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CHEMICAL TECHNOLOGY DIVISION
UNIT OPERATIONS SECTION
MONTHLY PROGRESS REPORT
JUNE 1958

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Chemical Technology Division

UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT

June 1958

J. C. Bresee
P. A. Haas
C. D. Watson
M. E. Whatley

Date Issued

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OAK RIDGE NATIONAL LABORATORY

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ABSTRACT

This is a record of the current developments in the projects of the section. The two reports previous to this are April, CF No. 58-4-123, and May, CF No. 58-5-50.

The interfacial area in a pulse column was measured using an α, n reaction. Externally mixing atomizing nozzles were tried unsuccessfully in the Druhm reactor. A Fluorox run gave a UF_6 recovery of 72.9% of the theoretical yield and rate constants of 18.6 hr^{-1} and 32.9 hr^{-1} . Satisfactory operation of a flame calcination apparatus was demonstrated with methyl alcohol feed slurries of thorium oxalate, with ethylorthosilicate treated ThO_2 , and with $650^\circ C$ fired ThO_2 . Thorium dioxide was efficiently collected from circulating slurries using a hydroclone and an induced underflow receiver. Tests show that classification of thorium dioxide with hydroclones is practical. The Darex equipment is being modified to provide automatic adjustment of recycle acid streams. Two Zircex hydrochlorination runs were made with HCl utilizations of 55%, uranium losses to the sublimate of 0.057% and 5.1% insoluble losses. Methods for disassembling SRE Core 1 fuel elements were explored. Bench scale equipment to test a flowsheet for the reprocessing of irradiated PWR blanket fuel elements has been installed in cell 2 of Building 4507 and tested for leaks and operability. Tests on radiation damage of protective coatings and glass-lined equipment have been continued. Experiments have demonstrated that dry salt mixtures of LiF and NaF instead of molten mixtures might be charged to the Volatility pilot plant hydrofluorinator. The concentration of Darex and Sulfex waste by evaporation was studied.

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SUMMARY

1.0 CHEMICAL ENGINEERING RESEARCH

The interfacial area in a pulse column with a fluorocarbon discontinuous phase was measured using the $F(\alpha, n)$ reaction; the area increased linearly with discontinuous phase throughput and holdup with little effect from pulse amplitude.

2.0 DRUHM

Use of externally mixing atomizing nozzles for sodium and UF_6 entrance to the reactor was not satisfactory because of plugs which developed on the UF_6 side of the nozzle.

3.0 FLUOROX

Further evaluation of the results from Run FBR-18 show that there was a total material balance of 95.9% and the UF_6 recovery in the cold traps and chemical traps was 72.9% of the theoretical amount. The two reaction rate constants which were determined for this run, 18.6 and 32.9 hr^{-1} , are somewhat higher than the extrapolated values from other sources.

A Chilsonator has been purchased and is being prepared for a study of the consolidation of UF_4 as part of the feed preparation step for the fluidized bed operation.

4.0 HR FUEL AND BLANKET PROCESSING

4.1 Slurry Preparation Development - Satisfactory operation of a flame calcination apparatus was demonstrated with methyl alcohol feed slurries of $Th(C_2O_4)_2$, with ethylorthosilicate treated ThO_2 , and with 650°C fired ThO_2 . Duplicate runs gave reproducible results with approximately 2.0 m^2/g ThO_2 product, with carbon reflectors and 1.2 m^2/g product with a ZrO_2 reflector.

4.2 Component Testing Studies - Simple, efficient collection of circulating ThO_2 slurries into an induced underflow receiver was demonstrated by 0.4 and 0.8 in. D hydroclones. Results of hydroclone performance studies for concentrated ThO_2 slurries (> 100 g ThO_2/l) show that classification of 0.5 to 5 micron diameter ThO_2 is practical and that preparation of clarified purge

water by a simple cascade with one pump may be practical.

5.0 ION EXCHANGE

An equilibrium constant, $K = 23.1$, was calculated for the anion exchange system IRA-400 sulfate and bisulfate using data from two different literature sources.

6.0 POWER REACTOR FUEL REPROCESSING

6.1 Darex - The Darex equipment is undergoing extensive modification which is about 70% complete. The work on the process equipment has been completed but the instrumentation is only about 30% complete. The modification when complete, will allow continuous adjustment and recycle of aqua regia to the dissolver, and automatic adjustment and recycle to the HNO_3 boiler of the HNO_3 recovered in the feed adjustment tank. Another HNO_3 stream of the same composition will feed the HNO_3 boiler on level control to supplement the adjusted HNO_3 recovery stream.

6.2 Zircex Engineering Studies - Two hydrochlorination runs, HC-79 and HC-80, were made at approximately 900°C. The element was not fully reacted in either run; in run HC-79, 64.3% reacted in 5-1/2 hr while 76.3% reacted in 5 hr in run HC-80. In both runs the HCl feed was passed through activated charcoal; the HCl utilization efficiencies were about 55%. Uranium losses to the sublimate were 0.057%, and 5.1% was insoluble in 10 M HNO_3 .

6.3 Decladding Studies - SRE Disassembly - Several methods of disassembling SRE Core I fuel elements were explored. Detailed drawings are being made of equipment to demonstrate the recommended method. Disassembly is to be accomplished by removing one end cap, applying hydraulic pressure inside the clad, removing the other end cap, and mechanically "ram-rod" the slugs from the expanded tube.

6.4 Solvent Extraction Studies - Flooding studies for the 42.5% TBP-Decalin and water system were completed. A plot of log flooding rate vs. pulse frequency showed a linear relationship over the frequency range 50 to 80 cycles per min.

6.5 Reprocessing of Irradiated PWR Blanket Fuel Elements - Laboratory scale process equipment and instrumentation designed to test this flowsheet on irradiated fuel samples has been installed in Cell 2, Building 4507, and tested for leaks and operability. Calibration is now in progress.

6.6 Materials Evaluation - Dimetcoat No. 3, a protective coating manufactured by Amercoat, and Amercoat No. 1649, a cover-coat for Dimetcoat No. 3, were irradiated to 10^{10} r gamma in water. Dimetcoat No. 3 showed no visible physical damage, while Amercoat No. 1649 became chalky with low abrasion resistance. Pfaudler's No. 53 glass on Inconel, 304-L stainless steel, and mild steel showed no visible physical damage when irradiated to 10^{10} r gamma in either air or water. The irradiated specimens were returned to Pfaudler for physical property testing.

7.0 VOLATILITY

HF-Fused Salt Dissolution of Zirconium - Homogeneous melts of NaF-LiF salt mixtures of 0.43 mol fraction NaF and 0.57 mol fraction LiF have been prepared by heating mixtures of dry 200 mesh powders in proper proportions at 700°C for two hr. This temperature is only 15°C above the melting point shown by the phase diagram and is 140°C and 290°C, respectively, below the melting points of pure NaF and LiF. This experiment demonstrates that dry salt mixtures might be charged to the hydrofluorinator rather than molten salt.

8.0 WASTE PROCESSING

When Darex waste was reduced to 1/4 volume, a decontamination factor of 10^4 was observed for the condensate, which contained all the volatilized activity. The condensate was quite viscous and solidified upon cooling. The experiment was repeated using formaldehyde as a denitrating agent and results were the same except the viscosity of the concentrate was reduced.

A packed bed caustic scrubber and a DC electrostatic precipitator were found to be effective in removing activity from off-gas streams.

The solids resulting from reducing Sulfex waste to dryness totalled 42% of the original weight. Sulfex waste neutralized with 50% NaOH formed a thick brown jell.

A stainless steel remote handling facility is being fabricated in Room 19, Building 4505. It will have 40 sq ft of floor space, a 4x7 ft entrance-way and will be equipped with a pair of master-slave manipulators. Unit shielding will be used inside and dry stacked shielding outside.

1.0 CHEMICAL ENGINEERING RESEARCH

P. A. Haas

Methods of measuring interfacial areas and interfacial diffusional resistances are being developed for application to solvent extraction contactors. Data obtained by these methods would give a better basis for selecting and designing solvent extraction equipment and operating conditions.

