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FLUIDIZED BED RECOVERY OF FLUORINE IN THE MANUFACTURE OF UF_6

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ABSTRACT

Union Carbide Corporation, Nuclear Division, contract operator of the AEC's Gaseous Diffusion Plant at Paducah, Kentucky, has developed and installed a fluidized bed reactor for the recovery of fluorine from process gas streams associated with the manufacture of UF_6. The all Monel reactor employs a bed of UF_4 and operates at temperatures in the range of 700 to 750°F. Fluorine recovery is based on the reaction between fluorine and UF_4 at these temperatures to form UF_6 and intermediate uranium fluorides (U_2F_9, U_4F_{17}, etc.). The system has demonstrated a fluorine recovery efficiency in excess of 98 per cent.

This paper discusses the pilot plant operations which led to the development and installation of the plant reactor system. A description of the design features is presented, along with a review of the economic factors leading to the reactor installation. Current operational experience is also discussed.

INTRODUCTION

Elemental fluorine is used in the Paducah Gaseous Diffusion Plant for the manufacture of uranium hexafluoride. The efficient utilization of this fluorine is essential to the over-all economical operation of the plant and, accordingly, the recovery of fluorine from process vent streams is an important phase of the plant's operation.

Prior to the installation of the fluidized bed reactor system, tower type cleanup reactors were used for fluorine recovery. These units are similar in design to the primary fluorination reactors and operate at temperatures in excess of 2000°F. While fluorine recovery with the tower type reactor is very efficient under normal operating conditions, this type of reactor does not adjust easily to variations in operating conditions. The application of fluidized bed reactors in other plant processes has generally resulted in more efficient systems requiring considerably less maintenance. For this reason, a plant scale investigation was made to determine the possible advantages of employing a fluidized bed reactor for the fluorine recovery process. Based on the results of this investigation, a prototype reactor was installed and later converted to a production size unit. Development of the fluidized bed reactor from pilot plant studies to the current plant system is presented in this paper. Since fluorine recovery is an integral part of the over-all uranium hexafluoride process, a brief description of the plant facility is also presented along with a discussion of the reaction chemistry.

DISCUSSION

Description of Plant Facilities

The process flow sheet for the fluorination plant is shown in figure 1. Essentially 85 to 90 percent of the UF_6 production is obtained from the primary reactors, which are water cooled, vertical towers fabricated from eight inch Monel pipes. The

UF_4 feed material to the fluorination system is a finely divided powder with a mean particle size of approximately 40 microns. The UF_4 is fed into the reactor through a high speed mixing unit, called a powder disperser, which is employed to keep the powder in a finely divided state. From the disperser, the powder falls by gravity into the top of the tower where it is mixed with preheated fluorine. The fluorine flow to the reactor is preheated to 600°F. and is suppled from an adjacent plant where it is produced by the electrolytic dissociation of hydrogen fluoride. The UF_4-fluorine reaction is highly exothermic producing a flame temperature in excess of 2000°F. Approximately two percent of the UF_4 passes through the reaction zone and is collected at the base of the tower in a small container or ash receiver. The product gas stream is cooled as it flows down the tower and is discharged near the bottom of the reactor through a series of gas coolers, cyclone dust separators and a sintered metal filter. The UF_6 is then condensed from the product gas stream in cold traps operated at a temperature of about 10°F.

Since the primary reactors are operated with a controlled fluorine excess of approximately 10 percent, the effluent gas stream from the cold traps, after condensing the UF_6, contains from 20 to 40 percent fluorine. This fluorine is then recovered in the secondary fluorination system. Two types of reactors are employed in the secondary fluorination system - the newly designed fluidized bed fluorine cleanup reactor and the obsolete tower type cleanup reactors which are currently used as stand-by units. The tower type cleanup reactors are similar to the primary towers except that an excess of UF_4 is provided rather than an excess of fluorine. Consequently, a cooling screw is employed at the base of the tower to keep the excess UF_4 in a free flowing state and to transport the powder to a recycle conveyor. As in the primary system, UF_6 is removed from the product gas stream by condensation in cold traps at a temperature of 10°F. In this case,

smaller backup traps, which operate at -50°F., are employed in series with the larger traps in order to minimize the carry over of UF_6 with the noncondensible gases. The effluent gas stream from the low temperature traps is then processed through the fluidized bed UF_6 absorber for the recovery of trace quantities of UF_6 before the inert gases are vented to the atmosphere.

