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CHEMICAL TECHNOLOGY DIVISION

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ABSTRACT

In a preliminary experiment, the integral diffusivity of 1 M FeCl_3 solution varied uniformly with the fraction diffused: from $0.3 \times 10^{-8} \text{ cm}^2/\text{sec}$ for 10 per cent diffused to 0.8×10^{-8} for 30 per cent diffused. A short Fluorox run made with crude UF_4 in the 4-in. fluidized bed showed that UF_6 could be produced from the impure feed. Denitration of $\text{Th}(\text{NO}_3)_4$ solutions on fluidized or mechanically agitated beds of ThO_2 or sand gave fine ThO_2 particles for all conditions tested. The rate of sorption of uranium into 40 micron Dowex 21K resin particles from a 0.0042 M uranyl sulfate solution was studied by measuring the uranium loading on individual beads as a function of time. Chloride concentrations of 28-51 ppm were produced in the solvent extraction feeds during five feed adjustment runs made with the Darax Reference flowsheet. Decladding of SS-clad $\text{ThO}_2\text{-UO}_2$ pellets with a continuous feed of $6 \text{ M H}_2\text{SO}_4$ gave essentially identical results as batch decladding. When a Mark I prototype assembly was sheared into 0.75-in. lengths with a "plane of contact" blade in the 126-ton Manco shear, 22.2 g of metal fines (304L stainless steel) 1680 microns or less in size was produced with 36.5% less than 150 micron. UO_2 was leached from sheared stainless steel cladding, 0.4 in. O.D. x 2.75-0.5 in. long, with 10 M HNO_3 at an average rate of 0.009-0.067 g/min/g of initial UO_2 , respectively, and at initial rates of 0.052-0.29 g/min/g. After four runs at approximately 700°C with NaF-LiF melts (initial concentration: 43 mol per cent NaF, final concentration: approximately 12 mol per cent 2rF_4), average corrosion rates varied from 0.25 mils/hr maximum (at the interface) to 0.12 mils/hr minimum (in the vapor space). Heat transfer calculations on the storage of cylindrical containers of waste showed that the allowable specific heat generation in the waste can be increased by 20-30% by storage of the waste in air cooled vaults rather than burial with a 1-in. air gap between the container and the ground media.

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SUMMARY

1.0 CHEMICAL ENGINEERING RESEARCH

An improved apparatus for measuring liquid phase diffusivities from capillary tubes was devised. In a preliminary experiment, the integral diffusivity of 1 M FeCl_3 solution varied uniformly with the fraction diffused: from $0.3 \times 10^{-6} \text{ cm}^2/\text{sec}$ for 10 per cent diffused to 0.8×10^{-6} for 30 per cent diffused. This variation would be expected from the chemistry of the ferric ion.

2.0 FLUOROX

The corrosion on Inconel in run FER-22 as determined by corrosion coupons within the reactor varied from 0.048 ipy in the gas phase to 0.70 ipy in the fluidized bed in the temperature range of 775-830°C.

A short run made with crude UF_4 in the 4-in. fluidized bed showed that UF_6 could be produced from the impure feed. However, close temperature control is necessary to reduce the severe corrosion which results when reactor temperatures exceed the relatively low melting point of the crude UF_4 (730-740°C).

3.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

Denitration of $\text{Th}(\text{NO}_3)_4$ solutions on fluidized or mechanically agitated beds of ThO_2 or sand gave fine ThO_2 particles for all conditions tested. The only particles produced in the desired 100-500 micron size range were agglomerates of fines with little mechanical strength. Both $\text{UO}_2(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ solutions denitrated to give dense particles by growth on seed material with very small amounts of fine oxides compared to ThO_2 .

Installation was completed of equipment for engineering tests of the electrolytic removal of nickel from HRT fuel solution. Evaluation is continuing of ThO_2 and mixed Th-U-Al oxides produced by flame denitration.

4.0 ION EXCHANGE

The rate of sorption of uranium into 40 micron Dowex 21K resin particles from a 0.0042 M uranyl sulfate solution was studied by measuring the uranium loading on individual beads as a function of time. Enriched uranium was used in the studies, and the sorption rates were measured with a gamma spectrometer. The beads became loaded to one-half their equilibrium value in 24 min and the "apparent" over-all diffusion coefficient was $9 \times 10^{-8} \text{ cm}^2/\text{sec}$.

5.0 POWER REACTOR FUEL REPROCESSING

5.1 Darex

Five chloride removal and feed adjustment runs were made in the 4-in. equipment using the Darex Reference flowsheet. In two of these runs a 2-hr reflux period was used, while in three, no reflux was used. Chloride concentrations of 28-51 ppm were produced in the solvent extraction feeds. Three runs using an abbreviated Reflux flowsheet with "heat" material resulted in chloride concentrations of 40-71 ppm in the solvent extraction feed.

Laboratory scale studies were made to determine the effect of reflux time and initial HNO_3 concentration on chloride concentration in boiling Darex solution. Solutions containing 0.58 M Cl^- , 100 g/liter APPR and 8, 9, 10, 12 and 14 M HNO_3 initially, were refluxed six hours with an updraft condenser. Chloride concentrations decreased with reflux time in all cases; at any reflux time, the chloride concentration varied inversely with the initial HNO_3 concentration.

5.2 Sulfex

Decladding of SS-clad $\text{ThO}_2\text{-UO}_2$ pellets with a continuous feed of 6 M H_2SO_4 gave essentially identical results as batch decladding. Stainless steel loading, reaction time, extent of foaming and uranium losses were the same for each decladding method. This result indicated that large assemblies (Consolidated Edison) could be decladded in a geometrically safe vessel.

5.3 Feed Clarification

In experiments with Darex solvent extraction feed prepared from APPR fuel elements, siliceous matter was removed by addition of coagulating and flocculating agents. The clarified supernate could be filtered no faster than a solution which was allowed to settle for 48 hr, but the settling time was reduced to 3 hr.

5.4 Mechanical Processing

Shearing. When a Mark I prototype assembly was sheared into 0.75-in. lengths with a "plane of contact" blade in the 126-ton Manco shear, 22.2 g of metal fines (304L stainless steel) 1680 microns or less in size was produced with 36.5% less than 150 micron. There was sufficient cold working to allow removal of all of the fines but 2.5 g with a small permanent magnet. A total thrust of 80 tons was required to shear the Mark I prototype bundle.

Two die sets and eight pairs of blades are being fabricated for use in a 200-ton thrust surplus press for evaluation of optimum blade shape,

blade life and blade velocity while shearing the Mark I prototype. An 18-in. long section of a Con Ed fuel assembly consisting of 100 stainless steel tubes with 30 mil wall thickness separated by 15 mil wall thick ferrules was successfully disassembled without any fracture of tube wall. The disassembly device was a wedge driven by a small portable air hammer which ruptured the Microbrazed 50 bond between the ferrules and tubes.

Abrasive Sawing. In tests of the abrasive sawing of three 1/2 in. O.D. stainless steel rods with a 16 in. dia, Manhattan No. 239, blade at 10,450 sfpm, a ratio of blade consumption volume vs. volume of metal removed of 1/4-1/2 was obtained over a feed rate range of 6-40 in./min. The stainless steel particle sizes produced from the sawing ranged from 43% < 149 microns to 1.6% > 2000 microns.

Leaching Studies. UO_2 was leached from sheared stainless steel cladding, 0.4 in. O.D. x 2.75-0.5 in. long, with 10 M HNO_3 at an average rate of 0.009-0.067 g/min/g of initial UO_2 , respectively, and at initial rates of 0.052-0.29 g/min/g.

SRE Decanning. The SRE decanning unit being fabricated by the Southern Machine Company of Chattanooga, Tennessee is 10-15% completed. A steam cleaning unit for cleaning the SRE slugs of surplus oil and NaK was designed and approved for construction. Tests on recanning of the slugs in a two-sectional can of spun aluminum, sealed by a press fit and a rolled edge, showed that the method would be more expensive and less feasible than the canning machine method.

5.5 Radiation Damage

Glass coated steel specimens from Pfadler were irradiated to 10^{10} r, gamma and returned to Pfadler for measurements of changes in physical properties. Seven types of Corning glass rods, bars and discs are undergoing irradiation to 10^8 , 10^9 and 10^{10} r, gamma at the MTR.

6.0 VOLATILITY

A preliminary dissolution was made to prepare a NaF-LiF salt containing 20 mol per cent of ZrF_4 as the starting composition in a proposed dissolution cycle to operate at a maximum temperature of 600°C. Two subassemblies could be dissolved in a 35-liter fluorinator batch without exceeding 600°C. The comparative dissolution rate for 600°C operation will be determined in the next test.

After four runs at approximately 700°C with NaF-LiF melts (initial concentration: 43 mol per cent NaF, final concentration: approximately 12 mol per cent ZrF_4), average corrosion rates varied from 0.25 mils/hr maximum (at the interface) to 0.12 mils/hr minimum (in the vapor space).

At the end of the fourth run, there was a failure of an Inconel fused salt transfer line due to localized overheating at an electrical resistance heater connection.

7.0 WASTE PROCESSING

Five calcination runs were made using Darax waste concentrate in a calcination pot 8 in. in diameter and 18 in. high, varying the temperature during solids deposition from 250-650°C. The average permissible feed rates increased with temperature from 2.5-4.5 liters of concentrate per hour while the bulk density of the calcined solids decreased from 0.9-0.6 g/cc. The decrease in density was attributed to the greater inclusion of gaseous decomposition products at the higher heating rates. A scouting run with steel Rashig rings in the pot showed no significant increase in calcination rates.

Heat transfer calculations on the storage of cylindrical containers of waste showed that the allowable specific heat generation in the waste can be increased by 20-30% by storage of the waste in air cooled vaults rather than burial with a 1-in. air gap between the container and the ground media. The allowable increase depends upon the diameter of the cylinder and the thermal diffusivity of the ground media.

