle size distribution throughout the run while the solids collected in the filter housing were relatively fine. This result indicates that a substantial quantity of the solids collected in the filter housing was the direct result of the fines that were introduced in the UF₄ feed.

Fig.2.2. Material Balance of the Constituents of each Stream from Run FBR-16

Theoretical amount of UF_6 from 5442 g of UF_4 reacting with O_2 -3050g
 Total UF_6 accounted for - 3042 g
 % of UF_6 accounted for - 99.7 %
 Recovery of UF_6 in cold traps - 67.3%

Fig. 2.3. Disposition of UF_6 formed during Run FBR-16.

Fig. 2.4. Comparison of Sieve Analyses of Different Solids from Run FBR-16.

The changes made prior to Run FBR-17 seem to have partially reduced the dusting problem; however, if the filters were placed directly into the top of the reactor itself and provisions made for systematic filter blowback, the intermediates formation would probably be reduced to a very small equilibrium amount in the bed.

The obvious way to reduce UF_6 loss to the uranium oxide side-reaction is to reduce the amount of uranium oxide which is present in the UF_4 feed. However, the quality of the feed material is probably representative of production green salt.

Loss of UF_6 to metal fluoride formation is probably the result of corrosion of the reactor walls. Investigations of the use of other materials of construction for the inner reactor surface, namely flame sprayed ceramic coating is being continued.

There was a negligible amount of UF_4 in the bed at any time as indicated by analyses of the overflow samples. Therefore, it was impossible to determine reaction rates for the UF_4 oxidation; however, it was obvious that the reaction was rapid and essentially complete.

2.3 Development of a Rotary Pump Feeder

The rotary pump feeder was revised by placing a plug on the inside front face. This revision appears to have solved the problem of powdered feed flowing through the feeder when the rotar is stationary. The feeder has been re-calibrated in the range 500-2500 g/hr and is ready for use.

Table 2.1 Change in Individual Compounds in Run FBR-16

Compound	Amount of Compound (g)		
	Entering Reactor	Leaving Reactor	Change
UF_4	6283	0	-6283
U_4F_{17}	0	976	+ 976
UF_6	0	2052	+2052
UO_2F_2	6563	11109	+4546
U_3O_8	202	117	-85
UO_2	465	0	-465
Metal Fluorides	19	281	+262
H_2O	48	51	+3*
O_2	353	-	353**
Totals	13933	14586	+653

* Assumed zero for calculations.

** The oxygen input was determined by the UF_6 balance.

3.0 HOMOGENEOUS REACTOR FUEL AND BLANKET REPROCESSING STUDIES

P. A. Haas

The Homogeneous Reactor studies include engineering development of processes and equipment for the preparation and reprocessing of aqueous homogeneous reactor core and blanket fluids. The present emphasis is on the preparation of thorium oxide for slurry blankets, including equipment development for slurry irradiation studies. Preliminary studies have begun on alternate methods for solution processing to obtain design data for future processing plants.

3.1 Component Testing

3.1.1 Hydroclone Collection of Loop Slurry - J. W. Snider; R. C. Early

Initial studies with the mockup as shown in Fig. 3.1 indicate that the use of a hydroclone for removing ThO_2 from in-pile loops is feasible. Three runs were made in which more than 99% of the ThO_2 was transferred from the feed tank to the underflow pot; in one run greater than 98% was transferred. All of the studies were made with a 0.40-in. hydroclone operated with a pressure drop of 44 ft of fluid at a flow rate of 1.7 liter/min.

Particle size analysis of two feed materials (Fig. 3.2) indicated mean diameters of 1.2 and 2.9 microns. The particle size distribution of the feed used for Run 2 (Fig 3.3) was not determined, but it contained more oversize ($> 5 \mu$) material than would be used for in-pile slurry loops.

The equilibrium concentration for Run 2 (Fig. 3.4) was approximately 1.25 g ThO_2 /kg H_2O for a feed concentration of 500 g ThO_2 /kg H_2O ; 99.9% of the ThO_2 was recovered in the induced underflow pot. This test was with a high underflow pot to feed tank volume ratio as compared to the other runs (Table 3.1).

The same feed material was used for Runs 4 and 5 (Material W-3-AB in Fig. 3.2) under identical conditions except for a greater feed volume for Run 5 and a different underflow pot geometry. The only effect that the greater volume of feed should have upon the equilibrium concentration would be a time delay for reaching equilibrium. If the two curves (Figs. 3.5, 3.6) are extrapolated to equilibrium concentration, it appears that Run 4 had an equilibrium concentration below 3 g ThO_2 /kg H_2O and that Run 5 had an equilibrium concentration below 5 g ThO_2 /kg H_2O . The difference in equilibrium concentrations may be due to the underflow pot geometry differences. In Run 4 a straight-walled underflow pot was used while in Run 5 a conical-shaped underflow pot was used. An induced flow into the underflow pot tends to induce a conical swirl which is parallel to the

Fig. 3.1. Schematic of Hydroclone Loop Slurry Collection Apparatus.

Fig. 3.2. Particle Size Distribution Of ThO_2 Feeds

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Fig.3.3. Particle Size Distribution for Run
2 ThO₂ Slurry W-2-A.

-25-

Fig. 3.4. Concentration Of ThO₂ In Feed Tank Versus Time For
Run 3

986 025

-26-

Fig3.5. Concentration Of ThO₂ In Feed
Tank Versus Time For Run 4

-27-

Fig. 3.6. Concentration Of ThO₂ In Feed Tank Versus Time For Run 5

conical walls and is propagated to near the flask bottom where it re-suspends previously settled material.

Table 3.1 Tests of a Hydroclone for ThO₂ Slurry Collection

Hydroclone: 0.40-in. dia

P_f-P_o: 44 ft

Feed Flow: 1.7 liter/min.

Run No.	ThO ₂ in Underflow Pot (%)	Underflow Pot Geometry (in.)	<u>Underflow Pot Volume</u> Feed Volume	Feed Volume (liter)
2	99.87	6 x 8	4.67	3.000
3	99.20	3 x 12	0.954	1.630
4	99.30	3 x 18	0.952	3.224
5	98.10	4 liter flask	0.951	4.410

The straight wall underflow pot tends to interfere with the induced flow and produces a region near the upper underflow pot volume of greater turbulence. However, this turbulence is not propagated as far and leaves an unagitated region into which the ThO₂ settles. It may be possible, with properly arranged baffles and different underflow pot geometries, to promote settling in the underflow pot and thus lower the equilibrium concentration in the feed tank. Further studies are to be made of the effect of underflow pot geometry and baffle arrangements.

The initial concentrations prepared for Run 3, 4, and 5 were 500 g ThO₂/kg H₂O, however, the graphs of concentration vs time indicate that only 420, 280 and 320 g of ThO₂/kg H₂O, respectively, were suspended at zero time. The only stirring utilized during these studies was a lab type stirrer. The feed tank is being modified to utilize recirculation by a centrifugal pump to improve the agitation.