1.1 Interfacial Area Measurement - C. V. Chester, S. G. Kent

Studies of the interfacial area produced between an aqueous phase containing polonium and a liquid fluorocarbon in a 2-in. pulse column were made. The α, n reaction of fluorine at the interface was used to measure the area. The interfacial area increased linearly with discontinuous phase throughput and holdup, and pulse amplitude had very little effect on operation. The fluorocarbon was the discontinuous phase, and its high density, 1.7, relative to water made throughput rather insensitive to pulse amplitude.

The column is a 12-in. length of 2-in. quartz tubing. The column is immersed in a 12-in. dia tank of water which acts as a neutron moderator and reflector. Eight BF_3 neutron detector tubes are immersed in the tank surrounding the column. Plates in the column were fabricated from 1/16-in. quartz plate and carry 1/16-in. holes on 1/8-in. triangular pitch. The plates are spaced one inch apart. The column is operated aqueous continuous, and the fluorocarbon is circulated by means of a pulse pump (Fig. 1.1).

The neutron production at the interface was determined by counting the total production with the column operating, and then subtracting from this the count rate with the column not operating. The count rate due to column operation was plotted as a function of discontinuous phase holdup (Fig. 1.2), throughput (Fig. 1.3) and pulse volume (Fig. 1.3). The count rate due to operation was a linear function of holdup which in turn was proportional to throughput. In two cases stable emulsions formed which persisted over the whole pulse cycle, and gave much higher average count rates. During normal operation, the droplets only existed for a part of the cycle, and the average count rate was proportionately lower than the instantaneous rate at the moment the drops existed.

The data indicate only a slight effect of pulse amplitude on holdup. The difference in densities between the liquids is so large that, with the existing (1/16" dia) hole size in the plates, the pulse need only start the liquid flowing through the holes, and it will continue until all the coalesced liquid on the plate has run through. At the greater amplitudes, the droplets formed tended to be smaller which gave a higher count rate, although holdup was not materially affected.

Fig. 1.1. Fluorocarbon Circulating System for Pulse Column.

INCREASE IN COUNT RATE DUE TO
COLUMN OPERATION (counts/min)

Fig. 1.2. Pulse Column Operation.

Fig. 1.3. Effect of Throughput and Pulse Volume on Interfacial Area.

2.0 DRUHM

C. D. Scott and W. G. Sisson

The Direct Reduction of Uranium Hexafluoride to uranium metal by use of sodium is being investigated. A continuous reaction study is being made with primary emphasis placed on the design of reactor entrance nozzle for the reactants.

2.1 Experimental Work

Several attempts were made to use externally mixing atomizing nozzles for introducing liquid sodium and UF_6 vapor into the reactor. The reactor used was described in the Unit Operations May Monthly 1958 (CF-58-5-50). The atomizing nozzle was composed of a center tube for liquid flow surrounded by an annulus for gas flow. These tests were made by heating the reactor to above $500^{\circ}C$, flowing helium through the gas side of the nozzle, starting a liquid sodium flow through the center tube, and then simultaneously cutting off the helium flow and initiating the UF_6 flow through the gas side of the nozzle. This latter step resulted in a gradual transition from pure He to pure UF_6 .

Several flow velocities within the design range of the nozzle were tried. The sodium flow could be maintained, but in all cases the gas side of the nozzle plugged shortly after the UF_6 flow was started. Increasing the UF_6 annular area by 100% did not prevent plugging.

In all cases, excess sodium was used and a sodium rich atmosphere was maintained in the reactor. A possible explanation for the plugging is the diffusion of some sodium into the gas side of the nozzle forming solid reaction products with the UF_6 . This theory suggests that there was a period of time during each of these tests when the gas velocity through the atomizing nozzle was very low or stopped. The prevention of occasional interruptions of flow may embody a difficult operational problem.

Other atomizing nozzles with different flowrate ranges have been designed for tests.

Another type of nozzle being studied is the three zone nozzle made of three concentric Inconel tubes (Chemical Technology Division November, 1957 Monthly Report, ORNL-2447). This nozzle introduces UF_6 through a center tube, a helium blanket through an intermediate annulus, and liquid sodium through an outer annulus. It has been found that this type of nozzle can be used with minimum corrosion when the helium nozzle velocity is equal to the UF_6 nozzle velocity; however, high helium gas rates tended to reduce the reaction temperature and disperse the reaction product making final uranium metal consolidation difficult. In the future test, the helium gas rate will be maintained at a low rate relative to the UF_6 rate.

3.0 FLUOROX

M. E. Whatley

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 being studied 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 .

3.1 Fluidized Bed Development - C. D. Scott, G. K. Ellis, D. H. Newman

The UF_4 oxidation process is being carried out in a 4" fluidized bed reactor. Sized UF_4 is continuously fed into a UO_2F_2 bed which is fluidized in dry O_2 at 800 to 850°C. The UF_6 which is produced is removed in the gas stream and subsequently recovered in cold traps.

Evaluation of Run FBR-18. Complete experimental and analytical results from run FBR-18 have made it possible to evaluate the run in a manner similar to that used in runs FBR-16 and FBR-17 (UNOP Monthly Reports for March, April, and May 1958). The over-all material balance for all entering and leaving streams was 95.9% (Table 3.1 and Fig. 3.1) or a loss of 810 g between the material entering and the material leaving the reactor. This apparent loss can probably be accounted for by a layer of material which built up on the reactor wall in the fluid bed zone and which was not entirely removed for material balance purposes. Analysis of this layer showed that it had a higher UF_4 content than the fluidized bed itself (21% and 1%, respectively).

The UF_6 balance showed that 98.7% of the theoretical amount of UF_6 could be accounted for (Fig. 3.2) and the actual recovery of UF_6 in the cold traps and chemical traps was 72.9% of the theoretical amount formed, the largest recovery of UF_6 from a continuous fluidized bed run. The largest loss of UF_6 by a side reaction was to the water reaction. Twelve per cent of the UF_6 formed reacted with water which was introduced with the feed into the reactor.

The water content of the feed ranged from 0.5% to 0.7%. It is felt that most of this water was absorbed during the feed preparation. In the future, attempts will be made to reduce water pick-up during feed preparation by use of proper handling techniques; however, a drying step may be added to the feed preparation step to reduce the water content.

Since two different feed rates were used during run FBR-18, it is possible to determine the reaction rate constant at 825°C from two different sets of operating data. The UF_4 material balances over the fluidized bed reactor (Fig. 3.3) make it possible to determine the rate constants by the ratio of the total UF_4 reacted per unit time to the UF_4 inventory in the bed.

Table 3.1. Change in Amounts of Individual
Compounds in Run FHR-18

Compound	Amount Entering Reactor, g	Amount Leaving Reactor, g	Change, g
UF ₄	12,426	673	-11,753
UO ₂ F ₂	6,108	12,535	+ 6,427
U ₃ O ₈	617	57	- 560
U ₄ F ₁₇		1,208	+ 1,208
Metal fluorides	20	170	+ 150
H ₂ O	77		- 77
UF ₆		4,377	+ 4,377
O ₂	<u>582*</u>	<u> </u>	<u>- 582</u>
Totals	19,830	19,020	- 810

Material balance = 95.9% (material leaving/material entering).

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

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Fig. 3.1. Material Balance of the Constituents of Each Stream from Run FBR-18.

Fig. 3.2. Disposition of UF_4 and UF_6 in Run FBR-18.

Basis: One Hour Of Operation

$$\text{Rate Constant, } k = \frac{790 \text{ g/hr}}{24 \text{ g}} = 32.9 \text{ hr}^{-1}$$

Feed Rate Of 985 g/hr

$$\text{Rate Constant, } k = \frac{894 \text{ g/hr}}{48 \text{ g}} = 18.6 \text{ hr}^{-1}$$

Feed Rate Of 1187 g/hr

Fig. 3.3. UF₄ Material Balances Across the Fluidized Bed Reactor in Run FBR-18. All Flow Rates are Averages Based on the Last Two Hours of Operation at Each Set of Operating Conditions.