1.0 CHEMICAL ENGINEERING RESEARCH

M. E. Whatley

1.1 Diffusion Measurements - C. V. Chester

A convenient and economical method of measuring molecular diffusivities in liquids is being sought as a technique to support measurements of interfacial diffusion resistance. The diffusion of a radioactive tracer from a capillary into an essentially infinite volume may be a desirable approach. Two requirements of the method are: (1) that it be capable of measuring diffusivities at high solution concentrations (up to 200 g/liter solute) and (2) that expensive and/or radioactive solutes be retained in a small volume.

The high concentration of expensive solute makes the recirculation of the bulk solution necessary. In the case of enriched uranium it would not be economical to prepare several gallons of the bulk solution for flow past the capillaries. A desirable system would be one in which a few hundred ml of bulk solution is recirculated past the mouth of a capillary at a rate sufficient to keep the diffusing solute concentration at the mouth of the capillary essentially equal to that of the bulk. The bulk solution should be kept well mixed, to keep the concentration of the diffusing species essentially zero. Evaporation and a consequent increase in density of the recirculating bulk solution must be guarded against in differential experiments to prevent convection currents from destroying the concentration gradient in the capillary.

The first model of a recirculation system was a stirred beaker of bulk solution in which the capillaries were immersed. However, it was determined that the apparent solute diffusivity was a function of stirring speed and impeller position.

To avoid the disturbance at the ends of the capillaries, a system was devised wherein the agitator acts as a pump impeller. The bulk solution is pumped to the top of a small tube, where it is allowed to flow gently past the tops of the capillaries and then back into the bulk solution. Figure 1.1 is a sketch of the apparatus. The flow past the capillaries is controlled by adjusting the variable speed impeller motor to maintain approximately a centimeter head in the capillary holder over the surface of the bulk solution. This apparatus was made of wax, and the integral diffusivity of FeCl_3 was determined for diffusion between 1 M FeCl_3 and 3 M HCl .

The data (plotted in Figure 1.2) are from 3-cm long capillary tubes and show an increase in diffusivity with the fraction diffused. This result is not surprising considering the tendency of the ferric ion to form complexes and polymers in concentrated solutions.

The complexed polymers disassociate in more dilute solutions and diffuse more readily. In the capillary experiments, this tendency may be observed by noting that an apparent diffusivity of $0.3 \times 10^{-6} \text{ cm}^2/\text{sec}$ for about 10% diffused increased to about $0.8 \times 10^{-6} \text{ cm}^2/\text{sec}$ for about 30% diffused.

Fig. 1.1. Recirculation System for Diffusion Experiments.

Fig. 1.2. Integral Diffusivity Plot for 1M Ferric Chloride Diffusing into 3M HCl.

2.0 FLUOROX

R. W. Horton

The Fluorox program is the engineering development of processes which produce UF_6 without the use of elemental fluorine. The process under study at present is the oxidation of UF_4 with oxygen ($2UF_4 + O_2 = UO_2F_2 + UF_6$) with subsequent recycle of the UO_2F_2 through reduction and hydrofluorination.

2.1 Fluidized Bed Development - C. D. Scott

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

Corrosion in Run FBR-22. Corrosion data on six Inconel corrosion coupons which were in the reactor attached to the center thermowell during run FBR-22 showed that corrosion on annealed Inconel was general with no noticeable pitting or intergranular attack. The corrosion rates which were based on 65.5 hr of reactor operation when the bed temperature was in the range of 775-830°C varied from 0.048 ipy in the gas phase to 0.70 ipy in the fluid bed. There were some large temperature variations when the run was terminated, and there was approximately 20 hr of heating-up and cooling-down time when the bed temperature was less than 775°C.

The corrosion rates listed below are based on continuous operation for a 300-day year with the assumption that no corrosion occurred at temperatures less than 775°C.

Table 2.1. Annual Corrosion Rate on Annealed Inconel
at 775°C-830°C in Run FBR-22

<u>Location of</u> <u>Corrosion Coupons</u>	<u>Average</u> <u>Corrosion Rate,</u> <u>ipy</u>
Gas phase	0.048
Bed interface	0.65
Middle of Fluid Bed	0.70

These rates are considerably higher than other measured rates calculated from thermowell corrosion or rates calculated from collection of corrosion products, probably due to the violent agitation in the center of the bed and to the apparent movement of the corrosion coupons in the fluid bed.

2.2 The Fluorox Reaction for Impure UF_4 from Ore Concentrate

Crude UF_4 (produced from unpurified mill concentrate) which was received from the Allied Chemical Corporation had a much wider particle size range than does the usual feed for the Fluorox fluidized bed (Figure 2.1). Some of the +20 mesh material appeared to be mainly corrosion products. In order to facilitate the use of this material in the solids feeding system of the Fluorox fluidized bed reactor, a size fraction in the -20 mesh to +150 mesh range will be used.

Analytical results from the "as received" material, although somewhat inconsistent, make it possible to determine the composition of the crude UF_4 if it is assumed that all of the uranium is present as U^{+4} and that all fluoride impurities are present as their highest, nonvolatile, fluoride. The use of these assumptions results in the following composition for the crude UF_4 :

<u>Compound</u>	<u>Wt, %</u>
UF_4	88.52
UO_2	2.72
AlF_3	0.56
CaF_2	0.12
CuF_2	0.20
FeF_3	4.89
MgF_2	0.08
MnF_3	0.10
NaF	1.72
NiF_2	0.10
VF_3	0.51
H_2O	<u>0.15</u>
Total	99.67

Further tube furnace tests on the reaction rate of the crude UF_4 in the Fluorox reaction ($2\text{UF}_4 + \text{O}_2 = \text{UO}_2\text{F}_2 + \text{UF}_6$) gave reaction rate constants comparable to other types of UF_4 in the temperature range of 700-720°C ($k = 0.20 \text{ hr}^{-1}$ at 700°C and $k = 0.42 \text{ hr}^{-1}$ at 720°C).

Although the crude UF_4 sinters at 690-710°C and melts at 730-740°C, severe sintering or agglomeration does not occur in a 90% UO_2F_2 -10% crude UF_4 mixture (wt %) until the approximate melting point of 730-740°C. Therefore, if the Fluorox fluidized bed is maintained at less than 10% crude UF_4 , the bed temperature can be maintained at 730°C where the reaction rate constant for the crude UF_4 is $k = 0.60 \text{ hr}^{-1}$ and the reaction half time is 1.15 hr.

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Fig. 2.1. Sieve Analysis of Crude UF_4 Received from Allied Chemical Corp.

Oxidation tests in a tube furnace also showed that essentially all the vanadium contained in the crude UF_4 is collected in the off-gas cold traps with the UF_6 .

Determination of Feed Rate for the Fluidized Bed Reactor. For any proposed run, the calculated feed rate to the Fluorox fluidized bed reactor is dependent on (1) the characteristics of the feed, (2) the UF_4 concentration to be maintained in the bed and (3) the reaction rate constant which is dependent on temperature and feed characteristics. The following equation yields the feed rate, F , as a function of the important variables:

$$F = \frac{k_t CW(1 - 0.51C)}{U - 0.49UC - IC - NC}$$

where k_t is the reaction rate constant, W is the bed weight, C is the weight fraction of UF_4 in the bed, and U , I , and N are characteristic of the feed with U the weight fraction of UF_4 in the feed, I the weight fraction of inert impurities in the feed and N the equivalent weight fraction of the feed which results in solids from reaction of other impurities with UF_6 .

If a run is made with crude UF_4 at a bed temperature of $730^\circ C$ with 10% UF_4 in the bed, then $U = 0.8881$, $I = 0.0831$, $N = 0.0595$, $C = 0.10$ and $k_{730} = 0.60 \text{ hr}^{-1}$. Since the bed weight is approximately 6000 g, the feed rate should be:

$$F = \frac{(0.60)(0.1)(6000) [1 - (0.51)(0.1)]}{0.8881 - (0.49)(0.8881)(0.1) - (0.0831)(0.1) - (0.0595)(0.10)} =$$

$$F = 368 \text{ g/hr}$$

Run FBR-23. Run FBR-23 was made to evaluate the use of crude UF_4 as the feed material in the Fluorox 4-in. fluidized bed reactor. The run was made with O_2 at a bed temperature of $690-725^\circ C$ and an average feed rate of 341 g/hr. Total operating time was 13.60 hr with 0.13 hr down-time for routine maintenance. The run was terminated when a leak developed in the reactor and in the thermowell.

A total of 4600 g of crude UF_4 was introduced to the reactor and 454 g of material was collected in the cold traps. Experimental apparatus and operating procedure were similar to that in run FBR-22 (Unit Operations monthly progress report for January 1959, ORNL CF 59-1-74).

All recorded outside wall temperatures were maintained below $750^\circ C$ except for one excursion to $800^\circ C$ which occurred in the vicinity of the hole in the reactor.

A 1/2-in. hole was corroded in the reactor wall midway up the 4-in. fluidized bed section (Figure 2.2) in the same general area in which a hot

Fig.2.2. Damaged Fluorox Fluidized Bed Reactor.

spot developed during the latter part of run FBR-22. The leak in the 1/4-in. Inconel thermowell (0.035 in. wall) was due to severe corrosion in a 4-in. section roughly opposite the hole in the reactor wall. It is felt that severe corrosion on Inconel occurred when the bed or reactor walls were operated at a temperature above the melting point of the UF_4 feed and the hole in the reactor was due to a hot spot caused by uneven external heating.

Following is the over-all material balance for run FBR-23:

Material Introduced (does not include O_2):

Original bed	5,950 g
Feed	<u>4,600 g</u>
Total	10,550 g

Material Removed:

Final bed	9,044 g
Overflow	1,173 g
Cold traps	<u>454 g</u>
Total	10,671 g

Analytical results are not available for this run.

Run FBR-24. The reactor has been repaired by replacing the damaged 4-in. section by new schedule 40 Inconel pipe. A second and final crude UF_4 run will be made (FBR-24) in which closer temperature control will be maintained. Following are the proposed operating conditions for this run:

Bed temperature	720-730°C
UF_4 concentration in bed	10%
Crude UF_4 feed rate	350-375 g/hr

Inconel corrosion coupons will be placed in the reactor by attaching them to the thermowell at three positions: (1) in fluidized bed, (2) at interface, and (3) in the gas phase. The reactor has been "vidigaged" to determine the wall thickness, and it will be measured again after the run.