3.1.2 Hydroclone Clarification of Purge Streams - P. A. Haas, J. W. Snider

Application of hydroclones has been suggested for producing a clarified water supply for purge streams and/or rinsing operations in loops or slurry blankets. The hydroclone operating conditions for these applications are outside the slurry concentrations and underflow-overflow volume ratios

Fig. 3.7. Hydroclone Purge Preparation Test Apparatus.

- a Eastern Model 3-J Centrifugal Pump
- b Dorrclone model X8A unit, 710 mm dia hydroclones
- c One 0.40 in D hydroclone
- d Small agitated reservoir, 17 liters

covered by previous development studies of slurry collection. An experimental program to obtain data for these conditions has been suggested. As a simple qualitative test, a two stage system using a multistage centrifugal pump and a Dorrclone Model X8A (see Unit Operations February Monthly Report, CF-58-2-139) unit as the first stage was installed for testing (Fig. 3.7).

3.1.3 Thorium Oxide Bomb Cooling Test - J. M. Holmes, F. N. McLain

Several tests have been run to determine the cooling rates on a mockup of the ORR thorium oxide bomb experiment. A tapered coolant channel cross-section minimized the temperature gradient along the bomb length. Results to date have indicated that air coolant alone will remove as much as 1.5 kw of heat produced by heating the bomb skin electrically. Above this rate, spray cooling water might be added to the air to increase its heat capacity. However, the use of a water-air mixture at the higher heat rates gave

erratic temperature readings on the bomb skin thermocouples. A new bomb with internal thermocouples is being fabricated and will be tested upon completion.

3.2 ThO₂ Preparation Development

3.2.1 Flame Calcination of ThO₂ - C. C. Haws, K. O. Johnsson, V. L. Fowler G. D. Judy

The first flame calcination of an oxalic acid dispersed methanol-thoria system was completed. Results show that chemical dispersion was superior to the mechanical dispersion previously used. The flame was enclosed within a graphite reflector (1-in. dia x 9-in. long) to achieve higher particle temperatures by lowering the rate of radiative heat loss from the particles. The furnace and burner assemblies built for this test operated satisfactorily. Succeeding tests may achieve higher temperatures using zirconia reflectors with this same chemically dispersed system. The apparatus for ultrasonic dispersion of ThO₂ powder was altered to improve the efficiency of energy transfer.

Reflective Burner Calcinations

An oxalic acid dispersed methanol-thoria system, containing 200 g thoria per liter, was prepared and fired in a reflected flame apparatus. The reflector was built by drilling a 1-in. dia hole lengthwise through a 2-1/2-in. x 2-1/2-in. x 9-in. graphite block. The reflector was then mounted in magnesia fire brick so that it would exhaust directly into the intake of the spray cooling system. A new type tubular torch was built capable of furnishing a fully carburetted alcohol-oxygen-acetylene gaseous mix to the intake of the reflector. Operation of the torch and feeding system was uneventful throughout the feeding of 1-lb of material with the exception of a few leaks in the feeding system. Service life of the graphite reflector was short (about 2 hr) and heat losses from the uninsulated ends of the block reflector were high. Reflector temperatures ranged from 1300°C at the exposed ends to > 1600°C in the insulated center section. Exhaust gases from the reflector were above 1750°C, the limit of available thermocouples.

The results obtained from Run 14 show an improvement over those from the most nearly comparable previous run (Run 9). Smaller surface areas were obtained, even neglecting the smaller particle sizes in the Run 14 feed (see Table 3.2 and Fig. 3.8). The dispersion of the feed material was considerably improved as indicated by the comparative increase of the particle sizes in the spray cooler (Fig. 3.8). The spray cooler product from Run 9 increased from 1.5 micron average particle size in the feed to 12 micron in the product from the spray cooler. The product of the spray cooler collected during Run 14 increased from 0.86 to 1.6 micron. The significance of a doubling of the percentage of material collected in the filter bag is not known, but a much greater increase should have been obtained

Fig.3.8. Flame Calcination: Comparison of Particle Size Distribution Data - Runs 9 & 14

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based upon the marked improvement in feed dispersion. The halving of the waste percentage was a result of using the better dispersed feed as well as a better focused burner.

Data are not yet available for a comparison of these results with those from gas fired furnace operation.

Ultrasonic Dispersion

Application of ultrasonic energy to disperse ThO_2 powder into a gas for flame calcination feed has only been moderately successful. It would appear that the major difficulty of transmitting the high frequency energy to the powder has been in the improper choice of the exponential horn (or coupling device) connecting the transducer and the feed cup. At a frequency of 25,000 kc the proper length for a half wave horn is 3.785-in. (for stainless steel) while the horn which has been in use measures 4.42-in. long. The feeding equipment is being modified by shortening the horn so as to transfer the energy to the powder in a more effective manner.

Table 3.2 Flame Calcination Experiments

Comparison of Data from Run Nos. 9 and 14

Product Location	Product Distribution				Surface Area (sq m/g)	
	Run 9		Run 14		Run 9	Run 14
	g	%	g	%		
Filter Bag	3.9	1.9	17	4.4	2.9	2.3
Spray Cooler	159.3	76	328	85	3.1	2.7
Misc. Waste	46.3	22	41	10.6	--	--
Feed Material	216.9	--	--	--	12.8	22.3

Note: Run No. 9 Feed Material was jet precipitated (JP).

Run No. 14 Feed Material was taken from current Pilot Plant production oxide (1043-650°C fired).

3.2.2 Hydroclone Classification of Thorium Oxide - E. L. Youngblood, R. D. Arthur

Single Hydroclone - Classification runs have been made with a single 0.40-in. dia hydroclone using 1600°C fired thorium oxide dispersed in demineralized water, methyl alcohol, 0.005 M oxalic acid, and 0.005 M sodium pyrophosphate solutions to determine the effect of various dispersing agents on hydroclone classification. All runs were made with 10 g/liter ThO₂ feed and a feed to overflow pressure difference of 15 psig. The underflow stream was throttled to give a 70% volume flow to the overflow stream. The particle size distribution curves for the feed and fines product (overflow) for each run (shown in Fig. 3.9) indicated that the particle size distribution of the fines product from the hydroclone was not greatly affected by the use of dispersing agents; however, dispersing agents may be desirable to increase the product yield.

The curve for particle size vs the separation of thorium oxide for a single hydroclone based on the size distribution curves in Fig. 3.2 and the operating conditions listed above has the shape (Fig. 3.10) which would be expected from theoretical hydroclone correlations.