The two rate constants which were determined for the operating temperature of 825°C were 18.6 hr⁻¹ and 32.9 hr⁻¹. These values are somewhat higher than the extrapolated values from laboratory thermobalance data and batch fluidized bed reactor runs (4 hr⁻¹ and 14 hr⁻¹, respectively).

The oxygen fluidizing gas rate in run FBR-18 was approximately 60 scfh or 242 cfh at the bed operating conditions, a superficial gas velocity in the reactor of 0.8 ft/sec. The oxygen utilization at a constant fluidizing gas rate will be directly proportional to the rate at which UF₄ reacts to UF₆. The oxygen utilization by this reaction, disregarding side reactions, in run FBR-18 was 1.6% for a feed rate of 985 g/hr and 1.8% for a feed rate of 1,187 g/hr. It would be desirable to increase the oxygen utilization by a factor of two or three; however, if it were increased much above 5%, the adverse affect of the higher UF₆ vapor pressure in the gas stream on the reaction rate might be prohibitive. The oxygen utilization will be increased by increasing the UF₄ feed rate while maintaining a constant fluidizing gas rate.

Equipment Changes. Further revision of the FBR system will include the installation of another tube furnace for gas preheating in series with the present oxygen preheater and a heater which will preheat the UF₄ as it progresses down the feed entrance line from the feeder to the reactor. In the next run, which will be made at a bed temperature of 825 to 850°C, the fluidization gas will be preheated to approximately 800°C and the UF₄ feed will be preheated to approximately 500°C.

3.2 UF₄ Feed Preparation

Fluorox UF₄ feed should be in the particle size range -40 to +100 mesh for proper fluidization. The available UF₄ meeting the chemical specifications is between 5 and 10% in the proper size range with 80% less than 100 mesh and 40% less than 325 mesh. Consolidation of the small particles and comminution to the usable size range is required in feed preparation for the fluidized bed reactor. The consolidation presents the most difficult problems.

Several unsuccessful attempts have been made using various types of equipment to consolidate UF₄ without introducing contaminating lubricants. In each case the erosive quality of the material galled the equipment. A device using compression rollers, a Chilsonator (Fig. 3.4), has been purchased for study. The UF₄ powder is fed continuously from a hopper by a screw feeder between two corrugated rollers operating to compact the powder between them. The rollers are spring-loaded. There are adjustments to vary the distance between the rollers, control the degree of scraping of pressed UF₄ from the corrugations, and to vary the feed rate of UF₄.

Planned alterations to the machine include provision for reversing the rollers to free them when they become jammed, and spacers to control the width of the feed application to the rollers. A ventilated hood is being built in which to operate the machine.

Drive Motor (7.5 h.p.)

Spring Loaded Rollers

Scraper

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Fig. 3.4. Chilsonator for UF_4 Consolidation (in a dis-assembled and incomplete condition).

4.0 HR FUEL AND BLANKET PREPARATION AND PROCESSING

P. A. Haas

These programs include the development of processes and equipment for preparation and reprocessing of aqueous homogeneous reactor fuel and blanket fluids. Emphasis at the present is on ThO_2 preparation methods including flame calcination to produce high temperature calcined ThO_2 and gaseous fluidized bed denitration to produce ThO_2 particles suitable for aqueous fluidized reactor blanket systems.

4.1 Slurry Preparation Development

4.1.1 The Arc Calcination of Thorium Oxide - K. O. Johnsson, C. C. Haws

There are three principal modes of operation for electrical arc heating or calcination of a material. One, the method used in steel and smelting operations as well as metal-arc welding, depends upon forming the arc between an electrode and a pool of molten metal. This method would not appear to be suitable in the case of thorium oxide. Another method utilizes a gas to transfer the energy from the electrical arc to the material to be heated. This method is employed in heliarc welding of the atomic hydrogen torch. Heating dispersed thoria particles in a gas by this method shows promise.

The third method of heating consists of dispersing the solid to be heated in a carbon matrix in the form of a consumable electrode, a relatively new process if the material added to the carbon is the desired product. Carbon with rare earth compounds added has been used for many years as a light source. Recent experiments in this laboratory show that a consumable electrode containing thoria can be used to produce very small ($< 0.1 \mu$) thoria particles.

Atomic Hydrogen Torch. The high temperature obtained with an atomic hydrogen torch is possible due to the high "heat capacity" of the hydrogen in dissociating from H_2 to 2H . The electrical energy of the arc is used to dissociate the hydrogen and then is recovered at temperatures in the order of 4000°K when the recombination of the hydrogen atoms takes place a few centimeters away from the arc. By using the hydrogen as a carrier gas for thoria dust it has been possible to fuse some of the thoria particles as they were suspended in the recombination zone of the hydrogen atoms. An electron micrograph of such particles is shown in Fig. 4.1. The arc in this run was formed between $1/16"$ tungsten electrodes at 30 amperes and 40 volts with a hydrogen flow of 10 cfh.

The major problems in this form of heating is getting a reasonable fraction of the thoria particles through the high temperature zone. In order to prevent melting of the electrodes it is necessary to remove the

Fig. 4.1. Thorium Oxide Passed Through Atomic Hydrogen Flame.

heat from the arc as it is generated. This heat removal requires an excess of molecular hydrogen gas which will not be dissociated and recombined but which will form an envelope around the atomic hydrogen flame (If the excess hydrogen is open to the atmosphere, it will burn at a temperature which is much lower than the recombination reaction temperature.)

According to H. G. MacPherson while a member of the National Carbon Research Laboratories* "It is more difficult than one might assume to heat a gas stream to high temperatures by normal heat-transfer methods. Where such a hot gas is needed, it is easiest to heat it directly by an arc discharge occurring in the gas."⁽¹⁾

The atomic hydrogen flame has been used at Mallinckrodt⁽²⁾,⁽³⁾ for the preparation of fused UO_2 . The process was aimed at forming maximum density UO_2 by a process similar to the Verneuil process for the preparation of monocrystalline sapphires. The produce was a fused solid rod or boule rather than fine particles.

Consumable Electrodes. The high intensity carbon arc is a suitable means for reaching extremely high temperatures. This type of electrical discharge is established above the sudden transition from an ordinary type of arc when the current density on the electrodes is increased beyond a critical point. This form of arc is familiar to illumination engineers since it is marked by a sudden increase in the brilliance of the arc. Another change, observed when the current density is increased beyond the critical value, is a rapid increase in temperature with increasing current from 3900°K to 7000°K or more.

It has been found possible by incorporating a metal salt or oxide in the electrode material to subject the material to the high temperature of the arc. This technique has been used on a pilot plant as well as a laboratory scale by the Vitro Laboratories with materials such as boron⁽⁴⁾, silica⁽⁵⁾, and manganese⁽⁶⁾. The Vitro Laboratories report that virtually any material which is incorporated into the electrodes can be vaporized and heated to temperatures in excess of 7000°K at power consumption of between 3 and 7 kwh per pound⁽⁵⁾. Their studies indicated that, for operation in air, electrode carbon is oxidized and passed off as carbon monoxide, whereas a metal oxide becomes a vapor and condenses as a fine fume. Their product condensed as solid spherical particles $0.01 - 0.1 \mu$ in diameter.⁽⁷⁾

*Present address: Reactor Projects Division, ORNL.

Carbide Formation. One factor to consider in a high temperature operation with carbon and a metal oxide is the possible formation of carbides. In the case of thorium, the reaction would be:

Calculations show that for this reaction, $\Delta F^\circ_{2000^\circ\text{K}} = +4.7$ kcal and $\Delta F^\circ_{3000^\circ\text{K}} = -38.3$ kcal indicating that ThC_2 would be more stable than thorium at temperatures somewhat over 2000°K and in the absence of other reactants. In Vitro's work with boron⁽⁴⁾ they were troubled with carbide formation; however, they were operating in an inert atmosphere in an effort to produce boron metal. If oxygen were present the reaction:

must be considered. Here calculations show that $\Delta F^\circ_{2000^\circ\text{K}} = -47,196$ kcal and $\Delta F^\circ_{3000^\circ\text{K}} = -72,694$ kcal, favoring the oxidation of any carbide formed. Sheer⁽⁷⁾ reports no carbide formation with metal oxide feed when operating the arc in air. No documented evidence has been found establishing the formation of carbides of thorium with an arc operating in an oxidizing atmosphere.