3.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

P. A. Haas

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

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

Development studies for application of fluidized bed denitration (UNOP progress report, ORNL CF 58-10-90) to produce 50-500 micron diameter thorium oxide particles for fluidized bed reactor fuels were completed. A final report is being written comparing the fluidized bed and agitated trough (UNOP progress report, ORNL CF 59-2-45) for denitrating an aqueous solution of $\text{Th}(\text{NO}_3)_4$.

During the operation of the fluidized bed, seven runs were made by spraying aqueous and methanol solutions of 1.5 M $\text{Th}(\text{NO}_3)_4$ into a fluidized ThO_2 bed using a superficial fluidizing air velocity of 0.8 ft/sec at temperatures between 550 and 600°C. The main problem was partial caking of the ThO_2 bed. The ThO_2 for the starting bed material consisted of irregular sintered agglomerates which were not easily fluidized, and the poor fluidizing properties of the ThO_2 increased the probability of cake formation within the bed.

The last four fluidized bed runs were made by spraying aqueous $\text{Th}(\text{NO}_3)_4$ or $\text{UO}_2(\text{NO}_3)_2$ solutions into an initial bed of classified sea sand. The conditions of these runs were as follows:

Table 3.1. Operating Conditions and
Product Nitrate Content for Fluid Bed Denitration

Run	Aqueous Feed	Bed Temp.	Superficial Fluidizing Air Velocity, ft/sec	Wt % NO_3 in Product
T-8	1.8 M $\text{Th}(\text{NO}_3)_4$	700°C	0.8	0.06
T-9	2.5 M $\text{Th}(\text{NO}_3)_4$	500°C	0.8	0.34
T-10	2.5 M $\text{Th}(\text{NO}_3)_4$	400°C	1.3	0.51
T-11	2.5 M $\text{UO}_2(\text{NO}_3)_4$	390°C	1.3	0.26

Caking of the bed occurred below the spray nozzle in runs T-9 and T-10. The bed remained fluidized during runs T-8 and T-11 (the latter run with $\text{UO}_2(\text{NO}_3)_4$ feed was made to duplicate results reported by Argonne National Laboratory). There was a high yield of ThO_2 fines in all three of the $\text{Th}(\text{NO}_3)_4$ aqueous feed runs as indicated by a rapid build-up of the pressure drop across the metallic bayonet filters. The yield of UO_3 fines in run T-11 was sufficiently low to maintain a minimum pressure drop across the bayonet filters.

Photomicrographs were made of the classified product from the two most successful fluidized bed runs, T-8 and T-11 (see Figures 3.1, 3.2 and 3.3). Samples A- UO_3 and C- ThO_2 were classified between 250 and 500 microns, and sample B- ThO_2 was classified between 500 and 840 microns. Each figure contains photomicrographs showing the particles as removed from the fluidized bed, after washing with H_2O , and after sectioning to show the internal structure.

Observations of the sectioned samples indicated that the UO_3 coating on the sand particles was more dense and homogeneous than the ThO_2 . Due to the poor contrast between ThO_2 and sand, the make-up of the ThO_2 particles is not shown clearly in the cross-sectioned photomicrographs. However, visual observation of the sectioned samples showed that each "particle" consisted of sand and loosely bound agglomerates of smaller ThO_2 particles. The UO_3 , however, formed a continuous coating around the sand particles which was not readily removed by attrition. These observations are consistent with the fact that there was a higher yield of fines in the Th runs than in the U run.

Particle size analyses (determined by sedimentation and neutron activation) on the product from run T-8 also indicated the presence of loosely bound ThO_2 agglomerates. The average particle size of ThO_2 in sample C- ThO_2 (screen classified between 250 and 500 microns) was 35 microns using aqueous 0.001 M $\text{Na}_4\text{P}_2\text{O}_7$ as a dispersing agent.

From the results of these runs, use of a fluidized bed denitrator is not considered feasible for producing dense, high strength, 50-500 micron diameter ThO_2 particles. There was a high yield of fines in all the Th runs, and bed caking was a problem in every Th run except T-8 (bed temperature 700°C). Neither of these troubles were encountered in the run with uranium to duplicate results reported for fluidized bed denitration studies at Argonne National Laboratory.

The agitated trough calciner has been operated as a Th denitration system with no caking problem in the trough, but the high yield of ThO_2 fines is still an unsolved problem (see Section 3.2). All of the future work on denitration of ThNT will be done in an agitated trough apparatus.

A-UO₃ MAGNIFICATION 15X

A-UO₃ (WASHED WITH H₂O) MAGNIFICATION 15X

A-UO₃ (CROSS SECTION) MAGNIFICATION 34X

CONDITIONS

AQUEOUS FEED 2.5 M UO₂(NO₃)₂
BED TEMPERATURE: 390°C
PARTICLES SCREEN CLASSIFIED
BETWEEN 250 AND 500 microns

Fig. 3.1. Photomicrographs of Particles from Denitration of UO₂(NO₃)₂ on a Fluidized Sand Bed.

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B-ThO₂ MAGNIFICATION 15X

B-ThO₂ (WASHED WITH H₂O) MAGNIFICATION 15X

B-ThO₂ (CROSS SECTION) MAGNIFICATION 34X

CONDITIONS
AQUEOUS FEED 1.8 M Th(NO₃)₄
BED TEMPERATURE: 700°C
PARTICLES SCREEN CLASSIFIED
BETWEEN 500 AND 840 microns

Fig. 3.2. Photomicrographs of Particles from Denitration of Th(NO₃)₄ on a Fluidized Sand Bed.

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C-ThO₂

MAGNIFICATION 15X

C-ThO₂ (WASHED WITH H₂O) MAGNIFICATION 15X

C-ThO₂ (CROSS SECTION) MAGNIFICATION 34X

CONDITIONS
AQUEOUS FEED 1.8 M Th(NO₃)₄
BED TEMPERATURE: 700°C
PARTICLES SCREEN CLASSIFIED
BETWEEN 250 AND 500 microns

Fig. 3.3. Photomicrographs of Particles from Denitration of Th(NO₃)₄ on a Fluidized Sand Bed.

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

Tests were continued with the agitated trough calciner (described in ORNL CF 59-2-45, UNOP progress report for February 1959) to prepare 50-500 micron diameter ThO_2 by denitration of aqueous $\text{Th}(\text{NO}_3)_4$ in an agitated bed of sea sand. The bed temperature in the vicinity of the nitrate feed line was varied between 150 and 250°C with no bed caking. However, there was no ThO_2 growth on the sand particles.

In an effort to use a nitrate feed which would give a cohesive oxide, a run was made feeding $\text{Al}(\text{NO}_3)_3$ to an agitated sand bed. The resulting bed material (see Figure 3.4) contained a high percentage of Al_2O_3 particles between 200 and 800 microns in diameter.

A material balance on the agitated trough run reported in the Unit Operations February progress report (ORNL CF 59-2-45) showed a loss of ThO_2 . The initial ThO_2 bed weight was 9080 g to which 2385 g of ThO_2 was fed as $\text{Th}(\text{NO}_3)_4$. No ThO_2 was found in the product tank and only 8790 g was in the bed. The unrecovered oxide (2675 g) was probably entrained from the trough through the off-gas line and discharged with the off-gas scrubber solution.

In an attempt to coat ThO_2 on agitated sand particles, the trough bed temperature in the vicinity of the nitrate inlet line was lowered to 150°C. During operation the temperature increase from the nitrate feed line to the product removal port was 100°C at an aqueous feed rate of 30 m./min. The packed glass column in the off-gas system was white with ThO_2 fines throughout the run, and there was no indication of ThO_2 growth on the sand under any operating conditions. A particle size analysis of a sample of the oxide fines from the off-gas system indicated that 40 weight per cent was less than 1 micron in diameter.

In an attempt to find a possible feed additive which would aid ThO_2 particle growth, a run was made pumping aqueous $\text{Al}(\text{NO}_3)_3$ into an agitated sand bed. The aqueous feed rate was 30 ml/min, and the trough temperature was between 425 and 450°C. There was no indication of fines collecting in the off-gas column, and the Al_2O_3 coated the sand bed particles. The initial sand bed weight was 13.6 lb, and 9.8 lb of Al_2O_3 as $\text{Al}(\text{NO}_3)_3$ was fed to the bed during the run. About 4.2 lb of sand and Al_2O_3 were removed in the product tank. Due to the difference in densities of the two compounds and the difference in initial and final bed volumes, a material balance may not be completed until the final bed volume has been removed from the trough and weighed. The only caking in the bed was on the nitrate feed line (see Figure 3.4).

Future runs with the agitated trough will be made using the existing Al_2O_3 and sand bed. Mixtures of Al and Th nitrates will be denitrated in the bed in an attempt to form a cohesive oxide product.

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Fig. 3.4. Interior View of the Agitated Trough After Pumping $\text{Al}(\text{NO}_3)_3$ into a SiO_2 Bed.

3.3 Electrolytic Removal of Nickel - E. L. Youngblood

Installation of the system for electrolytically removing nickel from simulated HRT fuel solution is 95% complete (see Figure 3.5). Reagents required for the light water runs were procured. Arrangements were made to obtain heavy water and low moisture content UO_2SO_4 required for subsequent heavy water runs.

The removal of copper and nickel from the fuel solution by electrolysis increases the acid content of the solution and thus its corrosiveness. Since condensate for washing the electrolytic cell is obtained by evaporation, it is desirable to know corrosion rates for various stainless steels during evaporation. Corrosion data were obtained by placing stainless tubing in the liquid and vapor phases of a boiling solution of 0.34 M UO_2SO_4 and 0.56 M H_2SO_4 . The specimens were washed with water and acetone before and after a 24-hr exposure to the boiling solution. Corrosion rates were measured by weight loss of the specimens (see Table 3.2). Stainless steel, particularly 316, appears to be acceptable for operation of the test equipment.