TM-3 Dorrclone - Three runs have been made with continuous product and waste removal using the three stage modified Dorrclone. In these runs, 1600°C fired ThO₂ (Batch LO-41-HF-100) in demineralized water was used as feed. The thorium oxide as received from the furnace and after agitation in the feed tank contained lumps of ThO₂ sufficiently large to plug the hydroclones and settle out in the system. Therefore, it was necessary to reduce the size of these lumps to less than 500 microns dia prior to feed slurry preparation.

The operation of the unit was at feed concentrations of 30 to 100 g/liter and feed rates of 1 to 2 gpm. The fines product stream from each run appeared under microscopic examination to have a uniform particle size of about 1 micron (particle size analyses are not yet available). The percent recovery of the feed ThO₂ in the fines product stream was low; further runs will be aimed at increasing the product yield.

3.2.3 Centrifugation of ThO₂ - J. M. Holmes, F. N. McLain

Particle size distribution data for the feed and overflow streams in the Sharples "Super D Canter" test on thorium oxide slurry are complete. Results indicate that a ThO₂ feed of 1.2-1.3 micron mean particle size was effectively concentrated to about 84% solids at flow rates between 0.3 and 2.0 liter/min. The overflow stream solids had a mean particle size of less than 1.0 micron at concentrations between 0.04 and 0.5 g/liter. Complete data are tabulated in Table 3.3.

One problem encountered during the test was contamination of the solids product with iron (300 ppm), nickel (57 ppm), and chromium (41 ppm). However, it is believed that this contamination was due to wearing between the stainless steel conveyor and bowl shell, possibly caused by worn conveyor bearings. Heating of the casing near the feed tube plus excessive noise at low liquid flow rates confirmed this theory. Product contamination should not be a problem after correction of the centrifuge alignment.

Fig. 3.9. Hydroclone Classification of ThO_2

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Fig. 3.10. Hydroclone Separation Factor vs Particle Diameter for ThO₂ Slurry.

Table 3.3 Sharples P-4 "Super-D-Canter" Thorium Oxide Centrifugation Test

"Super-D-Canter" RPM = 6000
Centrifugal Force (XG) = 2100
Percent Solids in Underflow Stream = About 84%

Test	Feed Stream				Overflow Stream					Remarks
	Rate (cc/min.)	Solids Concen- tration (g/liter)	Mean Particle Size (microns)	Standard Deviation (microns)	Solids Concen- tration (g/liter)	Mean Particle Size (microns)	Standard Deviation (microns)	Appearance	Percent Solids Removed (%)	
A	300	16.0	1.2	+ 0.6	0.039	---	---	Slight Haze	99.76	Insufficient Solids in Overflow for Particle Analysis
B	820	89.6	1.2	+ 0.6	0.132	0.7	+ 0.6	Hazy	99.85	-----
C	2000	47.8	1.3	+ 0.7	0.523	0.6	+ 0.3	Milky	98.91	-----
D	1460	89.6	1.3	+ 0.5	0.396	0.6	+ 0.4	Milky	99.56	-----
E	375	44.9	1.2	+ 0.6	0.050	---	---	Slight Haze	99.89	Insufficient Solids in Overflow for Particle Analysis

4.0 ION EXCHANGE

J. B. Adams

Kinetic Studies on Uranium Anion Exchange

A hand solution of the equations for complex formation in UO_2SO_4 - H_2SO_4 - Na_2SO_4 - H_2O solutions (UNOP Monthly Report February, CF-58-2-139) was made for a few points over a representative range of total sulfate concentration. Values of C_U , total uranium concentration, C_S , total sulfate concentration and $[\text{H}^+]$, hydrogen ion concentration were chosen and concentrations of various ions were solved for. Calculation of each point required three iterations and from 1 to 1-1/2 hr.

Columns 1-8 (Table 4-1) were calculated using complexing constants as determined by K. E. Allen⁽¹⁾: $K_{\text{US}}(I=0) = 580$, $K_{\text{US}_2}(I=0) = 3450$ and

$$K_{\text{US}_3}(I=0) \approx 100.$$

The variation with ionic strength was estimated by: $K_{\text{US}} = f_{\text{US}}$
 $K_{\text{US}}(I=0)$, and $K_{\text{US}_3} = f_{\text{US}_3} K_{\text{US}_3}(I=0)$ where $f_{\text{US}} = f_{\text{US}_2} \approx$

$$\exp_{10} \left(- \frac{4.072 I^{1/2}}{1 + 2.3 I^{1/2}} \right) \text{ and } f_{\text{US}_3} = 1. \text{ For comparison, Column 9}$$

(Table 4-1) was calculated using complexing constants as determined by Ahrland⁽²⁾.

$$K_{\text{US}_I=1} = 53, K_{\text{US}_2 I=1} = 410 \text{ and } K_{\text{US}_3 I=1} = 2500 \text{ with the first two}$$

corrected for ionic strength by the same function $f \approx \exp_{10} \left(\frac{-4.072 I^{1/2}}{1 + 2.3 I^{1/2}} \right)$

$$\text{so that } K_{\text{US}}(I=0) = 900, K_{\text{US}_2}(I=0) = 7000 \text{ and } K_{\text{US}_3}(I=0) = 2500. \text{ A comparison}$$

of the two calculations (Columns 5 and 9, Table 4-1) reveals a wide difference in the distribution of uranium among the various complexes. This arises almost entirely from the difference in value of K_{US_3} used. It is difficult to determine which is correct though the low value seems to carry a little more weight. However, there is no effect on the overall composition in terms of sodium sulfate, sulfuric acid and uranyl sulfate.

A comparison of two calculated solutions compositions which approximated closely two actual solutions made in the laboratory (Table 4-2), showed a lack of agreement in some respects. In particular it appears that more H_2SO_4 is needed to reach an $a_{\text{H}^+} = 0.01 \text{ M}$ (pH = 2) than is required to attain $[\text{H}^+] = 0.01 \text{ M}$ in the calculation. This results mainly from using the tacit assumption that solutions can be compared on the basis of the $\text{pH} = -\log \text{H}$ rather than $\text{pH} = -\log a_{\text{H}^+}$, where a_{H^+} is the hydrogen ion activity. Corrections