Production Rate. In order to obtain some conception of the size of equipment required for small scale production of fused thorium by the carbon arc method, some conservative estimates have been made for the production from a single small unit. Vitro⁽⁴⁾ operated an arc at 300 amperes and 65 volts using an electrode 5/8" diameter containing 35% carbon (65% borax) and obtained an electrode erosion rate of 3-1/2" per minute. Making the following assumptions for a thorium-containing electrode:

Electrode diameter	1.0 cm
ThO ₂ content (by wt)	50%
Electrode density	6.0 gm/cc
Consumption rate	3.0 cm/min

There would be vaporized 3.5 gm per minute of ThO₂ or approximately 11 pounds per 24 hour day.

Tests Made at ORNL. Some arc calcination tests were made about a year ago by C. E. Curtis of the Ceramics Research group. His method consisted of dusting ThO₂ powder through a hollow refractory tube into an arc using carbon electrodes. The product consisted of a mixture of solid and hollow spheres 100 to 300 μ in diameter. This material was not considered suitable for reactor slurry use.

Recently a test was made by C. S. Morgan⁽¹⁰⁾ and C. E. Curtis using a hollow carbon electrode for feeding 15 to 30 μ agglomerates of ThO_2 particles into the arc. The product appeared unchanged by X-ray analysis but proved much poorer than the feed material in a Waring Blender degradation test.

Experiments in the Unit Operations Section have consisted of using 3/16" carbon electrodes having a 1/8" core packed with a thoria-carbon mixture. It has not been possible to collect significant amounts of the product but samples of the "smoke" from the arc have been taken. A photomicrograph of such a sample is shown in Fig. 4.2. Most of the particles appear to be spheres with a diameter of 0.02 to 0.04 μ . Sheer⁽⁷⁾ stated that particles up to 0.1 μ diameter can readily be obtained by surrounding the arc with an insulated chamber and diluted the ThO_2 vapor stream (lowering the dew point).

Electrode Preparation. It was reported^{(4),(5),(7)} that satisfactory operation cannot be obtained with a loosely packed cored electrode but that a compact homogeneous electrode is needed. Vitro reports^{(4),(7)} that satisfactory electrodes can be made using as much as 80% metal oxide content while MacPherson⁽⁹⁾ feels that with a refractory material like ThO_2 , the oxide content should be limited to 10 to 15%.

Experimental work will be necessary to produce a satisfactory electrode since the ThO_2 present will affect the electrical and physical properties of the electrode. Apparently the best mixture of one of the many types of carbon (coke flour, coal flour, carbon black, etc.) with binder and oxide must be determined by trial and error.

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- (8) Homogeneous Reactor Project Quarterly Progress Report for Period Ending Oct. 31, 1957 ORNL 2432.
- (9) MacPherson, H. G., Oak Ridge National Laboratory. Personal communication June 19, 1958.
- (10) Morgan, C. S., Oak Ridge National Laboratory. Personal communication June 1958.

Fig. 4.2. Thorium Oxide from High Intensity Arc Vapor.

4.1.2 Flame Calcination Experiments - C. C. Haws, K. O. Johnsson,
V. L. Fowler

Examination of the product of duplicate flame calcination runs shows the process capable of excellent reproducibility. Thorium oxalate slurries were fed and calcined in the experimental unit as effectively as thorium oxide, suggesting the elimination of present intermediate drying-calcining steps from the flowsheet. A zirconia-reflected flame attained temperatures near the particulate fusion point.

Reproducibility Tests. Four runs were carried out to assess the reproducibility of a flame calcination process insofar as the standard slurry evaluation parameters would allow. In two runs (Runs 23 and 24) the standard 200 gm/liter thorium oxide feed was used while in another pair of runs (Runs 20 and 21) the operability of the equipment for the feeding of a thorium oxalate slurry was also tested. The feeding of the thorium oxalate was as satisfactory operationally as previous feedings of thorium oxide. Reproducibility for all standard parameters was within the range of analytical error as shown by the data in Figs. 4.3 and 4.4 and in Table 4.1, with the exception of the surface area for Run 20. This high surface area has been verified, but no explanation can be offered for the wide departure from the other values.

Two results of significance were obtained from Run No. 19. These were:

1. The product exhibited a zero yield stress.
2. Electron micro-graphs of the product give evidence of having reached near fusion temperatures for the particulates.

The probable importance of this run led to a check of the tabular data presented last month. The original and the check results (Table 4.1) showed good agreement and verified the low yield stress. Unfortunately the mean particle size increased during firing, partially offsetting the decreased yield stress observation. Production material of this same average particle size is estimated to have a yield stress of at least 0.05 lb per sq ft.

A spherical shape and a smooth, hard, fused surface for ThO_2 particles would be expected to give desirable slurry properties with respect to erosion-corrosion, yield stress, slurry stability, and other properties. The potential long range value of flame calcining lies in the possibility of producing such a material. Spherical, fire polished powders of a wide variety of materials varying from low melting plastics to high temperature refractories are commonly produced. Alundum (M.P. approximately 2200°C) had been spheroidized in this study, but no previous evidence was obtained that temperatures necessary to fuse thorium (M.P. approximately 3200°C) had been approached. The electron micrographs of Fig. 4.5 show a definite difference in particle shape between the feed and product of Run 19, the first such

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RUN NO. 19 - THORIA FEED
MATERIAL

1 MICRON

RUN NO. 19 - FLAME CALCINED
THORIA PRODUCT

Fig. 4.5. Flame Calcination Experiments, Effect of Passing Thoria Through a Zirconia Reflected Flame.

Table 4.1. Flame Calcination Experiments

Summary of Data for Recent Tests

Run No.	Reflector Material	Feed Material		Product Material		
		Description	Average Particle Dia (microns)	Average Particle Dia (microns)	Surface Area, sq m/gm	Yield Stress, lb/sq ft
19	ZrO ₂	ThO ₂	0.86	2.4	1.2	0
		LO43		2.6	1.4	0
20	Graphite	Thorium Oxalate	1.4	1.6	2.5 ^a	-
21	Graphite	Thorium Oxalate	1.4	1.8	5.5	0.20
23	Graphite	ThO ₂ LO43	0.86	1.1	2.5	0.25
24	Graphite	ThO ₂ LO43	0.86	1.15	2.4	0.27
Pilot Plant Product	-	LO43	0.86	1.6	1.6	0.25-0.35

a. Residual thorium oxalate in product = < 0.4%.

Fig. 4.3. Flame Calcination Experiment; Particle Size Distribution for Runs 23 and 24.

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Fig. 4.4. Flame Calcination Experiment; Particle Size Distribution for Runs 20 and 21. Test Firing of Thorium Oxalate.

difference noted. The feed has many sharp (or square) corners and has the rectangular platelet particulate shape characteristic of the thorium oxide feed. The product has few sharp curves, and no rectangular platelets survived the firing. The 3-fold increase in particle size can also be observed qualitatively between the two photographs. Test firing using a zirconium reflector will be continued.

4.1.3 Fluidized Bed Denitration of $\text{Th}(\text{NO}_3)_4$ - E. L. Youngblood, H. L. List

Drawings were prepared and work orders issued for fabrication and installation of a system to test direct decomposition of $\text{Th}(\text{NO}_3)_4$ in a fluidized bed to produce over 100 micron dia ThO_2 . Equipment was installed for room temperature tests of fluidization and product classification for the proposed equipment geometry.

4.2 Component Testing Studies

4.2.1 Hydroclone Preparation of Purge Streams - J. W. Snider, R. C. Early

Two four-stage cascades of 0.4 in. diameter hydroclones were tested with constant pressure drop per stage. The Bicclone, Model BI-40SS-1 (ORNL Dwg. D-21270) was fabricated and is being installed for testing.