<u>Chemistry of Reaction Process</u>

The feed material for the fluorination system is produced by a two step reaction process consisting of the reduction of UO_3 to UO_2 followed by the hydrofluorination of UO_2 to UF_4. Since there are unreacted products from these reactions, the impure UF_4 (green salt) contains both uranium oxides and uranium oxyfluorides. Analyses of the green salt product usually range over the following compositions:

UF_4	- 95 to 98	percent
UO_2	- 0 to 4	percent
UO_2F_2	- 0 to 1.0	percent

These compounds combine with elemental fluorine to produce UF_6 according to the following reactions:

$$(1)\quad UO_2 + F_2 \xrightarrow{200°F.} UO_2F_2$$
$$(2)\quad UO_2F_2 + 2F_2 \xrightarrow{500°F.} UF_6 + O_2$$
$$(3)\quad UF_4 + F_2 \xrightarrow{450°F.} UF_6$$

All of the above reactions are exothermic and the temperatures shown are the approximate initiating reaction temperatures. Since the primary reactors are operated at temperatures above 2000°F. with an excess of fluorine, all the reactions proceed essentially to completion. Greater than 98 percent of the green salt is converted to UF_6.

In addition to the above reactions, fluorine and UF_6 may react with UF_4 to produce a group of metastable compounds commonly referred to as uranium fluoride intermediates. Reactions between UF_4 and UF_6 are shown below:

$$(4)\quad UF_6 + 7\ UF_4 \rightleftharpoons 2\ U_4F_{17} \quad (UF_{4.25})$$
$$(5)\quad UF_6 + 3\ UF_4 \rightleftharpoons 2\ U_2F_9 \quad (UF_{4.5})$$
$$(6)\quad UF_6 + UF_4 \rightleftharpoons 2\ UF_5$$

These compounds are unstable solids which dissociate into UF_6 and either UF_4 or a fluoride intermediate between the parent compound and UF_4. Consequently, there is an equilibrium UF_6 vapor pressure associated with each intermediate fluoride as shown in figure 2. By way of illustrating the use of these curves, consider a small sample of UF_4 enclosed with a large volume of UF_6 at a total pressure of 6.0 psia. At temperatures above 800°F. there is no tendency for UF_4 and UF_6 to react. As the system is cooled below 800°F., UF_4 and UF_6 react to form U_4F_{17} which then reacts with more UF_6 at temperatures below 710°F. to produce U_2F_9. Finally, the U_2F_9 is converted to UF_5 at temperatures below 570°F. The intermediates and UF_4 react readily with UF_6 even at relatively low temperatures. With fluorine, the initiating reaction temperature increases progressively with the fluoride to uranium ratio.

The ability of UF_6 to react with the intermediates, which then decompose into lower fluoride compounds, can result in the formation and growth of solid crystals. Crystalline formations have been observed to vary in consistency from that of a hard fused salt to a soft matting of needles resembling fur. This type of interaction between intermediates is responsible for the coalescence tendency of uranium fluoride powders in the presence of UF_6 or fluorine. Unfortunately, crystallization or coalescence can occur over a wide range of operating conditions and is the major source of operational problems in the secondary fluorination system. On the other hand, formation of solid fluoride intermediates affords a unique method of recovering trace quantities of UF_6 as in the fluidized bed UF_6 absorber. However, at the

normal operating temperature (300°F.) of the absorber, the rate of dissociation of the intermediates is too low to promote crystallization or agglomeration of the powder.

Origination of Fluorine Cleanup Reactor Investigation

As a result of the successful adaptation of fluidized bed systems in other process operations involving uranium fluorides and oxides, the decision was made to investigate the possibility of employing a fluidized bed reactor for fluorine recovery. The obvious advantages of the fluidized bed reactor are:

(1) The relatively large inventory of green salt in the reactor would provide assurance that an excess of UF_4 would always be available regardless of the inlet fluorine concentration - a condition that is not always true with the tower type reactors.

(2) The large heat capacity of the bed would tend to minimize the effect of cyclical variations in fluorine concentration.

(3) The simpler reactor design with fewer moving parts and the ability to operate at much lower temperatures should minimize maintenance requirements.