Table 3.2. Corrosion by Simulated
Electrolysis Cell Product

Material	Liquid Phase Corrosion Rate, mil/yr	Vapor Phase Corrosion Rate, mil/yr
347SS	0.8	6.3
316 SS	2.9	1.5
304SS	1.8	29.0

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

The study of the ceramic properties of mixed Th-U-Al oxides was initiated with the Ceramics Research group located at Y-12. The group will determine melting points and compositions for mixed oxides of U:Th = 0.08:1 containing from 0 to 10 weight per cent Al_2O_3 . Evaluation tests were continued of the mixed Th-U-Al oxides and ThO_2 from aqueous solutions or sols reported in previous monthly reports.

Fig. 3.5. Electrolytic Nickel Removal System.

4.0 ION EXCHANGE

M. E. Whatley

Mechanism and Kinetic Studies - J. S. Watson

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.

The rate of uranium sorption on Dowex 2LK was studied by measuring the uranium sorbed on single beads in an agitated bath as a function of time. The bath contained enriched uranyl sulfate solution, and the uranium-235 content of each bead was determined by counting with a gamma spectrometer. The beads were removed from the agitated bath with a wire net. Since a very small quantity of beads was required for the measurements, the solution concentration remained essentially constant. The procedure was described in a previous report (UNOP progress report, ORNL CF 59-2-45).

The beads were in the sulfate form at the beginning of the run and were 1198 ± 40 micron in diameter. The solution was 0.0043 M uranium, 0.020 M sulfuric acid, and 0.20 M total sulfate. The solution was stirred during the entire run, and approximately 8% of the solution volume was lost due to evaporation.

The results of the first single bead run are shown in Figure 4.1. The results are in the form of an "S" curve. One-half of the equilibrium loading of the beads occurred in approximately 24 min.

A very simple and probably erroneous model was used to provide a preliminary correlation of these data. The resin was assumed to be completely ionized so that all of the uranium in the bead was free to diffuse. Furthermore, the uranium was assumed to exhibit a constant diffusion coefficient. With these assumptions the data may be fit to the equations for diffusion into a sphere with a constant surface concentration. It must be noted, however, that this is only a preliminary model and may differ from the actual physical case in one or more of the following ways:

1. A substantial portion of the uranium may be attached to the positive resin sites and be unable to diffuse.
2. The uranium which is free to diffuse may not exhibit a constant diffusion coefficient, since the uranium exists as several species, UO_2^{++} , UO_2SO_4 , $UO_2(SO_4)_2^-$, and $UO_2(SO_4)_3^{--}$. Each of these species will diffuse due to its own concentration gradient and will have its own diffusion coefficient. In addition one species may be

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Fig. 4.1. Bead Loading in Run No. 1 as a Function of Time.

converted to another along the diffusion path. The diffusion rate which will be observed is the sum of all of these processes.

3. The film diffusion resistance may be significant and the surface concentration not be constant.

The concentration gradient for each uranium specie is affected by the fact that along the diffusion path, all of the species as well as sulfate and hydrogen ions are constantly reestablishing chemical equilibria. For solutions in which the sulfate concentration is much greater than the uranium concentration, one can show that each uranium specie essentially constitutes a constant fraction of the total uranium concentration. Furthermore, under these conditions, an apparent constant diffusion coefficient for uranium might be observed. However, these conditions will probably not be met within the resin bead.

With all the previously stated assumptions, the loading of the spheres as a function of time may be written²:

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

where

M_t = loading

M_∞ = equilibrium loading

a = sphere radius

t = time

D = diffusion coefficient

Note that M_t/M_∞ may be considered as a function of only the group $(Dt/a^2)^{1/2}$. To determine a value for D and to see how the data agreed with the equation for a constant D , experimental value of M_t/M_∞ were plotted as a function of $(t/a^2)^{1/2}$. Then on the same plot curves for M_t/M_∞ vs. $(t/a^2)^{1/2}$ were calculated from equation (1) were plotted for various assumed values of D . (shown in Figure 4.2). The data shows a moderately good fit to a curve for D of about 9.02×10^{-8} cm²/sec.

This low value of the diffusion coefficient does not take into account the porosity of the bead and therefore should be a function of the cross-linkage (DVB) of the resin. However, real evaluation of this treatment will require data with different solution concentrations and bead size. The treatment is expected to be too simple to describe the system in general so better methods are to be developed.

²Crank, J., The Mathematics of Diffusion, Oxford Press, (1956), pp 85-91.

Fig. 4.2. Correlation of Data from Run No.1 with Particle Diffusion Equation.

5.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

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

The purpose of the Darex process is to convert SS-U and SS-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. In the present investigation, a batch flowsheet is being developed in which dissolution product is treated with 61 wt per cent HNO₃ to produce solvent extraction feed which contains 2-3 M HNO₃ and less than 350 ppm chloride.

Chloride Removal and Feed Adjustment. A total of eight batchwise runs were made in the 4-in. feed adjustment equipment. Five runs were made with APPR dissolution product using the Darex Reference flowsheet, while the other three were simplified procedures for processing "Heat" material.

The flowsheet referred to in past reports as the "double recycle" flowsheet (a nondistinguishing title since the Recycle flowsheet also has two recycle streams) will henceforth be known as the Darex Reference flowsheet. The distinguishing characteristics are: a batchwise Darex flowsheet using only virgin 61 wt per cent HNO₃, a continuous addition of recycle acid (12 M HNO₃ plus a trace of chloride), and a variable period of reflux. Important variables are the method of condenser operation and the use of gas sparging.

Data for five Reference flowsheet runs (two with and three without reflux) are presented in Table 5.1. A detailed description of the Reference flowsheet for APPR (2% plant scale) is as follows: (see Figure 5.1)

1. Charge 5.4 liters DP (5-1/2 g/liter U, 60 g/liter total metals) to the feed adjustment tank.
2. Boil off 1.5 liters acid waste.
3. Add continuously 4.7 liters recycle acid (12 M HNO₃, trace Cl⁻) while distilling off 4.7 liters mixed acid.
4. Add 3.3 liters virgin 13.3 M HNO₃ (61 wt per cent).
5. Reflux - (zero reflux time was required in the 1/50 scale equipment).
6. Distill off 4.7 liters recycle acid (12 M HNO₃, trace Cl⁻).
7. Dilute with water to 6.2 liters of solvent extraction feed (2-3 M HNO₃, < 350 ppm Cl, < 5 g/liter U).

Table 5.1. Data for Recycle Flowsheet and "Heat" Runs

Col No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	
Run No.	Air Spurge	Condenser	Dissolution Product			Acid Waste			At Constant Level				Add 13.3M HNO ₃	Acidified Concentrate			Reflux Time Hours	Recycle HNO ₃ (Trace Cl ⁻)		Solvent Extraction Feed			
			Vol	H ⁺	Cl ⁻	Vol	HNO ₃	Cl ⁻	Add 12M HNO ₃	Aque Regia Recycle				Vol	HNO ₃	Cl ⁻		Vol	HNO ₃	Vol	HNO ₃	Cl ⁻	
			l	M	M	l	M	M	l	Vol	HNO ₃	Cl ⁻		l	l	M		M	l	M	l	M	ppm
51	None	UPDR	5.4	2.92	1.75	1.5	0.45	0.20	4.7	4.7	5.6	1.2	3.0	~6.8	11.0	0.19	2	4.7	12.0	6.2	2.33	28	
52	None	UPDR	5.4	2.92	1.75	1.5	0.35	0.20	4.7	4.7	5.55	0.9	3.3	~7.1	11.2	0.13	2	4.7	12.0	6.2	2.91	33	
53	None	UPDR	5.4	2.92	1.75	1.5	0.47	0.20	4.7	4.7	5.7	1.1	3.3	~7.1	11.3	0.10	None	4.6	12.0	6.2	3.04	51	
54	None	UPDR	5.4	2.92	1.75	1.5	0.40	0.25	4.7	4.7	5.8	1.0	3.3	~7.1	11.3	0.10	None	4.7	12.1	6.2	2.29	48	
55	None	UPDR	5.4	2.92	1.75	1.5	0.41	0.22	4.7	4.7	5.8	1.0	3.3	~7.1	11.3	0.12	None	4.7	12.1	6.2	2.40	40	
									13.3M HNO ₃ Batch														
Heat 5	None	DWDR	6.0	4.31	1.65	None			3.5	5.2	4.0	1.1	None	4.0	9.7	0.004	None	None		12.0	3.23	40	
Heat 6	None	DWDR	6.0	4.31	1.65	None			2.6	4.5	3.4	1.4	None	4.0	8.4	0.006	None	None		12.0	2.80	71	
Heat 7	None	DWDR	6.0	4.31	1.65	1.0	1.18	1.17	3.0	5.0	5.2	0.92	None	~2.75	9.1	0.004	None	None		8.3	3.03	~40

Fig. 5.1. The Darex Process
Reference Flowsheet for Batchwise Operation Using 61 wt % HNO₃
Run No. APPR-52

Comparison of Three Batch Darex Flowsheets Using 61 Wt Per Cent HNO_3 . The Reference flowsheet will be used first in the Darex pilot plant for APPR fuel reprocessing since it incorporates more desirable features than any other 61 wt per cent flowsheet (see Table 5.2). The waste volume, 27% of the aqua regia feed, is not the lowest (19% in the Reflux flowsheet) but is less than the Recycle waste (32%). The continuous HNO_3 addition is desirable for high efficiency of Cl^- removal and recovery in that the HNO_3 concentration in the metals-bearing solution increases while the Cl^- concentration decreases. Thereby, unnecessary decomposition from boiling a high HNO_3 , high Cl^- solution (as in the Reflux flowsheet) is avoided. The over-all effect of the continuous addition is to produce lower Cl^- concentrations at the beginning of reflux.