The first cascade run, Run F-1, was made with an initial feed concentration of 753 gm ThO_2 /kg H_2O . The concentration was reduced to 21 gm ThO_2 /kg H_2O (Fig. 4.6) with 160 ft of liquid pressure drop across the cascade. If a B/F ratio of 0.5 had been maintained from stage to stage the final concentration would have been below 5 gm ThO_2 /kg H_2O .

The second cascade run, Run F-2, was made with an initial feed concentration of 290 gm ThO_2 /kg H_2O and 0.003 M oxalic acid added as dispersant. The purpose of this run was to determine if the high shear field of a hydroclone disperses the ThO_2 particles as they pass through the hydroclone. The value of C_o/C_f is lower without a dispersant than with a dispersant at the same concentration, pressure differential and B/F ratio (Fig. 4.7). This tends to support the argument that the high shear field of a hydroclone does not completely prevent interaction between the ThO_2 particles.

A Pressure Bridge Density Meter* is being constructed to measure ThO_2 concentrations for axial flow hydroclone studies. The flowrates of this hydroclone are too high for graduated cylinder measurements, and a venturi meter with water purged taps is being installed. More economical methods

*Wichner, R. P., VandenBulck, C. F., "The Pressure Bridge Density Meter For Continuously Metering Densities of Flowing Streams", ORNL CF-57-1-49, January 10, 1957.

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Fig. 4.6. Concentrations (in g/liter) for a Four Stage Hydroclone Cascade at a Constant Pressure Drop of 40 Feet Per Stage.

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Fig. 4.7. Overflow to Feed Concentration Ratio Versus B/F for a 0.4 in. Diameter Hydroclone at Different Pressures With and Without Dispersant.

of fabricating the vaned core (Fig. 4.8) are being investigated.

One improvement to be made in a cascade hydroclone system would be to have a large, low shear, low pressure hydroclone to remove agglomerates. A 3-in. glass hydroclone (Fig. 4.9) has been built and will be tested to determine its usefulness on ThO_2 .

4.2.2 Hydroclone Collection of Loop Slurry - J. W. Snider, R. C. Early

Induced underflow ratios were determined for five different underflow pots geometries with and without baffles using both a 0.4 in. diameter and a 0.8 in. diameter hydroclone. The 0.8 in. diameter hydroclone has a higher induced underflow ratio than the 0.4 in. diameter hydroclone for the same underflow pot geometry (Table 4.2). The use of a baffle (Fig. 4.10) reduces the induced underflow ratio.

A series of tests to measure the performance of a 0.8 in. D hydroclone with concentrated ThO_2 slurries was completed. One run with an initial concentration of 1332 gm ThO_2 /kg H_2O was made with a conical frustum underflow pot. In 45 min 99.8% of the ThO_2 was transferred from the feed tank into the underflow pot (Fig. 4.11). With an initial concentration of 801 gm ThO_2 /kg H_2O (Run 9 of Fig. 4.12) only 71% of the ThO_2 was transferred to the underflow pot in three hours. The use of a baffle reduced the B/F ratio such that not enough liquid is exchanged between the hydroclone and underflow pot for the slurry to be carried down into the underflow pot. The apparent hydroclone efficiency was lower (Table 4.3) than for other runs.

With an initial concentration of 101 gm ThO_2 /kg H_2O (Run 10 of Fig. 4.12) 99.1% of the ThO_2 was transferred into the underflow pot in 3 hours. However, for this run the efficiency was not reduced as in Run 9. An effort to determine the initial ThO_2 removal rate as a function of feed concentration for the 0.8 in. diameter hydroclone, applicable to an infinitely large feed volume did not give an exact correlation for the three points determined. The three points for the 0.8 in. D hydroclone may be represented by:

$$(1) \quad R = 0.5 C_f^0$$

where

R is the initial ThO_2 removal rate in gm ThO_2 /min

C_f^0 is the initial feed concentration in gm ThO_2 /kg H_2O

Although the apparent efficiency of Run 9 is somewhat lower than the apparent efficiencies for the other two runs (Table 4.3) the average removal rate falls within the expected range and curve family (Fig. 4.13).

Housing

Pinned Clone Core

Underflow - Overflow
Divider

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Fig. 4.8. Axial Flow Hydroclone Components.

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Fig. 4.9. Three Inch Class Hydroclone.

Fig. 4.10. Hydroclone Underflow Pot Baffle Components.

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Fig. 4.11. Concentration of ThO₂ in Feed Tank Versus Time for Run 8.

Fig. 4.12. Concentration of ThO_2 in Feed Tank Versus Time for Runs 9 and 10.

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Fig. 4.13. Average ThO_2 Removal Rate for 0.8 in. Diameter Hydroclone at Room Temperature Versus Time.

Table 4.2. Induced Underflow Ratio Determination
Using LiCl at ΔP of 57-58 Feet of Fluid

Run No.	Hydroclone Dia, in.	Underflow Pot Geometry	B/F Ratio, %
LC-1	0.8	Conical frustum* "A"	2.52
LC-2	0.8	Conical frustum** "B"	2.47
LC-3	0.4	Conical frustum "A"	1.53
LC-4	0.4	Conical frustum "B"	1.06
LC-5	0.8	6-1/2"x6-1/2" + baffle	0.88
LC-6	0.4	6-1/2"x6-1/2" + baffle	0.25
LC-7	0.4	6-1/2"x6-1/2"	1.26
LC-8	0.4	5-1/4"x10-1/2"	1.64
LC-9	0.4	5-1/4"x10-1/2" + baffle	0.58
LC-10	0.4	4-3/4"x13-3/4" + baffle	0.17
LC-11	0.4	4-3/4"x13-3/4"	1.28
LC-12	0.8	4-3/4"x13-3/4" + baffle	0.29

*2" and 8" diameters x 12" high.

**2" and 6" diameters x 16" high.

Table 4.3. Slurry Collection With 0.8 in. Diameter Hydroclone

Conditions: $\Delta P = 55$ Feet

Loop Volume/Underflow Receiver Volume = 1.0

Run No.	Initial Concentration gm ThO ₂ /kg H ₂ O	Apparent Efficiency, %	Initial Removal Rate* gm ThO ₂ /min	Underflow Pot Geometry
8	1332	1.69	> 700	Conical frustum 2"x6" dia 19" high
9	801	0.09	> 250	5-1/4"x10-1/2" + baffle*
10	101	1.88	> 70	4-3/4"x16-3/4" + baffle

*Obtained by extrapolation of Fig. 4.13 to time zero.

Feed: 1600°C fired ThO₂

$\sigma = 1.25$

50% < 1.2 microns

The underflow pot assemblies used are shown in Fig. 4.14. One method which will be tried in an effort to increase the B/F ratio for the baffles will be to put a by-pass line from the underflow pot to the overflow line of the hydroclone.

4.2.3 Loop P-1 Inspection - J. W. Snider

The pump and the main loop, including the pump scroll case, were removed from the container can. Surfaces including the pump impeller appeared clean without signs of localized corrosion. Release of Pu activity was not hazardous and did not handicap disassembly operations. Cross sectioning of components such as the hydroclone and the flow restrictors for additional examination and measurement of corrosion rates has been scheduled.

0.4" Diameter Hydroclone Assembled
with 4 3/4" x 13 3/4"
Underflow Pot

0.8" Diameter Hydroclone and
Baffle Assembled with
5 1/2" x 10 1/2"
Underflow Pot

Fig. 4.14. Hydroclone Underflow Pot Assembled With and Without Baffle.

5.0 ION-EXCHANGE

J. B. Adams

A study is in progress to determine the mechanism and the kinetics of the anion exchange of uranium in a sulfate system. The current phase of the work is concerned with the solution equilibrium of the sulfate, bisulfate and uranyl sulfate complexes and the equilibrium of these with strong base anion exchange resins.

