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ORNL
CENTRAL FILES NUMBER

CF-58-9-72

COPY NO. 6

DATE: September 25, 1958
SUBJECT: Summer Quarter, 1958, Co-op Report
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ABSTRACT

This report covers work done by the author during the summer of 1958. Information has been gained on the Fluorox fluidized bed oxidation process, feed preparation for the fluidized bed reactor and two runs made in this reactor. A resume' of work done on a mercury cleanup project is also included.

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1.0 INTRODUCTION

Fluorox is a process which produces UF_6 without the use of elemental fluorine. At the present time the method being developed to accomplish this is the oxidation of UF_4 to UF_6 .

This reaction is carried out in a 4 inch diameter fluidized bed reactor. To date three runs have been made with this reactor. Runs FBR-19 and FBR-20 were made while this student was assigned to the project. The results obtained by the use of the fluidized bed reactor have demonstrated the feasibility of the oxidation reaction on a small pilot plant scale.

Several problems present when other types of reactors are used for the oxidation of UF_4 are eliminated by the use of the fluidized bed reactor. The general advantages of the fluidized bed reactor over previous types of reactors are:

1. It allows good heat transfer to the reacting material.
2. It has good temperature control and by having the temperature more consistent throughout the reactor higher temperatures may be used.

There were three especially difficult problems, which were solved, using the fluidized bed reactor to carry out this reaction problem.

1. Plugging of the UF_6 off-gas line by UF_6 freezing out in the line and by solid material entrained in the UF_6 .
2. Feeding the UF_4 feed which is under a condition of atmospheric pressure into the reactor which is operated above atmospheric (3-5 psig).
3. Separating the intermediate product, U_4F_{17} , formed by the reaction of UF_6 and UF_4 , from the UF_6 product.

The UF_4 feed used in the process must be sized so that the UF_4 will be in the proper size range (-40 mesh +100 mesh) for the most efficient fluidized bed operation. The feed must be compacted, granulated and sized before it is used in the process. The abrasive and hygroscopic nature of this material make this an especially difficult procedure. The operations used in preparing UF_4 feed material are diagrammed in Figure 3.1. The distribution of the particle sizes of the UF_4 feed before and after it goes through each operation and the percentage of product obtained after each operation is also shown. Two batches of feed were prepared. Forty pounds of feed was prepared for run FBR-19 and seventy pounds for run FBR-20.

The mercury cleanup job consisted primarily of removing thorium impurity from approximately 8 tons of mercury and readying it for shipment to another plant facility. Dilute nitric acid was used to dissolve the thorium. The maximum allowable limit of thorium in the mercury was 2 ppm.

2.0 THE FLUOROX PROCESS

Fluorox is a process which produces UF_6 without the use of elemental fluorine. During the summer of 1958 two runs were made with the fluidized bed reactor to produce UF_6 by the oxidation of UF_4 . In this process a sized green salt feed, UF_4 , is fed into the bottom of the reactor. Oxygen at a temperature of $800^\circ C$ fluidizes the bed and oxidizes the UF_4 feed producing UF_6 gas and uranyl fluoride, UO_2F_2 . The fluidizing section of the reactor is shown in Figure 2.1.

The mixture of UF_6 and O_2 gas then passes through four porous sintered nickel filters connected to the top flange of the reactor to remove entrained solids (see Figure 2.2). The filters are cleaned periodically by an automatic blowback system which blows O_2 through the filter in a direction opposite that of the regular gas flow (see Figure 2.3). After leaving the reactor, the gases go through two cold traps where the UF_6 is frozen out (see Figure 2.4). The cold traps are maintained at a temperature of approximately $-75^\circ C$ by immersing them in a tank of trichloroethylene and dry ice. This is below the sublimation temperature of UF_6 . The oxygen which is a non-condensable gas at this temperature, then passes through three chemical traps containing anhydrous calcium sulfate which adsorbs HF and any UF_6 which was not trapped in the cold traps. The O_2 gas then goes to the hot off-gas system.

During the reaction, about 50% of the UF_4 is converted to UO_2F_2 which is collected in an overflow trap. The contents of this trap are periodically removed during the run. This UO_2F_2 formed by the reaction may be used to recharge the bed for a future run.

Before a run is started the bed must be charged with about 6 kgs of UO_2F_2 . The top level of the UO_2F_2 in the reactor is just below the overflow line at fluidization so that UO_2F_2 will begin being collected in the overflow container soon after the start of the run. Next the bed is heated to a temperature between 800° and $850^\circ C$. Approximately 6 hours are required for the bed to reach this temperature.