The possible elimination of the reflux step itself (dependent on the performance of larger equipment) would be an obvious advantage. In the absence of reflux, the question of gas sparging during reflux would be automatically resolved. However, the availability of a reflux step, should it be necessary, lends flexibility to the Reference flowsheet and is an advantage compared with the Recycle flowsheet which has no such provision.

If refluxing is necessary, the addition of virgin 13.3 M HNO_3 dilutes the chloride present without introducing additional chloride as is the case with the Recycle flowsheet. The batchwise addition results in a solution more dilute in metals (45 g/liter) than the original DP, compared with the Recycle (90 g/liter) and the Reflux (100 g/liter) flowsheets. In the Reflux flowsheet the metal loading is as high as 270-300 g/liter prior to the second HNO_3 addition.

All three flowsheets have essentially the same over-all HNO_3 consumption per batch. The Reflux flowsheet requires no HNO_3 recycle and uses virgin 13.3 M HNO_3 in both additions. One fewer titanium vessel is required in the pilot plant. If provisions for a recycle stream are provided, however, the Reference flowsheet has the advantage of countercurrent operation with respect to chloride. Virgin 13.3 M HNO_3 is added for final chloride removal. The strong nitric acid becomes contaminated with chloride and is recycled upstream as 12 M HNO_3 . The final recycle is back to the dissolution step as 6 M HNO_3 -1 M HCl where the aqua regia is adjusted to 5 M HNO_3 -2 M HCl and reused as dissolvent.

The smallest volume reached in the Reference flowsheet (35% of DP) is encountered after the recovery of the recycle acid, compared with 30% for the Recycle flowsheet (after recycle recovery) and 20% for the Reflux flowsheet. The Recycle flowsheet requires further HNO_3 distillation and H_2O dilution to obtain 2-3 M HNO_3 in the solvent extraction feed. The Reference flowsheet gave better chloride removal (28-51 ppm) without reflux than did the Reflux flowsheet (135-330 ppm with 2-hr reflux and sparge) or the Recycle flowsheet (220 ppm, no reflux or sparge but larger volume of recycle HNO_3).

TABLE 5.2. COMPARISON OF THREE BATCH DAREX FLOWSHEETS USING 61 WT % HNO_3

	REFERENCE	REFLUX	RECYCLE
WASTE VOL. (% OF AQUA REGIA VOL.)	27	19	32
1ST HNO_3 ADDITION	CONTINUOUS 12M	BATCH 13.3M	CONTINUOUS 13M
2ND HNO_3 ADDITION (13.3M)	BATCH	BATCH	CONTINUOUS
COMPOSITION OF "ACIDIFIED CONCENTRATE"			
HNO_3 (M)	11.1	9.0	9.2
Cl^- (M)	0.1-0.2	0.5-0.9	0.12
REFLUX	IF NEEDED	NECESSARY	NO PROVISION
VOL. OF ACID RETURNED (% OF AQUA REGIA VOL.)	167	90	225
MAX. METALS LOADING (g APPR/LITER)	170	290	200
Cl^- IN SOLVENT EXTRACTION FEED (ppm)	28-51	135-330	220

Chloride removal was accomplished much more easily in the case of the "Heat" material than with APPR. Neither reflux nor recycle HNO_3 was required to remove chloride to less than 100 ppm. In the first run (see Table 5.1, run Heat 5) only a single 13.3 M HNO_3 addition and mixed acid recovery was necessary to yield a chloride concentration of 40 ppm. However, the mixed acid could not be adjusted to 5 M HNO_3 -2 M HCl without water removal or the total volume would exceed slightly the original dissolvent volume.

The second run was identical to the first except that smaller volumes of HNO_3 and mixed acid were involved. The chloride content in the solvent extraction feed was reduced to 71 ppm and the mixed acid could probably be recycled without water removal. In the third run a small waste cut was taken initially to allow more flexibility in the process and in turn to increase its reliability. Chloride removal was to approximately 40 ppm and the mixed acid could be recycled. The volume of the waste cut must be minimized since HNO_3 and HCl molarities in the waste were considerably higher (see columns 7 and 8, run Heat 7) even though the waste cut was a smaller percentage of the DP volume. An abbreviated Reference flowsheet using a continuous virgin 13.3 M HNO_3 addition with no recycle or reflux should be readily adaptable to the "Heat" material if it is to be processed in the same equipment used for APPR.

Chloride Removal by Refluxing. Laboratory scale studies were made to determine the effect of reflux time and HNO_3 concentration on the dissolver product chloride concentration. The results are presented in Figure 5.2 for five runs using a dissolver product containing 100 g/liter APPR metals loading, 0.58 M Cl^- , and variable initial HNO_3 concentrations of 8 M, 9 M, 10 M, 12 M, and 14 M.

Note that very low chloride concentrations may be reached (< 100 ppm before acid recovery and dilution) by decomposition during six hours of reflux (without sparging) with initial nitric acid concentrations in excess of 12 M. The data indicate that for a given reflux time the chloride concentration in the dissolver product varied inversely with the initial HNO_3 concentration. Below an initial HNO_3 concentration of approximately 10 M there was very little change in the chloride concentration with reflux time. Higher HNO_3 concentrations increased the chloride decomposition and decreased the chloride in equilibrium with the liquid phase. Initially the chloride concentration decreased very rapidly and then leveled off for all runs indicating that for each initial acid concentration there is a reflux time beyond which there would be no further decrease in chloride concentration. The chloride concentration at any given reflux time would be decreased further by distilling HNO_3 from the dissolver product and then diluting the final concentrate with water to produce solvent extraction feed. The relative amounts of acid removed and diluent water would be dependent on which flowsheet was being used.

The test solutions were prepared by concentrating a single batch of product from chloride removal and feed adjustment runs made in the 4-in.

Fig. 5.2. Dares Dissolver Product Chloride Concentration as a Function of Reflux Time for Various Initial Nitric Acid Strengths.

I.D. feed adjustment tank using 61% HNO_3 with a Reflux flowsheet. HCl , HNO_3 , and water were added to obtain solutions with 100 g/liter APFR metal loading, 0.58 M Cl^- , and the various HNO_3 concentrations indicated. A run was made by charging 900 ml of solution to a 2-liter flask and boiling the solution, without sparging, at total reflux using an updraft condenser at a constant boilup rate/liquid volume ratio of approximately 1/150 per min.

5.2 Sulfex - J. B. Adams, G. B. Dinsmore

Experiments were made on the continuous dissolution of 304L stainless steel (simulating the decladding of prototype Consolidated Edison pins) using a small dissolver with a feed of 6 M H_2SO_4 .

There were several preliminary runs to adjust flow rates and to observe the dissolver operating characteristics with lengths of $1\frac{1}{4}$ in. O.D. stainless steel tubing with a 0.035 in. wall. Batches of 100-400 g were dissolved in a heated 1-in. dia glass tube. A $1\frac{1}{2}$ g piece of steel wool was included to start the reaction, and 6 M H_2SO_4 was metered in at the base of the tube at rates of 1-3 cc/min and allowed to overflow through a seal leg to a receiver. The off-gas passed through a glass condenser, and the hydrogen evolution rate was measured with a wet test meter. Over-all solution loadings of 50-75 g SS/liter were obtained.

The average off-gas rate was consistently $1.20 \pm 1\%$ g mole H_2 per "mole" of dissolved stainless steel ("molecular weight" of stainless steel = 55).

A layer of foam extended to the top of the stainless steel tubing or to the overflow port, whichever was higher. The foam was broken a short distance above these levels regardless of the acid flow rate or the charge of stainless steel. The instantaneous hydrogen evolution rate was erratic; the dissolution rate cycled approximately 50% over approximately 10-min intervals.

A single prototype Consolidated Edison pin ($\text{ThO}_2\text{-UO}_2$ clad in 20 mil 304L stainless steel tubing $7\text{-}3\frac{3}{8}$ " long x 0.311" dia) was declad in the 1-in. glass dissolver. The decladding process took an excessive length of time (150 min) and resulted in a low solution loading (43 g/liter) because of the relatively small volume of stainless steel in a large dissolver. When a single pin was declad in a $1\frac{1}{2}$ -in. dissolver of a similar design at the same acid flow rate (approximately 2.4 ml/min), the reaction took about 100 min and a stainless loading of 65 g/liter was attained. The rates and loadings are only slightly different from those in a typical batch reaction. The continuous decladding process could be further improved if more pins per unit dissolver volume were in the dissolver. Preliminary analyses of the product acid indicated uranium losses of $\sim 0.1\%$, approximately the same as have been reported earlier.

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

Four filtration runs were made with a 1-1/2 in. dia sand filter using a Darex solution (HS-5-A) which had been treated for chloride removal and nitric acid recovery. The runs were made with and without certain reagent additions to aid solution clarification. In each test the clear liquor from settling was first filtered and then the thickened slurry was filtered.

The results (Figure 5.3) gave almost identical slopes on cumulative volume vs. the root of time plots for both supernate and thickened slurry fractions for the four tests. The only significant difference in the results was that "Mistron"* caused sedimentation of the solids to a higher settled density which produced a greater volume of clear liquor and a decreased volume of slurry with a correspondingly shorter filtration cycle. Also only 3 hr settling time was needed after the silica-gelatin treatment compared to 48 hr normally required with the other methods.

The test solution, HS-5-A, contained 4.32 g U/liter, 28.3 g Fe/liter, 3.10 N H^+ and 21 ppm SiO_2 . The solution density at 28°C was 1.22 g/cc and the viscosity, 1.83 cp. The silica sludge was much blacker than any encountered previously and contained slightly more SiO_2 (5.8%) but was otherwise similar to that found in previous batches. A sample of clear filtered solution formed coarse white crystals when evaporated to one-third its original volume. When the crystals were dried to 56% H_2O , they turned red. The sample contained 79% SiO_2 and 3% Fe on a dry basis.

A coarse, granular, well-dehydrated silica was formed from water glass (40 BÉ $Na_2O \cdot 3.25 SiO_2$) in HNO_3 and in Darex solutions. Evaporation and reflux procedures were followed which simulated those used in Darex head-end treatment. The resulting wet silica cake contained 45-50% SiO_2 . Since the same procedure did not dehydrate silica contained in the dissolved stainless steel fuel elements, the basic colloidal properties of the two are obviously different.