Bisulfate-Sulfate Solution Resin Equilibrium

An equilibrium constant $K = 23.1$ was calculated for the system IRA-400, sulfate, bisulfate ions in terms of a mass action expression. Data on the solution resin equilibrium were obtained from a report by T. O. O'Connor*, and data on the solution ionic equilibrium were obtained from a report by C. F. Baes, Jr.**. The ion transfer can be written as $\text{SO}_4^{2-} + 2 \text{RHSO}_4 \rightleftharpoons \text{R}_2\text{SO}_4 + 2 \text{HSO}_4^-$ where R refers to the resin sites.

The thermodynamic equilibrium constant is:

$$K_A = \frac{a_{\text{HSO}_4^-}^2 a_{\text{R}_2\text{SO}_4}}{a_{\text{SO}_4^{2-}} a_{\text{RHSO}_4}^2} \quad (1)$$

where a_i are the activities of the ion involved. Substituting $a_i = \gamma_i N_i$, where γ_i = the activity coefficient and N_i = the concentration in g mols/liter for the solution and in g mols/g for the resin, gives:

$$K_\gamma = \frac{N_{\text{HSO}_4^-}^2}{N_{\text{R}_2\text{SO}_4}} \frac{N_{\text{R}_2\text{SO}_4}}{N_{\text{RHSO}_4}^2} \quad (2)$$

*ACCO-61, O'Connor, T. O.

**JACS 79 5611 (1957) Baes, C. F., Jr.

incorporating the activity coefficients in the equilibrium constant. Converting to equivalent fraction units results in the form:

$$K_{\gamma} = \frac{\epsilon \bar{X}_1}{\bar{Q}} \frac{\bar{X}_{R_2SO_4}}{\bar{X}_{SO_4}} \frac{\left(1 - \bar{X}_{SO_4}\right)^2}{\left(1 - \bar{X}_{R_2SO_4}\right)^2} \quad (3)$$

where

$\bar{X}_1$ = the total gram equivalent per liter of $SO_4^{--} + HSO_4^-$ in solution

$\bar{Q}$ = total capacity of resin in gram equivalents/gram of resin
(0.00389 for IRA-400 in the dry chloride form)

$\bar{X}_{R_2SO_4}$ = equivalent fraction of the total resin sites occupied by SO_4^{--}

$\bar{X}_{SO_4}$ = equivalent fraction of SO_4^{--} of total equivalents $SO_4^{--} + HSO_4^-$ in solution

Values of K_{γ} were obtained by calculating the phase compositions from the original data and the ionic concentrations from the data of Baes. With the exception of two values the variation in K_{γ} was not excessive. The original data for these two points, where the deviation was considerable, contained misprints which necessitated correction in order to make the data consistent. The average value of K_{γ} for all the points was 20.4; with the two doubtful points excluded the average value of K_{γ} was 23.1. A series of curves of $\bar{X}_{R_2SO_4}$ vs. $\bar{X}_{XO_4}$ were calculated from Equation 3 with $\epsilon \bar{X}_1$ as a parameter using $K_{\gamma} = 23.1$ (Fig. 5.1, Table 5.1).

Fig. 5.1. Resin-Solution Equilibrium $HSO_4^- - SO_4^{=}$ on IRA-400.

Table 5.1. Resin-Solution Equilibrium

 HSO_4^- - SO_4^{2-} on IRA-400

Point	Original ^a Solution Makeup		Calculated Values of Solution Composition				Measured ^a Resin Composition	Calculated Equilibrium Constant
	Molarity		Molarity		Total Anion Equivalents	Equivalent Fraction SO_4^{2-}	Equivalent Fraction SO_4^{2-}	
	H_2SO_4	Na_2SO_4	HSO_4^-	SO_4^{2-}	$\sum X_i$	$\bar{X}_{\text{SO}_4}$	$\bar{X}_{\text{R}_2\text{SO}_4}$	
1	0.4238	-	0.316	0.108	0.532	0.405	0.146	24.0
2	0.1095	-	0.0786	0.0309	0.1404	0.440	0.366	23.4
3	0.02736	-	0.0163	0.0112	0.0387	0.579	0.630	14.1 ^b
4	0.05473	-	0.0366	0.0181	0.0728	0.497	0.504	19.4
5	0.01095	-	0.00615	0.0048	0.01575	0.609	0.801	20.6
6	0.4378	0.4698	0.485	0.422	1.329	0.636	0.210	23.9 ^b
7	0.1095	0.0484	0.0969	0.061	0.2189	0.557	0.449	29.2
8	0.01095	0.01242	0.00717	0.0157	0.03907	0.804	0.784	8.1 ^b
9	0.05472	0.06210	0.0608	0.056	0.1727	0.649	0.538	21.2

^aACCO 61, O'Connor, T. O.^bInconsistencies found in original data for these points were corrected as appeared most reasonable.

6.0 POWER REACTOR FUEL REPROCESSING

C. D. Watson

6.1 Darex - F. G. Kitts, B. C. Finney, F. L. Rogers, J. Beams, W. E. Dunn

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 solvent extraction equipment. Chloride must be added to effect dissolution of SS in HNO₃ and then removed to avoid corrosion of feed adjustment, solvent extraction, and waste handling equipment. In the present concept of Darex, dissolution and chloride stripping are accomplished in a loop system; HNO₃ is recovered from the highly acidic stripped product and the concentrated solution containing the metallic salts is adjusted, by dilution, providing feed for solvent extraction. Continuing investigations will study the effect of system operating conditions on dissolution rates, chloride removal and recovery, off-gas losses, HNO₃ recovery and feed adjustment when dissolving fuels with various SS/U ratio.

6.1.1 Equipment Modification

The Darex equipment has not been operated during the past month because extensive modifications are being made (see Fig. 6.1). The purpose of the modifications is to make the operation of the stripper, dissolver, and feed adjustment tank integrated loop as nearly automatic as possible. Equipment modifications have been completed and the installation of the instruments that are available is approximately 30% completed.

A tank has been installed to receive the overhead condensate from the stripping column. An attempt is being made to instrument this tank so that concentrated HNO₃ and HCl can be added continually to adjust the tank contents to the proper aqua regia concentration. This tank will also serve as an aqua regia feed tank for the dissolver. A jack-leg liquid take-off will be used to maintain a constant level in the tank. There is no instrument commercially available that will continually analyze a solution for HNO₃ and HCl and maintain the HNO₃ and HCl content at a designated concentration. To accomplish this adjustment, it will be necessary to obtain a correlation between two independent variables. A lab scale investigation is being made to determine if a correlation can be obtained between the boiling point and density. It may be necessary to sample periodically the tank contents, titrate for HNO₃ and HCl, and readjust manually the addition rates of HNO₃ and HCl. Concentrated HNO₃ and HCl (22.5 N and 12.4 N) will be used as make-up to minimize the amount of water added to the system at this point.

A similar tank has been installed to receive the HNO₃ recovered overhead in the feed adjustment tank. Density control will be used to adjust the HNO₃ concentration in this tank. The use of 22.5 N HNO₃ for make-up will

Fig. 6.1. Schematic Diagram of Darex Equipment Including Instrumentation.

effectively serve the purpose of removing water from the system. The overflow from this catch tank will be fed to the HNO_3 boiler. A second HNO_3 make-up stream will enter the boiler directly and will be regulated by level control. The composition of this stream will be the same as that maintained in the feed adjustment overhead catch tank and its magnitude will be the difference between the recycle stream and the amount of stripping vapor required.

The dissolver, HNO_3 boiler, and feed adjustment tank will be heated electrically. The heat inputs to the dissolver and HNO_3 boiler will be adjusted manually while that of the feed adjustment tank will be automatically controlled by temperature to give a uniform concentrated product of suitable H^+ concentration and metals loading. The addition of diluent to the concentrated product will be made manually.

6.2 Zircex - J. J. Perona, G. B. Dinsmore

Currently, a series of runs is being made attempting to determine losses, HCl utilization efficiency and specimen temperatures for a reaction time of 6 hr on 4.2 kg sections of zirconium-based fuel element subassemblies. The shortest total reaction time previously achieved has been 12 hr.

Run HC-79 was shut down after 64.3% of the specimen had reacted in 5-1/2 hr due to boiling in the caustic filled scrubbers used for absorption of excess HCl .