The disadvantage of the fluidized bed reactor was the possible effects that agglomeration of the powder might have on the heat transfer and fluidization properties of the bed under the proposed operating conditions. Preliminary laboratory and pilot scale tests of the fluid bed fluorination process had been conducted at Paducah and other plant sites.(1)(2) These studies indicated that scaling of the internal surfaces of the reactor might be expected, particularly with high fluorine concentrations. These studies had also shown that the use of solid diluents such as MgF_2 or CaF_2 were effective in preventing the formation of scale. Nevertheless, the possibility of using solid diluents in the fluorine cleanup reactor was discarded because the cleanup reactor effluent solids were to be blended with the feed material for the primary fluorination reactors in order to provide a solids "bleed-off" stream.

Because of the similarity in operation, the UF_6 absorber$^{(3)}$ appeared to be an ideal unit in which to conduct a plant scale evaluation of the fluidized bed fluorine recovery process. Essentially the only modification required to convert the absorber to a fluorine cleanup reactor was extending the operating temperature range from 200-400°F. to 600-900°F. The reactor, shown in figure 3, is 27 inches in diameter with a bed height of approximately 40 inches. Process gas enters the reactor through a conical inlet section equipped with a ball check to prevent back flow of solids. Distribution of the gas is obtained by natural dispersion around the ball. The effluent gas is removed from the reactor through a large conical settling chamber to minimize powder entrainment to the off-gas system. From the top of the settling chamber, the effluent gas stream flows through a cyclone dust separator and a bank of porous metal filters to the plant exhaust system. Green salt is fed into the reactor by a screw feeder located approximately one foot above the gas inlet. Powder is removed by means of an overflow line to a product or ash hopper which is then blended with the green salt fed to the tower reactors.

During the normal operation of the reactor as a UF_6 absorber, the inlet gas stream contains from 300 to 1,000 ppm UF_6 and from three to seven percent residual fluorine. The concentration of UF_6 in the reactor off-gas stream corresponds to the equilibrium UF_6 vapor pressure of the intermediates for the operating conditions of the reactor. At an optimum temperature of approximately 300°F., the concentration of UF_6 in the effluent gas stream is less than 20 ppm. Some fluorine is also absorbed at this temperature by reaction with the small quantity of UO_2 that is present in the green salt. Heat released by these reactions is insufficient to maintain the reaction temperature; consequently, heat is supplied externally from Calrods attached to the reactor. Emergency water cooling is also provided in the event that a fluorination reaction should occur.

PILOT PLANT OPERATION

The primary objectives in operating a pilot plant reactor were to determine the effect of operational variables on fluorine recovery efficiency, the effect of scaling on reactor onstream efficiency, and the effect of agglomeration or particle growth on the fluidization characteristics of the bed. The secondary objective, if the initial operation of the reactor proved successful, was the collection of engineering data for the design and installation of a prototype reactor. Using the previously mentioned laboratory data as a guide, the pilot plant investigation was to cover a concentration range of 5 to 30 percent fluorine and a temperature range of 600 to 900°F.

In order to utilize the absorber for this investigation, the reactor was relocated process wise to a position in parallel with the existing tower type cleanup reactors. Modifications to the reactor, other than extending the operating temperature range of the control system, consisted essentially of piping revisions. Dry air and fluorine lines were tied into the inlet gas header and the normal process gas flow to the absorber was vented to the plant exhaust system. The air line was equipped with flow controls which could be operated either automatically to maintain a minimum gas fluidization velocity through the reactor or manually in conjunction with a fluorine flow to maintain the inlet fluorine concentration at any desired value. A fluorine analyzer was located on the inlet gas header to continuously monitor the fluorine concentration, and gas sample taps were provided for periodic analysis of the effluent gas stream. Temperature measurements were made from three exterior surface thermocouples and five internal thermocouples located at various depths in the bed and in the dispersed phase above the bed.

A total of eight test runs were made varying in length from 20 to 70 hours. For the first two runs, a mixture of fluorine and air was used to obtain the low fluorine concentrations. The reactor was completely isolated from the remainder of the plant in order to prevent the high inert gas flow from interfering with the operation of other plant equipment. During these runs, the UF_6 produced was collected in two parallel low temperature cold traps (-50°F.) and the inert gases were vented to an air-jet evacuation header. For the remaining runs, the outlet gas stream was combined with the existing cleanup reactor effluent gases.