Table 4-1

Calculated Composition of Uranyl Sulfate Solutions

Column No.	1	2	3	4	5	6	7	8	9
Species	Fixed Composition Parameters (mols/liter)								
C_{S^-} Total Sulfate	0.05	0.10	0.15	0.20	0.25	0.25	0.25	0.25	0.25
C_{U^-} Total Uranium	0.005	0.005	0.005	0.005	0.005	0.001	0.005	0.001	0.005
H^+	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01
Species	Calculated Ionic Composition (mols/liter)								
UO_2^{++}	0.0009536	0.000588	0.000395	0.0002865	0.0002204	0.00004323	0.0002512	0.00004858	0.0000794
UO_2SO_4	0.003341	0.002971	0.002588	0.002218	0.001938	0.0003862	0.002069	0.0004075	0.001063
$UO_2(SO_4)_2^{-2}$	0.0007023	0.001412	0.001937	0.00228	0.002605	0.0005203	0.002478	0.0005016	0.001803
$UO_2(SO_4)_3^{-4}$	0.000004	0.000030	0.0000786	0.000149	0.000236	0.0000502	0.000205	0.0000430	0.002059
SO_4^-	0.03514	0.07992	0.1258	0.1731	0.2202	0.2265	0.2014	0.2069	0.2181
HSO_4^-	0.009896	0.01419	0.01745	0.1975	0.0215	0.02188	0.04096	0.04159	0.2107
Na^+	0.07017	0.1658	0.2624	0.3605	0.4576	0.4678	0.4290	0.4365	0.4575
Species	Other Calculated Data								
I-Ionic Strength	0.114	0.269	0.402	0.548	0.692	0.703	0.655	0.663	0.701
H_2SO_4 (mols/liter)	0.0099	0.0121	0.0138	0.0147	0.0162	0.0151	0.0305	0.0308	0.0162
Na_2SO_4 /liter	0.0351	0.00829	0.1312	0.1803	0.2288	0.2339	0.2145	0.2182	0.2288
UO_2SO_4 /liter	0.0050	0.0050	0.0050	0.0050	0.0050	0.0010	0.0050	0.0010	0.0050

for this activity effect have been estimated for $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions⁽⁴⁾. However, these extend only to an ionic strength of 0.2 and therefore are of little use in the present work. It is planned to determine a usable $[\text{H}]$ - vs - a_{H} correction over the range of variables of interest for the particle type^H of uranium-bearing solutions being used in experiments. This involves calculating compositions of solutions in the range of interest, making these experimentally and measuring a_{H} to compare with the $[\text{H}]$ calculated for each solution. The assumption that addition of small amounts of UO_2SO_4 do not effect the experimental data derived from $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions⁽³⁾ is inherent in this procedure.

Table 4-2 Comparison of Actual and Calculated Solution Compositions

Solution Comparison (moles/liter)	Solution No. 1 ($C_s \sim 0.15$)		Solution No. 2 ($C_s \sim 0.05$)	
	Calculated	Actual	Calculated	Actual
C_s Total Sulfate	0.1500	0.1566	0.0500	0.0521
C_u Total Uranium	0.0050	0.00499	0.0050	0.00498
H^+	0.01	-	0.01	-
a_{H} Hydrogen ion Activity	-	0.01	-	0.01
Na^+	0.2624	0.2616	0.07017	0.0670
Na_2SO_4	0.1312	0.1308	0.0351	0.03352
H_2SO_4	0.0138	0.0208	0.0099	0.01356
UO_2SO_4	0.0050	0.00499	0.0050	0.00498

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5.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

5.1 Darex - F. G. Kitts, B. C. Finney, F. L. Rogers, J. Beams,
G. E. Woodall

5.1.1 Dissolution and Stripping Studies

The Darex head-end treatment consists of dissolving the fuel in dilute aqua regia and stripping out the chloride before the resultant nitric acid solution is concentrated, adjusted, and solvent extracted.

A continuous run of 32 hr was made at an average V/L of 0.98 in which 304 L stainless steel was dissolved in 5-2 aqua regia and chloride stripped from the dissolver product with 15.8 N HNO_3 stripping vapor rather than 15.3 N usually used. Continuous operation of the equipment was difficult and constant attention was required to sustain operation. The material balance for the run is presented in Fig. 5.1. Again, the average material balance is very good and chloride was removed to 100 ppm. The 87% balance on HCl in the stripper includes only the liquid streams; the remainder of the chloride left the stripper as decomposition gases.

The HNO_3 and H_2O balances in the dissolver were not expected to be 100%. The water should be increased by 5% due to the formation of water in the dissolution reaction. Also 2.85 moles of HNO_3 theoretically combine with a "mole" of stainless steel, the remainder leaving the dissolver in the offgas. Losses to the offgas by differences were approximately 1.5 moles HNO_3 and 0.25 moles HCl per mole of stainless steel dissolved. Based on analytical results and rotameter readings the losses to the offgas were 0.7 moles of HNO_3 and 0.2 moles HCl per mole of stainless steel. No oxygen was bled into the column during the run.

Even though chloride was stripped to an acceptable figure during this run, the column throughput was below earlier figures. The chloride stripping column was dismantled and siliceous deposits were found plugging the slits of the bubble caps and severely restricting the flow of stripping vapor. The column was reassembled using clean plates and bubble caps, leak-tested, and insulated. The plates and bubble caps with the siliceous deposits were used to evaluate a 10% NaOH cleaning solution recommended by Battelle Memorial Institute. A 20:1 water-HF mixture dissolves the deposits according to the Analytical Chemistry Division but it cannot be used because of its deleterious effects on titanium and glass.

5.1.2 Pre-Solvent Extraction Feed Adjustment Studies

The Darex dissolver solution whose chloride content has been stripped to less than 100 ppm requires the removal and concentration adjustment of nitric acid and adjustment of salt concentration prior to solvent extraction. To accomplish this, a continuous feed adjustment step is being investigated to: (1) determine the path and fate of the trace chloride; (2) determine

Basis:
13 min/mole SS diss.

Fig. 5.1. Material Balance for Darex Run No 53.

the extent of nitric acid removal without the salts solidifying in the hot concentrate; and (3) measure the residence time required at boiling temperature to dehydrate silica.

The installation of the pre-solvent extraction feed adjustment equipment was completed and a continuous run of 22 hr at 125°C was made with synthetic feed at 130 ml/min. Because of feeds of somewhat different compositions, the run results were divided into two parts, those of the first 16-1/4 hr and the last 5-1/2 hr.

The Part I feed contained 41.55 g SS/liter, 170 ppm Cl^- , and was 13.36 molar in HNO_3 ; the Part II feed contained 34.1 g SS/liter, 114 ppm Cl^- , and was 11.8 molar in HNO_3 . Both were concentrated by a factor of approximately 4. The resultant holdup time in the feed adjustment tank was approximately 1-1/2 hr. The results indicated that steady state may have been obtained approximately 2 to 4 hr after the start of operations. Material balances (out/in) based on analytical results and the assumption that densities and volumes are additive for Part I were: HNO_3 , H_2O , S.S. $(\text{NO}_3)_{2.85}$, and Cl^- ; 97.3%, 114%, 102.3% and 68.1%, respectively (see Fig. 5.2). For Part II the results were: HNO_3 , H_2O , S.S. $(\text{NO}_3)_{2.85}$, and Cl^- ; 99.8%, 100.5%, 116.7%, and 99.4%, respectively (see Fig. 5.3).

The slight difference in the composition of the overhead and products of Part I and Part II operation was expected since there was a difference in the composition of the feeds. The addition of an equal volume of water to the product in each case resulted in a solution approximately 3 molar in HNO_3 . Solids first started appearing in the concentrated product after remaining at room temperature for 24 to 36 hr.