Prior to feeding oxygen into the reactor the oxygen is preheated to a temperature of $800^\circ C$ by two tube furnaces with a capacity of 2.5 kilowatts each (see Figure 2.5). One furnace is maintained at a temperature of $900^\circ C$ and the other at $600^\circ C$ during the run. A clamshell heater with a capacity of 750 watts is attached to the UF_4 feed line to preheat the UF_4 feed before it enters the reactor bed. A schematic of the Fluorox Fluidized Bed Reactor is shown in Figure 2.6.

3.0 FLUOROX FLUIDIZED BED FEED PREPARATION

Before the UF_4 feed may be used in the Fluorox process it must first be prepared so that the size of the UF_4 particles will be less than 40 mesh and greater than 100 mesh. The preparation of UF_4 product consists of three principal operations: (1) compacting, (2) granulating, (3) sizing.

Fig. 2.1. Fluorox Fluidized Bed Reactor.

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Fig. 2.2. Automatic Oxygen Blowback System for Filters in Fluorox Fluidized Bed Reactor.

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Fig. 2.3. Filters in UF_6 -Oxygen Off-Gas Stream in Fluorox Fluidized Bed Reactor.

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Fig. 2.4. Cold Traps for UF_6 Product Collection in Fluorox Fluidized Bed Process.

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UO₂F₂ OVERFLOW LINE

(TWO-2.5 KW TUBE FURNACE)

Fig. 2.5. Preheaters for Oxygen Fluidizing Gas in Fluorox Fluidized Bed Reactor.

Fig. 2.6. Fluorox Fluidized Bed Reactor Equipment Schematic as of August 15, 1958.

The UF_4 when first obtained is in a fine powdery state. The first step in preparing this UF_4 is compacting it into a hard brittle form. A machine called a Chilsonator, which consists of two heavy, spring loaded, corrugated rollers, compacts the material (see Figures 3.2 and 3.3). The UF_4 powder is fed between the rollers at a rate of approximately 20 pounds per minute by a screw feeder. The capacity of the feed hopper allows about 50 pounds of UF_4 to be fed through the Chilsonator per batch. Several adjustments on the Chilsonator must be used to get maximum efficiency from the machine. There is an adjustment for: (1) the distance between the rollers, (2) a scraper which keeps the grooves in the rollers from becoming clogged, and (3) the rate at which the UF_4 is fed into the Chilsonator. Approximately 19% of the UF_4 product, which is collected in plastic bags beneath the Chilsonator, is in the compacted form. This was the best result that could be obtained after trying many variations of the adjustments on the machine.

Since only 19% of the UF_4 run through the Chilsonator was compacted, a means had to be devised to separate the compacted UF_4 from the UF_4 powder. In the past this operation was accomplished by sifting the Chilsonator product by hand through an eight mesh screen. This method was unsatisfactory due to the large amount of time consumed and the UF_4 dust problem which required the wearing of masks. Now a "Ty-lab tester" has been installed to accomplish this operation. The Ty-lab is a large box like machine which shakes in a vertical motion and does the job quite satisfactory. A 16 mesh screen is used in the Ty-lab for it was found that the size distribution was such that a large amount of the compacted material was being lost through an 8 mesh screen, which was tried earlier.

After the compacted UF_4 is separated from the UF_4 powder, the compacted UF_4 is sent through a rolling mill which breaks the compacted material down into smaller particles. The compacted UF_4 is then granulated. The "Stokes" granulator contains a 40 mesh screen and granulates about 60% of the compacted UF_4 into the proper sized particles. Approximately 34% of the remaining UF_4 is oversize and 6% is undersize. The Ty-lab is again used to separate the proper size particles (-40 +100) from the fines and oversize. Before this operation is started the 16 mesh screen in the Ty-lab is replaced with a 40 mesh and a 100 mesh screen.

4.0 RUNS FBR-19 AND FBR-20

Run FBR-19 lasted 15.75 hours, but the actual feeding time was 14.17 hours. 16,745 grams of UF_4 feed was fed into the reactor bed at an average rate of 1182 grams per hour. The normal pressure in the reactor was between 3 and 5 psi. The average temperature of the bed during the run was approximately 850°C. Two sudden pressure increases during the run caused by the filters becoming plugged with solid material made it necessary to momentarily stop the UF_4 feed to the reactor. The correct rate of fluidizing gas flow was obtained by increasing the blowback flow to maximum and vibrating the filter housing. 12.5 pounds of UF_6 was recovered in the first cold trap and .5 pounds of UF_6 was recovered in the second cold trap. The disposition of the UF_6 formed during the run is shown in Figure 4.1.