In general, the operation of the reactor during this test series was quite successful. Fluorine recovery efficiencies greater than 95 percent were obtained even at low fluorine concentrations. Fluorination efficiency varied rather sharply with reaction temperature; for instance, at a temperature of 600°F., only 50 to 60 percent of the fluorine reacted, while at 750°F. and above approximately 95 to 98 percent of the fluorine was recovered. At the lower operating temperatures, the fluorination efficiency was also dependent on the UF_4 feed rate which was usually maintained between 50 and 100 percent in excess of the stoichiometric rate for the total conversion of UF_4 to UF_6.

Powder samples withdrawn from the reactor indicated that the bed attained an equilibrium composition corresponding to a fluoride to uranium ratio of 4.2 to 4.3. The samples showed no apparent tendency toward particle growth nor were there any major changes in fluidization characteristics of the powder.

Scaling of the reactor was not a serious problem although a thin scale was observed after extended operating periods. The effect of this scale on the transfer of heat from the reactor was estimated by means of heat and material balances. While the estimates were not very accurate, the results did indicate that the overall coefficient of heat transfer was reduced by a factor of 2.0 or more during some of the

test runs. At the higher fluorine concentrations, a hard scale formed on the tip of the UF_4 feed screw which created difficulties in feeding UF_4 to the reactor.

Scale formation in the expansion section above the reactor was a more serious problem. Here, coalescence of the fines that were entrained with the off-gas and subsequently settled on the conical sides of the expansion section resulted in the formation of a thick, soft scale. Growth of this scale virtually filled the expansion chamber and eventually restricted the flow of gas through the reactor. However, most of the operational problems were caused by coalescence of fines trapped by the sintered metal filters, Powder collected by the filters had the consistency of wet sand and could not be removed by normal blow back procedures.

In summarizing the operation of the reactor during this investigation, one aspect of processes involving uranium fluoride intermediates which became very clear was that a high degree of agitation was required when handling the intermediates in the presence of UF_6 or at temperatures above 300°F. This point was vividly demonstrated when, at the conclusion of the initial test run, the reactor was left in standby operation for a period of two days. During this time, the reactor was maintained at a temperature of 600°F. without agitation and, as a result, the powder bed (composed primarily of intermediates) fused into a solid mass. This difficulty was eliminated in all subsequent runs by cooling the powder bed to below 300°F. before discontinuing fluidization. Similar difficulties were experienced in the ash hopper as evidenced by frequent bridging of powder over the screw conveyor. This problem was minimized somewhat by operating the screw conveyor on a continuous rather than an intermittent basis.

Conclusions from Pilot Plant Investigation

The results of the investigation clearly demonstrated that the fluidized bed reactor was a very efficient process for the recovery of fluorine from dilute gas streams. On the other hand, the study failed to indicate that a reasonable onstream efficiency could be achieved with the pilot plant reactor in view of the difficulties experienced with the general coalescence properties of the intermediate fluorides. In the areas where operational problems were incurred, it was felt that most of the difficulties could be eliminated or minimized by altering the design of the equipment. However, because of the size of the pilot plant reactor, alterations for test purposes were not practicable.

Considering the limitations of the tower type reactors and the comparatively greater maintenance requirement of these units, it was decided to install a prototype fluidized bed reactor of moderate capacity designed for further studies.

DESIGN AND OPERATION OF PLANT REACTOR

The design of the prototype reactor installation, shown in figure 4, was based on the experiences and ideas conceived during the pilot plant investigation. The reactor was 18.5 inches in diameter with an over all bed height of 3.5 feet. Except for the size, the basic design of the prototype reactor was similar to the UF_6 absorber. However, considering the extent of scaling observed in the expansion chamber of the pilot plant reactor, the space above the bed was held to a minimum. The idea, in this case, was to allow high velocity particles to impinge on the upper portion of the reactor and thus, minimize the tendency for scale formation in this area.

No provisions were made for heating the reactor externally, although the process gas stream to the reactor was preheated to 600°F. Heating the bed to reaction temperature from a cold start required about two hours. A dry air purge was used to supplement the process gas flow during start up or shut down operations and to automatically maintain a minimum gas flow through the bed. Cooling the reactor was accomplished by means of two parallel water cooling coils attached to the reactor shell. Dilution cooling by increasing the excess powder feed rate to the reactor was also used to control bed temperature.