The greatest discrepancy in the data appeared to be in the Cl^- concentration. In Part I there was approximately 32% or 0.0021 moles of Cl^- unaccounted for whereas in Part II the Cl^- material balance was approximately 100%. This discrepancy may be the result of analytical error or there may be the possibility that some of the Cl^- in the feed was in the form of a volatile chloride which was lost in the offgas. It appears that the Cl^- concentration on a mole basis in the product was approximately 1/3 to 1/2 that which was initially in the feed, with approximately an equal amount in the overhead. The addition of water to the product for the final feed adjustment prior to solvent extraction reduced the Cl^- concentration by 38%, when the concentration was measured in parts per million. The moles of Cl^- present were the same, and the normality was decreased by 50%.

The feed adjustment tank (Fig. 5.4) is a 30-in. high x 6-3/8-in. i.d. stainless steel cylinder. A riser 13-in. high x 2-3/8-in. o.d. was installed in the tank to decrease the volume. The static volume is approximately 6 liters, but it was found that during operation the liquid hold-up was approximately 3 liters. A shell and tube heat exchanger with water flowing through the tubes is used for condensation of the acid overhead. Four 115 v - 150 watt calrod heaters are wrapped around the outside of the tanks and the power to the heaters is regulated by means of a temperature-recorder-controller and an air-driven powerstat. The product is removed from the

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Fig. 5.2. Run F.A.R.-4 Part I Material Balance (16 hr)

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Fig. 5.3. Run F.A.R.-4 Part II Material Balance (5.5 hr)

Fig.5.4. Darex Pre-Solvent Extraction Feed Adjustment Equipment.

bottom of the tank through a jack-leg for level control.

The equipment was modified slightly and a run (F.A.R. 4) of 21.75 hr duration was made at 125°C and a feed rate of 130 ml/min. The results of the run are not yet available.

5.2 Mechanical Processing - G. A. West, J. C. Rose

The objectives of mechanical processing of spent heterogeneous power reactor fuels prior to chemical operations for the recovery of fertile and fissionable materials are: (1) to decrease diluent materials; (2) to remove nitric acid insoluble cladding to make possible the direct reprocessing by nitric acid chemistry and; (3) to break the cladding so that the fuel can be leached out and the clad discarded.

5.2.1 Rolling and Shearing Studies - Studies of mechanical separation of clad and fuel were continued on two fuel types; (1) Yankee Atomic, 0.395-in. o.d. x 30-in. long S.S. clad UO₂ pellets, 0.359-in. o.d. x 0.375-in. long, and; (2) Consolidated Edison, 0.315-in. o.d. x 30-in. long S. S. clad UO₂-ThO₂ pellets, 0.240-in. o.d. x 0.7-in. long. The fuels were passed through a Mackintosh-Hemphill rod straightening machine in an attempt to crush the pellets to determine the percent uranium lodged in tubes after shearing off the end cap and removing the fuel by gravity. This procedure was not completely effective on either type fuel; however, the UO₂ was easier to remove than the UO₂-ThO₂ pellets. About 98% of the UO₂-ThO₂ (Consolidated Edison) fuel remained in the cladding and from 0 to 98% of the UO₂ (Yankee Atomic) fuel remained after rolling and shearing off the end cap. Due to the distortion of the cladding after shearing of the end cap the pellets must be crushed into fine particles to assure removal. The UO₂-ThO₂ pellets in stainless steel cladding were recompacted by the rolling action of the Mackintosh-Hemphill machine and did not separate and flow freely from the clad. In most cases the UO₂ pellets were crushed into small particles which could be dislodged by shaking. The data obtained from this study indicate that complete separation of core and cladding by mechanical means can not be accomplished to insure complete recovery of the fuel.

5.3 Zircex Engineering Studies - J. J. Perona, G. B. Dinsmore, J. S. Taylor, G. E. Woodall

In a gas phase run of 24 hr duration, a 4.24 kg section of a fuel element (unirradiated) was hydrochlorinated at an average rate of 177 g/hr to completion with a constant HCl rate of about 10 g-mole/hr. The average reaction rate, based on half of the original surface area, was 1.5 mg/sq cm/min. The temperature of the reaction was not measured. The uranium loss to the sublimate was 0.065%, with 1.67% recovered from a glass-wool filter in the line to the ZrCl₄ condenser. The filter was maintained at 375°C throughout the run. Of the uranium chlorides recovered from the hydrochlorinator, 6.3% was insoluble in 10 M HNO₃.

Hydrogen evolution produced by the reaction as measured with a wet test meter showed an induction period of about 8 hr at the start of the run,

after which the reaction rate remained the same during the period 8-16 hr. This result indicates that the area reacting remained essentially constant (Fig. 5.5). During the period 16 to 24 hr, the reaction decreased gradually as the area available for reaction diminished to zero.

Uranium chloride passed from the hydrochlorination vessel into the line to the $ZrCl_4$ condenser by both entrainment and vaporization. Particles occluded in a filter in this line were measured with an electron microscope and they ranged from about 0.1μ to about 3μ in size. The gas velocity in the hydrochlorinator was sufficiently high (superficial velocity was about 0.01 ft/sec) to entrain particles of this size. A significant uranium loss could take place due to vaporization of uranium chloride if the gases leaving the hydrochlorinator were above $500^\circ C$ or if a significant fraction of the uranium chloride was present as UCl_4 . Therefore, the essential characteristics of the offgas filter are that it must de-entrain particles as small as 1μ and that offgases passing through it must be cooled to 375 to $400^\circ C$.

The utilization of hydrogen chloride in this run was about 70%, compared to about 90% for the previous two runs (see January and February issues of this report, CF-58-1-137 and CF-58-2-139, respectively). The lowering of the utilization was caused partly by the higher HCl flowrate (10 g-mole/hr vs 6 g-mole/hr in previous runs) which decreased residence time and partly by completely reacting all metal to a zero heel.

Fig. 55. Hydrogen Evolution as a Function of Run Time.

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6.0 VOLATILITY

M. E. Whatley

HF-Fused Salt Dissolution of Zirconium - M. E. Whatley, R. W. Horton,
L. E. McNeese, G. Jones, Jr.

The dissolution of zirconium metal in molten baths of NaF-ZrF_4 sparged with HF is being studied as a head-end step for reprocessing zirconium matrix, MTR type fuel elements by a volatility process. The study is being carried out with dummy fuel element sections fabricated from zircalloy-3 rolled plate. The principal measurements include the operating conditions, the hydrogen evolution rate, and the depletion of metal. The test facility includes a copper-lined dissolver, an Inconel salt preparation vessel, resistance heated transfer lines, an HF feed system, an HF recovery system, and a hydrogen off-gas metering system.