All split feed filtration tests reported here were made with 1 liter of a single Darex solution, HS-5-A, with 5 in. Hg vacuum at room temperature. The sand filter was 8 in. deep and 1.5 in. dia precoated with 1 g Celite 545 filter aid. Two grams of Celite 545 was added to the supernate (550-700 cc) and 12 g to the thickened slurry.

5.4 Mechanical Processing

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

Mark I Assembly. When a Mark I prototype assembly filled with porcelain rods was sheared into 0.75-in. lengths with a "plane of contact" blade in the 125-ton Manco shear, 22.2 g of metal fines (304L stainless steel)

*Mistron - 25 micron magnesium silicate reported to have adsorptive power for siliceous materials, Sierra Tube and Clay Co.

Test No.	Symbol	Reagent and Treatment
1	○	No reagent; settled 48 hr.
2	△	Agitated 10 ppm Mistran* in feed for 2 hr; added 8 ppm Np-10**; settled 48 hr.
3	□	Agitated 10 ppm Mistran in feed for 2 hr; settled 48 hr.
4	▽	Heated feed + 200 ppm soluble SiO ₂ + 100 ppm gelatin for ½ hr at 85°C; settled 3 hr.

**Mistran, 25 μ magnesium silicate, Sierra Tube and Clay Co.

**N.P.-10, flocculating agent, Dow Chemical Co.

Fig.5.3. Filtration of Darex Solvent Extraction Feed Solutions: Comparison of Various Reagent Treatments.

1680 microns or less in size was produced. There was sufficient cold working of these fines to allow removal of all but 2.5 g with a small permanent magnet. Size distributions of the metal-porcelain mixture and the metal fines alone are shown in Table 5.3.

In the previous monthly report (ORNL CF 59-2-45), it was erroneously reported that 4.8% of the fines were less than 149 micron. The correct value was 36.5% of fines are less than 149 micron size. The size distribution of fines produced in the lower range may be independent of blade shape, for essentially the same amount was produced using a "line of contact" blade (Table 5.3, ORNL CF 59-2-45). A total thrust of 80 tons was required to shear the Mark I prototype bundle. This experimental result compares favorably with a calculated required thrust of 70 tons on the basis of 80 per cent of metal tensile strength plus 20 per cent of the ceramic compressive strength.

UO₂-Filled Zirconium Assembly. A 5x5 tube, 27 in. long dummy fuel assembly was prepared by brazing together individual 0.5-in. dia, 10-in. long rods. The amount and size distribution of zirconium fines will be determined and the possible hazard of zirconium metal fines in the nitric acid dissolution step will be evaluated after shearing with a "plane of contact" blade.

Surplus Press. The surplus 200-ton thrust press will be installed by April 30, and the dies and blades will be fabricated for evaluating the effect of blade shape and velocity on blade life.

Fabrication has begun on two die sets and two pair of blades for use with the 200-ton press for shearing the Mark I porcelain filled prototype assembly. The first die assembly and 2 stationary blade shapes are shown in Figure 5.4. The advantage of blade arrangements shown over the types previously used is that use is made of a horizontal force component to press the fuel bundle together. Thus void spaces may be eliminated so that the bundle may be sheared as a solid integral unit. Different shapes of punches for use in these evaluation tests are shown in Figure 5.5. In addition to the shearing operation, the die sets will contain provisions for preliminary pressing and holding operations. With the type of blades and dies being used in this die set, it will be necessary to lift the bundle from the shear anvil after each shearing before material transfer of the bundle through the shear throat.

The tendency to shorten blade life by "wiping" bits of metal between blades is increased if a pair of blade types are used which allow the bundle to spread extensively so that the cutting action is on individual tubes rather than on the bundle as a solid integral unit. "Wiping" is exhibited in Figure 5.6 at several locations along the anvil with a "plane of contact" shear and no side retaining force on the fuel bundle.

Material Transfer and Collection. A detailed study is being made of the material transfer problem from shear to dissolver to disposal and back to the

Table 5.3. Size and Weight Distribution of Porcelain and Metal Fines from Shearing of Mark I Prototype Fuel Assembly

Conditions: (a) Shear - 125-ton Manco
 (b) Blade type - "plane of contact"
 (c) 65 cuts at 0.75-in. lengths of a 4 ft Mark I prototype at 0.33 in./sec
 (d) Physical properties of porcelain
 Tensile strength 5-10,000 psi
 Compressive strength 90,000 psi
 Flexural strength 10-20,000 psi
 Hardness 7-9 moh scale

Portion	Size, microns		Total, Metal and Porcelain		Total Metal			Nonmagnetic Metal	
	Over	Under	Weight, g	Per Cent of Total	Weight, g	Per Cent of Metal	Per Cent of Total	Weight, g	Per Cent of Metal
1	1680		72.0	3.3	0.38	2.6	0.53		
2	840	1680	193.5	8.9	7.09	47.9	3.66	0.22	2.9
3	297	840	661.9	30.4	4.24	28.7	0.06	0.13	3.1
4	149	297	454.5	20.9	1.25	8.4	0.28	0.12	9.6
5		149	<u>793.9</u>	<u>36.5</u>	<u>1.82</u>	<u>12.4</u>	0.23	<u>1.18</u>	64.8
Totals			2175.8	100	14.78	100		1.65

NOTE:
ALL DIMENSIONS IN INCHES

Fig. 5.4. Die Assembly for Use With Various Blade Shapes in Mechanical Processing Blades Evaluation Studies.

Fig. 5.5: Various Interchangeable Punches and Anvils for Use in Mechanical Processing Blade Evaluation Studies.

Fig. 5.6 "Wiping" of Stainless Steel Pieces Between Blades of 125-ton Manco After Shearing a Mark I Prototype Assembly Filled with Porcelain.

shear, by the Mechanical Processing group in the REE Division in conjunction with an outside contractor, Burns and Roe. Conceptual drawings were prepared of various methods of materials collection from the shear while shearing either under water or in a dry atmosphere. Sheared materials will be collected either in lined or unlined porous baskets. If a lining is used, it will be either aluminum foil or porous teflon cloth.

125-Ton Manco Shear. Modification of the Oil Gear and Manco units was completed to allow for cooling of the hydraulic oil, remote operation of the Oil Gear and replacement of two 5/16-in. dia, 1-ft long, channels in the Manco with a 1-in. dia direct inlet and outlet to the hydraulic cylinder to minimize excessive pressure drop at higher blade speeds.

A support framework for the Manco was designed and is being fabricated. Design is continuing on a bin for enclosing the shear during cutting with provision for transfer of sheared pieces into either a porous basket for batch dissolver operation, or through a connecting pipe and a star valve for isolating the shear to a feeding mechanism for either of several continuous solids discharging dissolvers under design or construction.

Solids Discharging Dissolvers. When a 2-g sample of 304L stainless steel fines (500 micron or smaller) was immersed for 5 hr in a boiling Thorex dissolver solution (13 M HNO_3 , 0.04 M F^- , 0.04 M Al^{+++}) 6% was dissolved. Under similar conditions, if a Con Ed fuel bundle of the Mark I size were leached after shearing, only 0.15 g would be dissolved.

Construction drawings were completed for a batch solids discharging dissolver and fabrication is approximately 20% complete. Fabrication was completed of two large auxiliary components of the continuous solids discharging dissolver installation, the de-entrainment separator and the off-gas scrubber. Installation is about 40% complete of the spiral vibrating dissolver and the auxiliaries which will also be used for either batch or continuous dissolvers.

Assembly drawings are 20% complete of the American Machine Foundry continuous dissolver concept in which solids transfer from the unit is by means of a revolving screw. The rotating slab dissolver is being studied in an effort to eliminate several difficulties of material transfer which may be inherent in this type of device.

Microbrazed Destruction. A Consolidated Edison fuel assembly consisting of 100 stainless steel tubes with 30 mil wall thickness separated by 15 mil ferrules was successfully disassembled without any fracture of tube wall using a wedge driven by a small portable air hammer to rupture the Microbrazed 50 bond between the ferrules and tubes (Figure 5.7). A similar impact tool was not successful in separating ferrules from single elements to provide a suitable feed for an automatic rod shear.

Extruding Die. An unsuccessful attempt was made to disassemble a 12-tube assembly (3x4 square array) simulating the Nuclear Ship Savannah

Fig. 5.7. Impact Wedge Used in Disassembling a Consolidated Edison Fuel Bundle by Separating into Slabs and Then into Individual Elements.

assembly by extruding through a die designed to cut the ferrules holding the assembly together (Figure 5.8). Failure occurred when one tube was bent out of the die path. A ferrule became wedged between one of the die cutting edges and the tube, causing it to bend rather than be extruded through the die. The extruding die will not be considered for fuel bundle disassembly because the trouble described above would be characteristic of irradiated fuel, and the close dimensions between tubes would make it impossible to anticipate the problem by die design.

5.4.2 Abrasive Sawing - G. A. West, R. O. Payne

Additional cutting characteristics were measured with a Ty-Sa-Man abrasive saw fitted with a 16-in. dia, Manhattan No. 239 blade. The abrasive saw is proposed for installation in the segmenting cell in Building 3026 for removing end boxes and separating fuel bundles of spent power reactor fuels.

Abrasive sawing of a triangular bundle of three 0.5 in. O.D. type 347 SS rods at a blade speed of 10,450 surface ft/min showed that ratio of blade consumption to metal removed was less (1:4) at a slow feed rate (< 10 in./min) than at higher rates (up to 40 in./min) where the ratio was 1:2 (see Figure 5.9). The mass ratio was 1:12 and 1:8 at feed rates of 6 and 40 in./min, respectively. The burrs produced on the underside cut extended as much as 1/8 in. on most of the cuts. The slow cutting rate, approximately 10 in./min, produced a rougher cut, heavier burrs and more metal discoloration from heat than the faster feed rates, 24 to 40 in./min.