Run HC-80 was shut down after 76.3% had reacted in 5 hr due to a plug in the outlet of the ZrCl_4 condenser. Uranium losses to the sublimate were 0.057% and insolubles in 10 M HNO_3 were 5.1%. The HCl was pretreated by passage through activated charcoal to remove water vapor and hydrocarbon. Hydrogen chloride utilization efficiency was 54.7%, compared to 78% for the 12-hr run. The interior of the specimen rose to a temperature of 920°C and was above 900°C during the first 3 hr of the run.

6.3 Solvent Extraction Flooding Studies - B. C. Finney, R. J. McNamee, J. Beams, W. E. Dunn

Flooding studies were made for the system, 42.5% TBP-Decalin and water, in a 2-in. i.d. sieve plate, pulse column. The flooding rate as a function of pulse frequency is presented in Fig. 6.2. The data follows the same general trend as data previously taken for other systems; an increase in pulse frequency results in a decrease in the flooding rate. These data will be used in conjunction with data from other systems in an attempt to obtain an empirical expression that may be used to predict flooding rates as a function of pulse frequency.

6.4 Decladding Studies - SRE Disassembly - G. A. West

Decladding studies are in progress to develop a method of removing the

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Fig. 6.2. Flooding Rate as a Function of Pulse Frequency for the System 42.5% TBP-Decalin and Water at A/O = 0.4.

stainless steel clad from the SRE, Core I, uranium slugs which are NaK bonded. The decanning operation will make possible the direct reprocessing of the uranium using nitric acid chemistry, and the hazards associated with handling the sodium-potassium eutectic alloy will be eliminated before the dissolution step. The element consists of twelve uranium slugs, 0.75" o.d. x 6" long, encased in stainless steel tubing, 92-5/16" long x 0.79" o.d. x 10 mil wall and a 10 mil NaK bond between slug and clad.

Several possible methods of dejacketing the SRE fuel have been explored. The method considered to be the most effective for positive dejacketing under all physical conditions was the mechanical "ram-rod" technique, Fig. 6.3. The other methods considered were: (1) to slit the entire length of the cladding with either a special roll cutter, a special lathe type "plow" cutting tool, or by using an abrasive disc, (2) to expand the cladding by applying hydraulic pressure or by rolling with a Mackintosh-Hemphill type rolling machine.

The equipment required for the "ram-rod" method consists of: (1) a special lead screw with a center hole for applying hydraulic pressure and an expanded head for pushing slugs out of the cladding, (2) a worm gear and reducer motor to drive the ram rod screw, (3) back-up blocks to contain the worm gear and provide support for the hub that is to be inserted inside the cladding and (4) a clamping vise to hold the clad on the hub. The decladding operation is to be performed under kerosene as follows: (1) remove one end cap using an abrasive saw or tubing cutter, (2) try removing clad and NaK by raising one end of the element, (3) if the slugs are not free to fall out by gravity continue operation by inserting the cut end of the clad on the hub and clamp to hold in position, (4) apply hydraulic pressure to expand tubing from the slugs, (5) remove second end cap and start ram-rod that will push the slugs out into a catch container for washing and transfer to dissolver. A complete detail design is being made of the "ram-rod" technique for cost estimation and possible fabrication of equipment.

6.5 Reprocessing of Irradiated PWR Blanket Fuel Elements - G. A. West, J. C. Rose, T. A. Gens, Chem. Development Section B and A. R. Irvine, Design Section.

The equipment, designed to test PWR flowsheets under actual reprocessing conditions, (1) has been installed and tested for leaks and operability. The first flowsheet test involves removing the Zircaloy-2 cladding with 6 M NH_4F and core dissolution in 7 M HNO_3 . (2) The second flowsheet test will involve jacket dissolution in HF followed by core dissolution in HNO_3 . (3)

Volume calibrations were completed for the feed tank, dissolver, catch pots and vacuum tank. Check valves and manually operated valves are being installed on the longer legs of the manometer lines to prevent back-surfing of radioactive liquid into the nitrogen supply lines. All fabrication is scheduled to be completed by July 1, 1958.

- (1) PWR Pin Decladding and Diss., ORNL Dwg. Nos. D-28867, E-21237.
(2) Chem. Dev. Sect. B Monthly Report, June, 1958, ORNL-CF 58-6-117.
(3) Clark, W. E and Kibbey, A. H., "Hydrofluoric Acid Decladding of Zirconium-clad Power Reactor Fuel Elements", ORNL 2460, July 1958.

Fig. 6.3. Schematic of Decanning Device for Removing SRE-Core 1 Material.

6.6 Materials Evaluation - G. A. West

Radiation Damage - Protective coatings and glass coated metals were irradiated in order to evaluate their usefulness in power reactor fuel reprocessing plants where radioactive materials and solutions are encountered. The Amercoat coating system Dimetecote No. 3, an inorganic protective coating, and Amercoat No. 1649, a white inorganic cover-coat for Dimetecote No. 3 was irradiated in water to 10^{10} r gamma. The glassed metals irradiated to 10^{10} r gamma in both air and water were Pfaudler No. 53 glass on (1) Inconel, (2) 304-L SS, (3) mild steel with No. A-5 ground coat and (4) mild steel with No. G-12 ground coat.

The Amercoat's Dimetecote No. 3 had no visible physical damage from the 10^{10} r exposure. This material offers promise for coating water canals where highly radioactive materials are stored. The coating has a light gray mat finish and offers poor visibility for handling materials underwater. For this reason, a white inorganic coating, Amercoat No. 1649, was developed for application over the Dimetecote. This material chalked after being irradiated to 10^{10} r in water, indicated that the inorganic binder was attacked and the coating would not adhere to the base coating over long periods.

There was no apparent physical damage on the Pfaudler glass 4 in. x 4 in. square adherence panels on Inconel, 304-L and mild steel after an irradiation exposure of 10^{10} r gamma in both air and water. These materials were returned to the Pfaudler Company for physical properties tests. Additional Pfaudler glass is to be irradiated for corrosion and adherence tests and to determine the effect of various convex radii.

7.0 VOLATILITY PROCESS

M. E. Whatley

HF-Fused Salt Dissolution of Zirconium - R. W. Horton, G. Jones, Jr.,
D. H. Newman

Homogeneous melts of NaF-LiF salt mixtures 0.43 mol fraction NaF and 0.57 mol fraction LiF have been prepared by heating mixtures of dry 200 mesh powders in proper proportions and heating to 700°C for 2 hr. This temperature is only 15°C above the melting point shown by the phase diagram and is 140°C and 290°C, respectively, below the melting points of pure NaF and LiF. This experiment demonstrates that dry salt mixtures might be charged to the hydrofluorinator rather than molten salt.

The NaF-LiF salt mixture is of interest because a greater weight of zirconium metal can be dissolved for a given volume of barren salt charged to the dissolver. The properties shown for the No. 1 systems in Table 7.1 are those existing when sufficient zirconium has been dissolved to bring the melting point of the mixture up to 700°C. The NaF-LiF-ZrF₄ mixture has a low melting point up to about 50 mol per cent ZrF₄ as shown by the phase diagram (Fig. 7.1) from ORNL 2295. A more useful comparison of properties of the two salts is based on a NaF-LiF-ZrF₄ mixture with a final melting point of 500°C and the NaF-ZrF₄ mixture melting at 650°C, as shown by the No. 2 system in Table 7.1. The lower melting point used for the Li bearing mixture could be assumed to counteract the greater corrosiveness which Li is expected to impart to this system, and a net gain of 0.1 lb of Zr per 1.0 cu in. of barren salt in the initial charge would still be achieved over the NaF-ZrF₄ system.

The use of NaF-LiF as the barren salt mixture would involve relatively small starting volumes of salt to dissolve a specified weight of zirconium (and uranium) and would also eliminate salt recycle since a satisfactory concentration of uranium for fluorination could be reached in one dissolving. For experimental work and possibly for larger scale operation, the small initial volume can be charged more easily and accurately as a dry salt added directly to the dissolver.