Several runs have been made with this system, three of which were completed during the last month. For the sake of comparison, the fourteen runs made at 650°C will be described and discussed.

Dissolution rates from 0.023 to 0.15 lb of zirconium per square foot of exposed area per hour (0.19 to 1.2 mg/sq cm/min) have been obtained using HF addition rates from 4 to 110 lb of HF/hr/sq ft of cross section area of the dissolver (Table 6.1). Previous tests have shown temperature to have little effect on the dissolution rate over the range of variables studied, and the effect of salt composition within the range 38 to 58 mole% ZrF_4 (necessary to maintain a low melting point) was masked by other more significant effects. The most important variables have been the rate of addition of HF and the geometric configuration during dissolution. The effects of geometry cover such a tremendous scope and appear so important that the studies reported here must be recognized as preliminary and little more than an identification of the problem.

6.1 Description of the Experiments

Three of the mock fuel elements were not dissolved completely at one set of conditions but were used over a series of runs. Examination of partially dissolved elements showed that dissolution occurred relatively uniformly over the surface so that the surface area could be assumed constant over the series of runs with small error. Further, three subsequent tests carried to completion with constant conditions, similar to those used in these series of runs with the same element, showed that the dissolution rate was fairly constant to the end of dissolution. Dimensions of test elements and of the equipment for each test are shown in Table 6.2. The weights and dimensions given apply to the test elements at the start of each series of runs.

Dissolution rates were determined by metering the hydrogen evolved, calculating the equivalent weight of metal dissolved per unit of time, and dividing by the surface area of the metal sample as it was charged to the dissolver.

Table 6.1 Dissolution Rates and HF Utilization of Zircalloy 3 in NaF-ZrF₄ Salts with HF at 650°C

Run No.	Zirconium Dissolution Rate (lb/hr/sq ft)	HF Feed Rate (lb/hr/sq ft)	HF Utilization (%)	Element Height (in.)
D-2 Phase III	0.0233	4.21	16.1	11.0
D-2 Phase IV	0.0343	6.29	15.8	11.0
D-2 Phase V	0.0368	8.38	12.8	11.0
D-2 Phase VIII	0.0384	12.75	8.63	11.0
D-4	0.0553	21.80	6.06	5.5
D-5	0.0714	63.20	2.71	5.5
D-6	0.0567	32.00	4.24	5.5
D-7	0.0236	5.67	9.96	5.5
D-8	0.0467	16.48	6.78	5.5
D-9	0.0744	110.80	1.61	5.5
D-10	0.0435	44.80	2.33	5.5
D-11	0.1428	26.70	2.83	3.7
D-12	0.1560	49.40	1.72	3.7
D-13	0.1224	11.20	5.83	3.7

The hydrofluoric acid feed rate was regulated by a rotameter but determined by the change in weight of the feed cylinder.

6.2 Discussion of Results

The relation between specific dissolution rate and HF flow rate for all tests at 650°C is shown in Fig. 6.1, and the values used in plotting Fig. 6.1 are compiled in Table 6.1. The data for each individual test run is shown graphically in Figs. 6.2 through 6.15.

The most reproducible effect found was the logarithmic relationship between zirconium dissolution rate and hydrofluoric acid addition rate. This relationship may be expressed analytically as:

$$R = K \log \frac{G}{G_0}$$

Where: R is the specific zirconium dissolution rate based on the element area (lb/hr/sq ft)

K is a constant (lb/hr/sq ft)

G is the HF mass velocity based on dissolver cross section area (lb/hr/sq ft)

G₀ is a constant (lb/hr/sq ft)

The data fell into two groups, the eleven inch and the five inch elements making one group and the 3.7 inch elements forming a separate group with much higher dissolution rates. For Runs D-2 through D-10, K was 0.0417 and G₀ was 1.18. For Runs D-11 through D-13, K was 0.0537 and G₀ was 0.0596. The constant K is the magnitude of the effect of increasing the HF rate, and is not significantly different for the two groups of data. The constant G₀ probably depends on the geometric configuration of the fuel elements, the distributor nozzle, and the dissolver. This constant is the extrapolated HF rate which would correspond to a zero dissolution rate, but this extrapolation extends so far beyond the range of the experimental data that this interpretation is meaningless.

At present it is believed that the controlling factor in the dissolution is the rate of removal of the ZrF₄ reaction product from the reacting surface. Presumably, when molten salt contacts ZrF₄, a NaF-ZrF₄ mixture of high ZrF₄ content (> 57 mol%) with a melting point in excess of 650°C is formed. The dissolution process is therefore reduced to a dilution of this mixture with additional molten salt until a composition is reached which melts at 650°C. The process is diffusional in nature and is relatively slow. As hydrofluoric acid addition rate increases, better mixing and movement of lower melting salt to the NaF-ZrF₄ surface is achieved, giving an increased dissolution rate as indicated by Fig. 6.1.

Fig. 6.1. The Effect of HF Addition Rate on the Zirconium Dissolution Rate in Molten NaF-ZrF₄ at 650°C.

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Fig. 6.2. HF Fused Salt Dissolution.

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Fig. 6.3. HF Fused Salt Dissolution.

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Fig. 6.4. HF Fused Salt Dissolution.

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Fig. 6.5. HF Fused Salt Dissolution.

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Fig. 6.6. HF Fused Salt Dissolution.

Fig. 6.7. HF Fused Salt Dissolution.

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Run Number D-6
N₂ Rate: 0.0016 CFM
Metering Temperature 33°C
Metering Pressure: 2.5 inches H₂O vacuum

Fig. 6.8. HF Fused Salt Dissolution.

Run Number D-7
N₂ Rate: 0.01 CFM
Metering Temperature 32°C
Metering Pressure: 2.5 inches H₂O vacuum

Fig. 6.9. HF Fused Salt Dissolution.

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ORNL-LR-DWG 29028

Run Number D-8
N₂ Rate: 0.015 CFM
Metering Temperature 31°C
Metering Pressure: 2.5 inches H₂O vacuum

Fig. 6.10. HF Fused Salt Dissolution.

Run Number D-9
N₂ Rate: Not Discernable
Metering Temperature 31°C
Metering Pressure: 2.5 inches H₂O vacuum

Fig. 6.11. HF Fused Salt Dissolution.

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ORNL-LR-DWG 29027

Run Number D-10
N₂ Rate: 0.01 CFM
Metering Temperature 31°C
Metering Pressure: 2.5 inches H₂O vacuum

Fig. 6.12. HF Fused Salt Dissolution.

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ORNL-LR-DWG 29021

Run Number D-11
N₂ Rate: 0.2 CFM
Metering Temperature
Metering Pressure: 2.5 inches H₂O vacuum

Fig.6.13. HF Fused Salt Dissolution.

Run Number D-12
N₂ Rate: 0.2 CFH
Metering Temperature
Metering Pressure: 2.5 inches H₂O vacuum

Fig. 6.14 HF Fused Salt Dissolution.