A total of 1,060 g of both metal and blade was produced from 204 cuts through a triangular bundle of three 0.5 in. O.D. stainless steel rods. The particle sizes produced from this cutting, as determined by U. S. Standard Sieve screens, were as follows:

<u>Particle Size, micron</u>	<u>% by Weight</u>
< 149	43.0
149-177	9.8
177-210	0.8
210-250	8.7
250-297	2.9
297-420	10.9
420-590	8.0
590-840	10.7
840-2000	3.6
> 2000	1.6

Fig. 5.8. Extrusion Die for Disassembling a 4x3-in Square Array Bundle Having the Dimensions of a Nuclear Ship Savannah Fuel Assembly Section.

Fig. 5.9. Wear Rate of Abrasive Disk Compared to Metal Removed at Various Feed Rates.

5.4.3 Leaching Studies - G. A. West, J. C. Rose

Leaching rates of sheared sections of Yankee Atomic prototype fuel, unirradiated sintered UO_2 pellets with stainless steel clad, in 10 M HNO_3 were measured to aid in the design of experimental solids discharging leachers.

Over-all average reaction rates for complete dissolution varied from 0.067 to 0.009 g/min/g of initial UO_2 for sheared fuel lengths of 0.5 to 2.75 in., respectively, of 0.400 in. O.D., 10 mil wall stainless steel tubing containing 0.370 in. O.D. UO_2 pellets (Table 5.4). Only 0.007 g/min/g were obtained on one run of 1.5 in. long elements, other runs at same conditions had rates from 0.025 to 0.043 g/min/g. Unclad pellets were dissolved at the rate of 0.04 to 0.10 g/min/g. The UO_2 particles dislodged from shearing were excluded from all of these tests.

Initial rates varied from 1.2 to 5.0 g/min on sheared elements of 0.5, 1.0 and 1.5 in. long (Table 5.4). The primary difference in dissolution rates resulted from the degree of fracturing of the pellets and closure of the sheared lengths from the shearing operation. The line-of-contact shearing resulted in an area decrease of 10-50% on the sheared ends.

5.4.4 SRE Decanning

The equipment for decladding the SRE (NaK bonded) fuel elements is being fabricated by the Southern Machine Company at Chattanooga, Tennessee. The estimated completion date is April 30, 1959, at which time the unit will be delivered to ORNL for cold tests.

A unit for steam cleaning the decanned uranium slugs to remove oil and surplus NaK was designed and is being fabricated. The cleaned slugs will be recanned for storage and subsequent charging to the Thorex dissolver. A two sectional can of spun aluminum, sealed by a press fit and by edge rolling did not appear as feasible in preliminary tests as the use of a home canning machine. Aluminum cans with 35 mil walls (type 303 food can size) are being fabricated for evaluation tests with a food canning machine seal.

5.5 Radiation Damage - G. A. West .

Effects of irradiation on glass is being studied in order to evaluate its usefulness as a material of construction for fuel reprocessing.

Specimens of Pfaudler glass coated mild steel were irradiated to 10^{10} r, 7 for measuring radiation effects on stress-strain, adherence to disc and various convex radii, and corrosion. The evaluation tests are being performed at the Pfaudler Company. Seven additional types of the Corning Glass solid glass rods, bars and discs are undergoing irradiation to 10^6 , 10^9 and 10^{10} r, 7.

A protective coating, Amercoat No. 1680 over Dimetecote No. 3, is being irradiated to evaluate its use as a cover-coat to increase visibility in storage canals.

Table 5.4. Leaching Rate of Various Sheared Lengths
of Stainless Steel Clad UO_2 in Boiling 10 M HNO_3

Conditions: Volume to mass ratio: 5 ml/g

Note: (1) Dislodged UO_2 particles from shearing excluded.
(2) Variable rates on same lengths show effect of
fracturing of the pellets and end closure of
cladding from shearing.

Sheared Length, in.	Initial Mass, g	Mass Dissolved, g	Time, min	Reaction Rate	
				Over-all Average, g/min/g	Instan- taneous, g/min
0.5	17	10.0	2.0	-	5.0
	16	7.5	2.0	-	3.76
	13.4	13.4	15	0.067	-
	14.9	14.9	35	0.029	-
	12.3	12.3	37	0.027	-
1.0	16.0	5.8	2.0	-	2.9
	14.9	5.6	2.0	-	2.8
	16.4	3.6	2.0	-	1.8
	15.4	15.4	27	0.037	-
	14.8	14.8	28	0.036	-
	15.4	15.4	30	0.033	-
1.5	26.2	3.8	2.0	-	1.9
	24.6	2.8	2.0	-	1.4
	23.0	2.4	2.0	-	1.2
	20.8	20.8	23	0.043	-
	23.0	23.0	38	0.026	-
	20.1	20.1	41	0.025	-
	23.4	23.4	140	0.007	-
2.75	46.5	46.5	115	0.009	-
Unclad Pellets	21.2	21.2	10	0.100	-
	20.8	20.8	23	0.043	-
	20.7	20.7	25	0.040	-
	27.8	27.8	120	0.004	-

6.0 VOLATILITY

R. W. Horton

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

The dissolution of zirconium metal in molten salt baths of NaF-ZrF_4 or NaF-LiF with anhydrous HF is a proposed head-end step for the reprocessing of zirconium matrix fuel sub-assemblies. The salt dissolution product is the feed material for the fluorination step. Dissolutions have been made using dummy sub-assemblies fabricated from Zr-2 rolled plate. The present program is directed toward: (1) corrosion studies in the newly constructed INOR-8 dissolver under dissolution conditions, and (2) the study of the effects of dissolver geometry on dissolution variables.

Two dissolution runs were made using the NaF-LiF system with sub-assemblies 100 per cent submerged. Run INOR-8 -4 (operating temperature range: $675\text{--}700^\circ\text{C}$) was terminated by a fused salt leak in the Inconel discharge line after reaching operating temperature. Run D-23 ($675\text{--}700^\circ\text{C}$) was terminated after 22.2 hr with 88% dissolution of the Zr-2 sub-assembly. An over-all dissolution rate of 0.11 lb/hr/sq ft was obtained for the second run. However, fluctuations in the HF feed gas rate made accurate evaluation of the HF utilization impossible.

Data and Results from Previous Runs. The analytical results from samples of various solids deposits collected after runs INOR-8 -1 and -2 are shown in Figure 6.1. The results are tabulated to show the location of each sample from the dissolver and off-gas system.

Vidigage readings on the INOR-8 dissolver and draft tube are shown in Figures 6.2 and 6.3. These thickness measurements were made after the salt residue on the dissolver surface was removed by boiling in 0.5 M ammonium oxalate solution for 16 hr.

6.1.1 Alternate Fused Salt Dissolution Cycle

Run D-23 was the first of two runs which are being performed to evaluate the fused salt dissolution of zirconium by an alternate cycle procedure. Table 6.1 lists the operating conditions for run D-23. The alternate dissolution cycle is shown in Figure 6.4. The method consists essentially of restricting the zirconium content of the NaF-LiF fused salt to the range 20-40 mole per cent ZrF_4 . Figure 6.5 represents the fused salt temperature profile for the NaF-LiF system as the ZrF_4 content is increased by fused salt dissolution with anhydrous HF ¹. As seen from Figure 6.5, lower dissolution temperatures can be used by limiting the zirconium composition

¹Thoma, R. E. and Grimes, W. R., "Phase Equilibrium Diagrams for Fused Salt Systems", p 54, ORNL-2295, June 24, 1957.

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RUN		TEMP	HF RATE	SUBMERGENCE	
INOR-8-1		800°C	4 LB/HR	100%	
INOR-8-2		675-700°C	4 LB/HR	100%	

RUN	SAMPLE DESCRIPTION	ELEMENT (WT %)									
		Na	Li	Zr	F	Mo	Ni	Cu	Fe	S	H ₂ O
1	OFF-GAS SOLIDS	0.12	0.05	4.91	12.45	0.32	1.40	68.9	0.08		
1	OFF-GAS SOLIDS	15.99	2.85	7.75	56.17		2.03				
2	OFF-GAS SOLIDS	17.63	6.59	11.14	60.27	1.22	1.85	<75 ppm			
1	OFF-GAS SOLIDS	15.19	5.13	10.76	54.94		1.89		0.38		
2	SALT DEPOSIT	11.50	18.99	1.08	68.49	24 ppm	0.12	155 ppm			
1	SALT DEPOSIT	4.62	20.66	6.82	66.84		0.89				
1	SALT DEPOSIT	20.14	6.90	17.70	56.68		1.52	0.11			
1	CORROSION PRODUCT	8.93	3.37	11.38	31.59		33.52		1.28		
1	SALT DEPOSIT	6.23	20.41	4.47	69.47		0.39	<0.5			
2	SALT DEPOSIT	10.50	16.00	7.60	66.20	0.11	0.46	333 ppm			
1	SALT TRANSFER	16.99	2.82	27.10	52.14		0.16	<0.1			
2	SALT TRANSFER	17.25	4.88	25.48	53.35	24 ppm	<50 ppm	<75 ppm			
1	NaF									0.28	0.52
1	LiF									140 ppm	0.53

Fig 6.1 Inor-8 Analytical Results for Various Solids Deposits.

Fig.6.2. Summary of Inor-8 Dissolver Corrosion Measurements.

1. TOTAL MOLTEN SALT TIME, 45 HR; TOTAL HF TIME, 27 HR
2. READINGS TAKEN ON LINE BENEATH LETTERS AS INDICATED BY 4-8
3. LINE C ADJACENT TO WELD SEAM
4. DRAFT TUBE CLEANED BY BOILING IN AMMONIUM OXALATE SOLUTION FOR 16 HRS

NOTE:
DIMENSIONS ARE IN INCHES

<u>READINGS IN MILS</u>											
<u>TIME OF VIDIGAGE READING</u>								<u>DECREASE IN</u>			
<u>ORIGINAL</u>				<u>AFTER INCR-8-4</u>				<u>THICKNESS</u>			
A	B	C	D	A	B	C	D	A	B	C	D
120	119	120	120	115	114	110	115	5	5	10	5
120	118	119	120	115	114	109	115	5	4	10	5
120	118	119	120	113	113	109	113	7	5	10	7
119	118	120	120	112	113	108	113	7	5	12	7
117	116	118	118	111	111	107	112	6	5	11	6

Fig. 6.3. Summary of Inor-8 Draft Tube Corrosion Measurements.