Four experiments have been performed to determine the possibility of adding the component dry salts, NaF and LiF, in the proper proportions and melting the mixture at the melting point. In the first two tests, the NaF used was in pellet form which was mixed with 200 mesh LiF powder. Heating this mixture to 960°C did not produce a homogeneous melt, nor did prolonged heating at 665°C. In both cases some of the NaF pellets appeared to have absorbed whatever initial melt had appeared.

Fig. 7.1. NaF-LiF-ZrF₄ System.

Table 7.1. Zirconium Dissolution Capacity, Melting Points, and
Densities of NaF-LiF-ZrF₄ and NaF-ZrF₄ Systems^a

System	Composition mol fraction		Melting Point, °C,		Dissolver Temperature, °C		Liquid Density at Dissolver, Temp., g/cc		Lb of Zr Dissolved per lb of Initial Mixture
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	
NaF-LiF No. 1	0.43 Na 0.57 Li	0.15 Na 0.20 Li 0.65 Zr	670	700	700	700	2.07	3.30	5.16
NaF-LiF No. 2	0.43 Na 0.57 Li	0.228 Na 0.302 Li 0.47 Zr	670	500	700	550	2.07	3.18	2.40
NaF-ZrF ₄ No. 1	0.38 Zr 0.62 Na	0.68 Zr 0.32 Na	560	700	650	700	3.0	3.30	0.96
NaF-ZrF ₄ No. 2	0.38 Zr 0.62 Na	0.63 Zr 0.37 Na	560	650	650	700	3.0	3.28	0.69

^aDensity data from ORNL 1702.

For the next two tests, 200 mesh NaF and 200 mesh LiF powders were hand mixed with a spatula and by pouring from one container to another. The first mixture was held at 665°C for 5 hr and was about 75% fused. This temperature is almost exactly at the melting point for the mixture. The second batch was heated to 700°C for 2-1/2 hr and was completely fused to a homogeneous melt. The melting points of the pure salts are 990°C and 840°C, respectively, for NaF and LiF, as shown in the phase diagram (Fig.7.2) from ORNL 2295.

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Fig. 7.2. NaF-LiF System.

8.0 WASTE PROCESSING

C. W. Hancher and J. S. Taylor

The purpose of the waste processing program is to develop methods of processing for ultimate disposal the high level radioactive waste solutions produced at ORNL. When the Chemical Technology Pilot Plant processes various types of reactor fuels, high level radioactive waste solutions of various types will be produced. The scope of the program will include Darex, Sulfex and 25 waste solutions. This report describes work with Darex and Sulfex wastes.

The Darex phase has covered (1) high temperature sintering, (2) evaporation, (3) chemical denitration, and (4) off-gas treatment. The Sulfex phase of the investigation is in the preliminary, nonradioactive, characterization stage.

8.1 Evaporation and Chemical Denitration

In the proposed flowsheet which appeared in last month's report, evaporation was one of the unit operations. Evaporation appears to be one means of separating the bulk liquid from the mass of fission products with little contamination carry-over.

When 200 ml of 1×10^8 cts/min/ml β and 3×10^7 cts/min/ml γ Darex solution was evaporated to 50 ml (see Fig. 8.1) (a volume reduction of 4), a decontamination factor of 10^4 was obtained for the condensate (see Table 8.1). All the fission product volatilized remained in the condensate; no detectable amount of fission products was carried by the off-gas from the condensate receiver. The concentrated waste was very thick after evaporation to 124°C . At room temperature it would be very difficult to pump.

The above experiment was repeated with formaldehyde added as a denitrating agent (see Table 8.2). The Darex solution contained 2.9 moles of free nitrate (NO_3) per liter. If formaldehyde is added slowly to boiling solution (108°C) a vigorous, but controllable, reaction can be sustained. The analytical results indicate that only a small percentage (1 to 5%) of the free nitrate was released when two moles of formaldehyde had been added per mole of nitrate present. However, the formaldehyde addition did reduce the viscosity of the concentrated waste. This should allow a further volume reduction, before reaching the point of high viscosity.

8.2 Off-Gas Processing

Two new processing devices have been used to remove fission products from the off-gas stream; these are (1) a packed bed caustic scrubber, (2) an

Fig. 8.1. Experimental Setup for Evaporation and Denitration Studies.

Table 8.1. Darex Evaporation

	Gross β cts/min/ml	Gross γ cts/min/ml	H ⁻ molar	NO ₃ ⁻	Vol., ml	Boiling Temp., °C	Viscosity Observed
Feed	1x10 ⁸	3x10 ⁷	2.9	6.1	200	107° (min)	Fluid
Condensate	7x10 ³	5x10 ³	4.0	4.5	150	-	Fluid
Sludge	4x10 ⁸	1.2x10 ⁸	0	2.7	50	124° (max)	Viscous- Hot (Solid at room temp.)

Table 8.2. Darex Evaporation and Chemical Denitration

Denitration Agent: 34 ml of Formaldehyde

	Gross β cts/min/ml	Gross γ cts/min/ml	H ⁻ molar	NO ₃ ⁻	Vol., ml	Boiling Temp., °C	Observations
Feed	1x10 ⁸	3x10 ⁷	2.9	6.1	200	108° (min)	Fluid
Condensate	1x10 ⁴	2x10 ³	1.66	3.3	170	-	Fluid
Sludge	4x10 ⁸	1.2x10 ⁸	1.1	2.0	50	115° (max)	Viscous when hot, Thick when cold

electrostatic precipitator.

The packed bed caustic scrubber consisted of an 18" long section of 1" glass pipe filled with 15" of 1/4" stainless steel rings. The liquid capacity was 100 ml of 10% NaOH. The flowrate was 10 gal/min/sq ft of cross-section. The packed bed scrubber, receiving the same off-gas stream, retained twice as much activity as did the 5 caustic bubblers previously used, with only 1/10 of the liquid volume.

A 1-in. diameter stainless steel electrostatic precipitator was used. The precipitator was operated using both A.C. and D.C. power supplies at 9000 and 6000 volts, respectively. The precipitator assembly was placed in an experiment, with no voltage applied to determine the "no-voltage" pickup of fission products. The "no-voltage" pickup was about equal to A.C. voltage pickup (see Table 8.3). The D.C. voltage pickup was 8 to 18 times better than that with no voltage or with A.C. voltage.

The fission products removed by the electrostatic precipitator were mainly Cs and some Zr and Nb. The recommended superficial velocity for operation of an electrostatic precipitator is a maximum of 100 to 400 ft/min. This unit was operated from 0.5 to 3.0 ft/min.

8.3 Sulfex

The Sulfex investigations to date have been nonradioactive; an attempt has been made to determine the physical-chemical properties not affected by radioactivity.

When Sulfex waste solution was boiled to dryness, a 42% by weight residue was left (see Table 8.4). The residue resembled melted sulfur. When Sulfex waste solution was neutralized with 50% NaOH a thick jell was formed with the brown color of FeOH.

8.4 Radioactive Handling Hood

A radioactive material handling hood is being fabricated in Room 19, Building 4505 (see Fig. 8.2). The general features of the hood are:

1. Complete stainless steel interior
2. 40 sq ft of floor space
3. 4x7 entrance door
4. Pair of master slave manipulators
5. 3x6 plexiglass window

Unit shielding will be used inside the hood and dry stacked shielding will be used outside to reduce personnel exposure. Lead brick, concrete block and lead glass blocks are on hand for dry stacked shielding.

Table 8.3. % of Fission Products in Original Mixture
Removed by the Electrostatic Precipitator

	% of Original F.P. in Feed Washed From Electrostatic Precipitator		Superficial Velocity	Potential
	% β	% β	ft/min	voltage
Blank	1.6×10^{-4}	3.3×10^{-3}	1.8	0
A.C.	3.3×10^{-4}	1.8×10^{-3}	2.3	9000 A.C.
D.C.	2.6×10^{-3}	3.3×10^{-2}	0.5	6000 D.C.

Table 8.4. Composition of Sulfex Waste Solution

6 M $[\text{SO}_4^{=}]$
33 g/liter Stainless Steel (304)

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Fig. 8.2. Remote Handling Hood.

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