Run Number D-13
N₂ Rate: 0.2 CFH
Metering Temperature
Metering Pressure: 2.5 inches H₂O vacuum

Fig. 6.15 HF Fused Salt Dissolution.

Table 6.2 Dimensions and Proportions Defining Dissolution Rate Test Conditions

Test No.	Code No.	Test Element Description						Dissolver Cross Section (sq ft)	Gas Dis-tributor (sq in.)	Volume of Salt	V/S (cu in.) (sq in.)	S/H (sq ft) (in.)	W/S (lb) (sq ft)	W/V (lb) (cu in.)
		Weight	Height	Plates		Total Area (sq ft)	Cross Section Area (sq in.)							
				Spacing	No.									
D-2 PIII	1	10.8	11.0	0.10	13	5.92	3.95	0.179	2.58	273.0	0.322	0.537	1.925	0.0395
D-2 PIV	1	See Note 1												
D-2 PV														
D-2 FVIII														
D-4	3	5.5	5.5	0.100	11	2.54	3.00	0.0935	2.51	147.0	0.40	0.462	1.732	0.0295
D-5	3	See Note 1												
D-6														
D-7	2	3.95	5.5	0.100	11	2.54	3.00	0.0935	2.51	147.0	0.40	0.462	1.552	0.0295
D-8	2	See Note 1												
D-9														
D-10														
D-11	A	1.475	3.7	0.100	6	0.563	1.55	0.0935	2.51	70.0	0.86	0.159	2.50	0.0211
D-12	B	1.800	3.7	0.100	6	0.579	1.55	0.0935	2.51	70.0	0.84	0.159	3.05	0.0257
D-13	C	1.785	3.7	0.100	6	0.567	1.55	0.0935	2.51	70.0	0.86	0.159	3.02	0.0255

V = volume of salt in dissolver

W = weight of element

S = surface area of element

H = height of element in inches

Note 1: Tests in these groups were run consecutively on the test element described for the start of the series. Dimensions at the start of each test were not measured.

The geometry of the system and possibly other factors influence the dissolution rates. The ratio of weight of element to salt volume (W/V) shown in Table 6.2 is a concentration term which was held within reasonably close limits (0.0211 to 0.0395); however, in this range, it was not an important factor. Since the maximum concentration range for the NaF-ZrF₄ system, because of melting point limitations, is 38 mol to about 58 mol percent ZrF₄, the effect of salt concentration was probably significant. Since the dissolution rates increased with HF velocity and the HF gas was used to provide mixing energy, the geometric factors involved are probably those having to do with mixing or contacting efficiency. Dissolution equipment designed to promote improved salt circulation should produce higher rate values than those which have been found.

Description of Equipment and Procedure

The determination of dissolution rates was accomplished in a 6.0-in. dia copper-lined steel vessel 32-in. high, heated by an external tube furnace. A rack which supports the test element in the salt directly on the HF distributor plate was connected to the removable flanged head. The anhydrous hydrofluoric acid was vaporized (bp 19°C) by heating the steel cylinder and was fed to the dissolver through a control valve and a rotameter. The gas emerged from the distributor, bubbled up through the salt surrounding the test element, and passed out the off-gas line carrying hydrogen with it. The HF was cooled, condensed at -75°C, and stored for recycle, while hydrogen and a small amount of nitrogen purged through instrument lines passed through a wet test gas meter.

In starting a test, the amount of zirconium tetrafluoride equivalent to the weight of zirconium present was calculated, and enough fused salt was added to the dissolver to make the final salt composition 58 mol percent ZrF₄. The dimensions of the dissolver and test elements were such that in all the tests the element was submerged, with a salt depth of 0.5 to 1.0-in. above the top of the element.

The original conformation of the dissolver was a straight cylinder 5.75-in. i.d. This dimension resulted in submergence of a test element having 11 to 13 plates 2.5-in. wide by 0.10-in. thick and 11.0-in. long. With this depth of salt in the vessel, there was a large amount of splash and entrainment of fused salt which made the use of high acid rates impossible. In order to achieve high HF velocity, shorter and smaller test elements were fabricated and a filler insert was placed in the bottom of the dissolver to reduce the dissolver cross-section in the area containing fused salt. This insert, 4.125-in. i.d. and 12-in. high, resulted in the change in dimensions shown in Table 6.2. The enlarged (5.75-in. i.d.) section above the insert formed a de-entrainment section and freeboard to reduce splash against the head of the vessel.

A further modification was made to assist in controlling entrainment and trapping the solids formed by condensation of sublimed ZrF_4 . This modification was a baffled pot placed in the offgas line about 4 ft from the dissolver. The pot was equipped with a water-cooled reflux leg on the outlet side to condense HF and return it to the pot, carrying with it any solid ZrF_4 particles trapped on the wet wall of the reflux column. The hot dissolver gas entering the pot (plus a steam coil if needed) served to reboil the HF from the pot. With good temperature control this system was effective in scrubbing the offgas stream, and substantial amounts of solids were removed from the pot after test runs.

Other modifications to the original system included shortening and steam tracing the acid feed lines to insure uniform flow and more accurate metering, adding absorber columns of marble chips between the HF accumulation and the wet test meter to remove traces of HF from the non-condensable gases, and eliminating all instrument bubbler lines from the dissolver because of the difficulties experienced in keeping them open.

7.0 WASTE DISPOSAL

C. W. Hancher and W. J. Boegly, Jr.*

Fixation of Waste Activity by Sintering

One of the purposes of the joint Chemical Technology Division and Health Physics Division Radioactive Waste Disposal Program is to study the fixation of fission-product waste activity in a heated clay structure. Hope-type aluminum nitrate waste was chosen for the initial tests. Mix 15, a clay formula was selected on the basis of preliminary tests by the Ceramic Group at Y-12. The amount and proportions of Mix 15 added to 1000 ml of liquid waste follow:

Mix 15, 890 g	{	1000 ml of 1.6 M $\text{Al}(\text{NO}_3)_3$
		170 g of NaCO_3
		170 g of limestone = 95% of CaCO_3
		550 g of Conasauga shale

When fission products are mixed with this mixture and are heated to 800-900°C, the fission products have reported to be virtually nonextractable. The sinter would then be acceptable for ultimate disposal.

During February two main projects have been active:

- (1) The field installation of the adiabatic self-sintering experiment.
- (2) A high activity hot cell experiment to determine offgas activity resulting from sintering and the solubility of fission products fixed in sinters.

7.1 Adiabatic Self-Sintering Experiment

Field Installation

The purpose of the adiabatic self-sintering experiment is twofold:

- (1) to heat by radioactive decay energy a mix of waste and clay inerts to form a ceramic sinter and, (2) to process and characterize the offgas problem resulting from heating the clay mixture containing fission products.