Table 6.1. Operating Conditions for Run D-23¹

Variable	Run D-23
Temperature	675-700°C
HF Feed gas rate	1-5 lb/hr ²
Salt charge	NaF-LiF (43-57 mol %)
Weight salt charge	NaF, 8.66 lb; LiF, 7.09 lb
Submergence	100%
Zirconium charged ³	10.92 lb

¹Run D-23 was performed in the copper-lined dissolver (see UNOP January, 1958 monthly report, ORNL CF 58-1-137, p. 37 for dissolver description).

²Feed rate range due to fluctuations in HF supply system.

³One Zr-2 rolled plate dummy sub-assembly of twelve 1/8"x2-1/2"x12" Zr-2 plates separated by 1/8"x1/4" x12" Zr-2 spacers.

NOTE:
HEAVY LINES REPRESENT FUSED SALT RECYCLE COMPOSITIONS
LIGHT LINES REPRESENT MAKE-UP AND PRODUCT COMPOSITIONS

Fig. 6.4. Alternate Fused Salt Dissolution Cycle for Volatility Pilot Plant.

Fig. 6.5. Fused Salt Dissolution Temperature Profile (NaF-LiF Composition Ratio Constant: 43/57 mole/mole).

to the 20-40 mole per cent ZrF_4 range. The 42.1 kg of zirconium in Figure 6.4 represents two 17-plate SIW-1 fuel sub-assemblies.

Run D-23 was the preliminary dissolution step of the alternate cycle and was performed to build the zirconium content of the NaF-LiF fused salt to 20 mole per cent ZrF_4 . The final step of the cycle will be a run to evaluate the dissolution rate and operating problems in the range 20-40 mole per cent ZrF_4 .

Discussion of Results. Run INOR-8 -4 was terminated shortly after reaching operating temperature by a fused salt leak in the 1/2-in. Inconel discharge line. (See Unit Operations February, 1959 monthly progress report, ORNL CF 59-2-45, for dissolver description.) Figure 6.6 shows the general location of the leak with respect to the lower INOR-8 dissolver section. Figure 6.7 is a longitudinal section through the Inconel discharge line at the leak site. Examination of Figure 6.7 reveals that the failure consisted of two holes (approximately 1/8 in. diameter) and a weld crack at the resistance heating contact. Since HF corrosion of the pipe in the immediate area was not extensive (primarily pitting), the cause of the leak has been attributed to the formation of a thermal "hot spot." Complete metallurgical examination of the section is now in progress.

Run D-23 was performed to prepare the fused salt starting composition shown in Figure 6.4. Unexplained plugging of the HF supply system caused occasional shut-downs during the duration of the run. In addition, the accumulation of large quantities of a viscous, sirupy mixture in the HF supply system caused wide fluctuations in the HF feed gas rate. The source of the contamination was probably the gradual accumulation of off-gas solids, corrosion products, and water in the HF supply system. Subsequent runs with the system will be delayed to permit equipment modifications to alleviate the problem.

The analytical results for runs INOR-8 -1 and -2 shown in Figure 6.1 indicated that both fused salt and INOR-8 dissolver corrosion products were entrained to the off-gas system. There appeared to be no appreciable segregation of the nickel corrosion product at any one point in the off-gas system. The off-gas column screen did, however, favor the collection of corrosion products rather than entrained fused salt. Of particular interest was the corrosion product sample removed from the interface of the INOR-8 dissolver after run INOR-8 -1. The sample, a gold colored metallic scale, was analyzed to be 33.52 wt per cent nickel. No such scale was apparent after run INOR-8 -2 or INOR-8 -3.

"Vidigage" measurements (accurate to $\pm 1\%$ of wall thickness) of the INOR-8 dissolver and draft tube are shown in Figures 6.2 and 6.3. These values are more accurate than results previously reported since fused salt residues were removed from the walls by boiling with ammonium oxalate solution. The corrosion rate of ammonium oxalate on INOR-8 was negligible (< 0.1 mil/16 hr exposure). Figure 6.3 shows that selective corrosion

Fig. 6.6. Location of INOR-8-4 Fused Salt Leak.

Fig. 6.7. Section of Inconel Pipe at Site of INOR-8-4 Fused Salt Leak.

7.0 WASTE PROCESSING

M. E. Whatley

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

The purpose of the waste process program is to provide engineering data for design of a facility to reduce radioactive waste to solids for ultimate disposal. This report contains results of Darex calcinations and equipment changes.

7.1.1 Calcinator Equipment Changes

A 6-in. diameter glass feed tank 6 ft long was installed to measure feed rates more accurately. A Milton Roy piston pump and steam traced feed lines were also installed (see Figure 7.1) which performed satisfactorily during the subsequent four runs.

7.1.2 Calcination of Evaporated Darex Waste

Evaporated Darex waste (Table 7.1) was calcined at four different furnace temperatures from 250-650°C. The feed pump was adjusted to feed between 0.5-1.0 ml/min. The feed pump was stopped when the liquid level reached the probe, 6 in. from the top of the pot. The demand feed rate was defined as the total volume fed divided by the feeding period.

Table 7.1. Composition of Evaporated Darex Waste at 25% of Original Volume

Fe(NO ₃) ₃	2.2 M	Fe 145 g/liter ¹
Ni(NO ₃) ₂	0.23 M	
Cr(NO ₃) ₃	0.51	
Al(NO ₃) ₃	0.39	

¹Fe = 36 g/liter average of original Darex waste.

The demand feed rate increased as function of the average furnace temperature, but the bulk density decreased (Figure 7.2 and Table 7.2). One run was performed with the calcination pot full of 1/4 in. Rashig rings, which were introduced to help decrease boiling splatter and increase conductive heat transfer to the liquid. The results of the run did not appear significantly different from the other calcining tests. If anything, the heat transfer to the liquid seemed to be decreased by the presence of the packing.

Fig. 7.1. Calciner Feed Equipment.

Fig. 7.2. Characteristics of Pot Calcined Darex Waste.

Table 7.2. Calcination of Darex Waste

Run No.	Feed Conc. g Fe/liter	Feed Rate (Demand) liters/hr	Furnace Temp. During Feeding °C	Feeding Period hr	Calcining Period hr	Maximum Center Cake Temp. °C	Calcined Cake Analysis				Waste ^d Volume Reduction	Fe Recovery in Cake %	Liquid Recovery in Condensate %
							Fe %	Water %	Nitrogen %	Density g/cc			
3	137	2.5	200-300	7.0	6.5	700			0.07	0.90	0.076		
4	130	3.9	400-600	7.0	3.0	700	43.9-44.6	1.8	0.25	0.82	0.1	98	88
5	142	4.1	400-900	4.0	6.0	^b	45-49	0.6	0.11	0.61	0.125	97	88
6 ^a	145	2.9	300-700	2.5	1.0	1000							
7	127	4.6	400-725	6.0	6.0	^c	44.6-45.5	0.74		0.60	0.130		92

^aCalciner pot packed with steel rings.^bThermocouple burned out.^cNo thermocouple.^dOriginal waste Fe concentration = 36 g/liter.

7.2 Temperature Rise in Stored Radioactive Solids - J. J. Perona

Temperature rise calculations were presented in recent issues of the Unit Operations monthly reports for January and February, 1959 (ORNL CF 59-1-74 and ORNL CF 59-2-45) based on a storage model of a very long radioactive cylinder separated from an infinite solid medium of soil, rock or salt by an air space. While this storage model has several practical advantages, it is one of the worst possible storage methods with regard to minimizing the temperature rise. The best possible situation from this standpoint, which might be feasible for long-term storage, would be to permit the radioactive cylinders to be cooled by a fluid from a constant temperature source circulating by natural convection. If water is not permissible because of possible corrosion of the cylinder containers, air could be used.

The temperature difference at steady state between the axis and the surface of a cylinder with uniform heat generation is given by¹

$$T_{\text{axis}} - T_{\text{surface}} = \frac{QR^2}{4K} \quad (1)$$

where:

T = temperature, °F

Q = heat generation rate, Btu/hr ft³

R = radius, ft

k = thermal conductivity, Btu/hr ft °F

The temperature difference across the air film at the surface of the cylinder is given by:

$$T_{\text{surface}} - T_{\text{air}} = \frac{QR}{2h} \quad (2)$$

where:

h = convection coefficient, Btu/hr ft² °F

Assuming the cylinders are in a vertical position and cooled by natural convection in air, the convection coefficient is given by²:

¹W. H. McAdams, "Heat Transmission", McGraw-Hill Book Co., Third Ed., p 19.

²G. G. Brown and Associates, "Unit Operations", John Wiley and Sons, p 444.

$$h = \left(0.27 \frac{T_{\text{surface}} - T_{\text{air}}}{2R} \right)^{0.25} \quad (3)$$

combining (2) and (3) yields

$$T_{\text{surface}} - T_{\text{air}} = 1.88 RQ^{0.80} \quad (4)$$

The axial temperature rise of the radioactive cylinders is given by:

$$T_{\text{axis}} - T_{\text{air}} = \frac{QR^2}{4k} + 1.88 RQ^{0.80} \quad (5)$$

Equation (5) was used to calculate a few cases of interest (Figure 7.3). In Figure 7.3, corresponding results based on the first storage model are also plotted, showing the range of temperatures which may be obtained between the two storage methods. By storing in an infinite salt medium rather than an infinite soil medium, the permissible heat generation rate is increased by about 25%. By storing in air with natural convection cooling, the permissible heat generation rate is increased by about an additional 50%.

Fig. 7.3. Maximum Axial Temperature Rise of Stored Radioactive Cylinders as a Function of Heat Generation Rate.

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