Fig. 3.1. Fluorox Fluidized Bed Feed Preparation.

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(CORRUGATED SPRING-LOADED
ROLLERS ARE GEAR DRIVEN)

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-13-

Fig. 3.3. Compacting Section of Chilsonator Machine Used in Feed Preparation for Fluorox Fluidized Bed Reactor.

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TOTAL UF_6 ACCOUNTED FOR - 8331G. OR 97.04%
RECOVERY OF UF_6 IN THE CHEM TRAPS - 70.8%
OF THEORETICAL

FIG.4.1. DISPOSITION OF UF_6 FORMED IN RUN FBR-19.

Prior to making run FBR-20 several changes were made in the fluidized bed reactor system. They were:

1. The capacity of the UF_4 feed container for the UF_4 feed line was increased from 1 kg to 5 kg.
2. An automatic blowback valve system was installed to replace the manually operated valves previously used to control the blowback on the filters in the reactor.
3. A vibrator was placed on the feed line just below the feed container to aid the feeding of the UF_4 feed into the reactor bed.

Run FBR-20, which had been scheduled to last approximately 25 hours, was terminated after 6.5 hours of erratic operation. Fluidization of the bed was lost frequently because of excessive pressure increases in the reactor. The pressure increase is believed to result from either a fusion of the solid mixture of UF_4 and UO_2F_2 in the reactor bed or corrosion product scale plugging the bottom of the reactor.

5.0 MERCURY CLEANUP PROJECT

During the first portion of the summer work quarter the writer was assigned to a mercury cleanup project. The objective of the project was the disposition to another plant facility of approximately 16,000 pounds of mercury which had been used in the Metallex Process. A maximum allowable-thorium specification was 2 ppm. The mercury contained over 1000 ppm thorium when used in the terminated Metallex Process. The two major problems of the project were the removal of thorium from the mercury and transferring of the mercury during the operation.

Two thorium compounds were present in the mercury: thorium oxide and thorium mercuride. There was no problem in removing thorium oxide from the mercury for the thorium oxide being less dense than the mercury floated on the surface of the mercury and could be easily removed. However, the removal of the thorium mercuride presented a problem for thorium mercuride is slightly more dense than mercury and had in some instances only partially settled from the mercury phase. There was in all cases a solid cake of ThHg_3 in the tank bottom. The mercury had been stored in five tanks for several months to allow the thorium mercuride to settle. The thorium content of the supernatant mercury ranged from less than .5 ppm to 200 ppm.

The first step in cleaning the mercury was to siphon it out of the tanks into stainless steel containers, leaving the ThHg_3 cake behind. Prior to siphoning into steel containers, dilute nitric acid was put into the containers. The purpose was to decrease the vapor pressure of the mercury and minimize the escape of poisonous mercury vapor into the surrounding air. Also, the acid oxidized the thorium mercuride and dissolved the resulting thorium oxide. The mercury in the bottom of the tanks having a thorium content of over 200 ppm was not removed.

Next, samples of the mercury in each container were analyzed for thorium content. Analysis of the mercury showed that much of it still contained greater than 2 ppm of thorium. By covering the mercury with 4 molar nitric acid and purging it with air from several hours to a day the thorium content of most of the mercury was decreased to less than 2 ppm.

Approximately 30 gallons of the highly contaminated mercury, including that which was left in the bottom of the tanks, was placed in 55 gallon stainless steel drums and stored to allow the thorium mercuride to settle so that the mercury could be separated from the thorium mercuride in about 3 months.

The mercury containing less than 2 ppm of thorium was transferred to pigs by pulling a vacuum on the pigs pulling the mercury out of the containers through a connecting hose into the pigs. These pigs were sent to the other plant facility in three shipments. On July 1, 1958 7,569.5 pounds of mercury was shipped in nine pigs. Eight more pigs containing 6,245 pounds was sent on July 11, and the last shipment consisting of three pigs containing 2,069.5 pounds was sent on July 22. The sum total of the mercury shipped was 15,974 pounds.

6.0 PERSONAL EVALUATION

The purpose of the co-op program is to teach the engineering student to apply the knowledge which he has gained at school to actual problems occurring in industry. After completing this first quarter of work in the Unit Operations Section of Chemical Technology Division, I now see this purpose of the co-op program is valid. A good understanding of the types of problems which face a chemical engineer has been gained and now I know how to better prepare myself in school to become a chemical engineer. I am sure the experience and knowledge gained this quarter will help much in my future schooling and work.

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