* Health Physics Division

The field construction is approximately 75% complete on March 1, 1958 (Table 7-1). The field work was temporarily discontinued on March 1, 1958.

During the adiabatic self-sintering experiment the heat from the fission products must supply 40,000 Btu/gal to 18 gal of waste and clay slurry, which is equal to 10 kilowatt-days of power, to produce a suitable sinter. This heating will take about 30 days if the heat loss from the sintering furnace is low (200-500 watts).

To reduce the heat loss a system of heaters have been placed around the sintering furnace. The amount of power to the heater system is automatically controlled to minimize heat losses from the sintering furnace. There are six heating zones in the system, one on top, three on sides, and two on the bottom of the sintering furnace (Fig. 7.1). Each zone is controlled at a set temperature lower than the corresponding sinter temperature by a set of thermocouples, one couple in the cake (see Fig. 7.2) and one on the adjacent heater zone (see Fig. 7.3). The resulting signal is sent to a step-less controller for raising or lowering the power to the heater zone (Fig. 7.4).

Table 7-1 Adiabatic Self-Sintering Field Construction Completion Schedule

Completion (%)	Scheduled Completion Date
Offgas 65	March 25, 1958
Electrical 70	March 20, 1958
Instrument 80	March 20, 1958
Heavy Construction 90	April 15, 1958
Sampler Design <u>95</u>	<u>March 10, 1958</u>
Total Project 75	May 1, 1958

7.2 Hot Cell Experiment

The objectives of the hot cell sintering experiment were: (1) the characterization of the offgases and possible processing procedures, and (2) the characterization of the leach liquor of Mix 15 sinter when contacted with distilled water.

The general experiment equipment consisted of a tube furnace in which the sample of Mix 15 was heated (Fig. 7.5) up to a maximum controlled

BOTTOM HEATER ZONE

Fig. 7.1. Bottom Two Heater Zones.

Fig. 7.2. Thermocouples in Sintering Furnace.

Fig. 7.3. Thermocouples for Heater Zones.

Fig. 7.4. Adiabatic Heater Control for Heater Zone B.

Fig. 7.5. Sintering and Off-Gas Study Setup for High Radioactive Level Sinter.

temperature of 900°C. The radioactive "Hope" waste solution (12 cc) was put into a 100 ml S.S. test tube and shaken with Mix 15 clay with a wrist action shaker for about 60 min. until a homogeneous gel was formed. The stainless steel test tube was placed in the furnace and heated at a predetermined rate. Attached to the furnace was a condenser (water-cooled) condensate trap, and two scrubbers, which were filled with 10% NaOH. Air was swept through the system at 0.2 to 0.5 cfh.

Six tests were made, one non-radioactive preliminary test (1C) and five radioactive tests (1R through 5R).

The analysis of the condensate solution and the caustic bubbles solution indicate that about 5×10^5 to 1×10^8 γ out of 1×10^{12} γ counts/min./ml were scrubbed from the offgas.

The percentage of original activity trapped in the offgas system was 0.004 to 0.09% β and 0.02 to 0.16% γ (Table 7-2). The offgas contained Ce, Sr, Ru, Cs and Zr-Nb. An analysis to determine the presence of other nuclides was not made. Activity trapped from the offgas by the bubblers appeared to be evolved linearly from the heated mix up to 1500 min. and leveling off at after approximately 2,250 min. of heating (Fig. 7.6). The count in the last gas scrubber was usually as high as the first bubbles which indicates that scrubbing of the radioactive aerosols was very difficult. The activity was classed as an aerosol, because when 1-liter gas-phase were taken there was no radioactivity.

For test 5R the middle bubbler was replaced with a "multibed" filter one layer of sand (300 cc), one layer of soda lime (NaO 300 cc), and one layer of granulated activated charcoal (200 cc). The flow rate through the multibed filter was 0.53 cm/sec. The decontamination factor using the multibed filter was 1 to 2. Since these preliminary tests indicated that the activity in the offgas was much higher than expected, more tests are planned.

Table 7-2 Percentage of β and γ Activity Scrubbed in the Offgas System

Run No.	Heating Time (min.)	Ratio Mix (15 grams) ml of waste solution	β %	γ %
3 R	800	3	0.09	0.09
4 R	720	1	0.004	0.02
5 R	1440	0.5	0.004	0.03
6 R	2200	0.5	0.007	0.16

Fig.76. β and γ Activity Trapped in Off-Gas System vs Heating Time Run -4 R.

Fig.7.7. Fission Product Activity in Distilled Water vs Leaching Time. Leachate (sinter of run 5R)

Table 7-2 Percentage of β and γ Activity Scrubbed in the Offgas System
(Continued)

Typical Scrubber Composition (10% NaOH)						
(counts/min./ml)						
Gross β	Gross γ	Ce β	Sr β	Ru γ	Cs γ	Zr-Nb γ
2×10^5	4×10^5	4×10^3	3×10^3	1×10^4	4×10^5	6×10^4

When a sinter of Mix 15 and waste was contacted with distilled water from 0.06 to 0.9% of the β activity and from 0.8 to 14% of the γ activity appeared in the leachate (Table 7-3). Analysis for Ce, Sr, Ru, Cs, and Zr-Nb showed all to be present. An analysis for other nuclides was not made. The β and γ activity appears to be equally soluble, (See Fig. 7.7).

It was concluded from these brief experiments that the radioactivity evolved from sintering was extremely difficult to remove and that sintered Mix 15 in its present form is not capable of retaining fission products in the presence of water.

Table 7-3 Percentage of β and γ Activity in Distilled Water Leachate of Mix 15 and Synthetic Radive Hope Waste

Run No.	Leaching Time (min.)	β %	γ %
3R	180	0.06	0.75
4R	180	0.07	0.41
5R	3660	0.52	1.80
6R	3660	0.90	14.0

Typical Leachate Composition						
(counts/min./ml)						
Gross β	Gross γ	Ce β	Sr β	Ru γ	Cs γ	Zr-Nb γ
1×10^7	1×10^7	3×10^4	2×10^5	8×10^3	3×10^7	6×10^6

7.3 Calcining of Waste Solids

A proposed waste processing flowsheet for the reduction of wastes to solids (Fig. 7.8) consists of the following steps:

The waste stream is neutralized and the metal hydroxides precipitated. The solids are then separated from the liquid. Strontium, cesium, ruthenium and nitrate ions remain in the liquid phase. The strontium and cesium are removed by ion exchange, and the ruthenium by an electrolytic cell. The solids are calcined or dried or possibly sintered to fix fission products, if deemed necessary prior to storage. The prior removal of ruthenium and nitrate ion by the precipitation step should decrease the offgas problem during the drying step. The precipitation will reduce the volume of waste which must be stored.

Fig.7.8. Proposed Reduction of Wastes to Solids Flowsheet.

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