Green salt was fed to the reactor by a gravity system consisting of a rotary feeder and an air buffered downcomer. With this arrangement, rapid mixing of the more reactive green salt with bed material was achieved, thereby avoiding a localized high reaction rate near the feed inlet.

The excess powder and effluent gases were removed from the reactor through a common, water cooled line to the ash hopper. Simultaneous cooling of the solids and off-gas streams was very effective in preventing bridging of the powder in the ash hopper and in improving the filtration characteristics of powder trapped by the filter. The ash hopper was made very large (five feet in diameter) in order to serve as a gas-solids disengagement section as well.

The filter unit was located directly above the ash hopper and contained 16 sintered Monel tubes. Since filtration was one of the areas where major difficulties were encountered during the pilot plant investigation, an automatic, on stream blow back system was incorporated on the filter for the prototype reactor. For automatic blow back, the tube bundle was divided into four equal banks. Each bank of tubes received a back flow of air, at a pressure of approximately 15 psig, once every 20 minutes on a five minute staggered cycle. In order to create a back pressure, the air was forced through venturi nozzles located on the tube sheet above each tube.

Operationally, the prototype reactor was very successful. The fluorine recovery efficiency was readily maintained between 95 and 98 percent and the reactor on stream efficiency averaged between 90 and 95 percent, which was comparable to the tower type reactors. Equipment maintenance requirements were negligible.

One problem that did develop was the formation and growth of scale in the off-gas cooler line near the reactor outlet. Following the installation of an inspection port in this line, the scale was removed daily requiring less than one half hour of reactor downtime for the cleaning operation. The anticipated scaling of the reactor wall did not cause any major difficulties, although the gradual growth of this scale did interfere with temperature control after a 20 to 30 day operating period. The other associated equipment remained relatively trouble free including the off-gas filter which had an average service life of approximately six months.

Plant Operational Changes

The prototype reactor, as the name implies, was designed with the idea of altering the equipment to a production size unit. The associated equipment for the prototype reactor, such as the feed hopper, ash hopper and filter, was originally sized to provide a capacity equivalent to the tower type cleanup reactors. Thus, the major modification required to alter the operation of the system consisted of replacing the prototype reactor with a larger diameter unit. The modified reactor designed for this purpose (see figure 5) was 27 inches in diameter with a bed height of 4.5 feet. Electric clam shell type heaters were added to assist in heating the bed during start up operations. Considering the anticipated higher heat flux, the capacity of the green salt feed system for the modified reactor was increased to provide up to five times the stoichiometric rate requirement. Under these conditions, dilution cooling could be used exclusively to control bed temperatures; however, water cooling was also provided for supplemental purposes. With dilution cooling, scaling has little effect on the transfer of heat from the reactor.

Problems were encountered with the sintered metal filters during the initial operation of the modified reactor due to high powder feed rates and the limited cooling capacity of the off-gas cooler line. For this reason, the filter was relocated over a secondary ash hopper in order to provide additional gas cooling capacity. The original filter shell was left intact to serve as a settling chamber. The revised arrangement increased the average filter life from one or two weeks to approximately 18 months.

The higher productivity of the modified reactor did not affect fluorine recovery efficiency. However, onstream efficiency for the modified reactor averaged approximately 90 percent reflecting the more strenuous operating conditions.

SUMMARY

Union Carbide Corporation, Nuclear Division, contract operator of the AEC's Gaseous Diffusion Plant at Paducah, Kentucky, has developed a fluidized bed process for the recovery of dilute fluorine. The fluidized bed fluorine cleanup reactor is 27 inches in diameter and employs a bed of UF_4 at a depth of 4.5 feet. Operation of the cleanup reactor depends upon the reaction of fluorine with UF_4 to produce gaseous UF_6 and several solid compounds with fluoride to uranium ratios between UF_4 and UF_6. The cleanup reactor is integrated with the UF_6 manufacturing process and operates at a temperature of approximately 750°F. The process gas stream for the fluidized bed reactor consists of the primary UF_6 process vent gas stream and contains from 20 to 40 percent fluorine.

The initial development work on the fluidized bed recovery process was conducted in an existing plant reactor. Because of the similarity in operation, the facilities of the fluidized bed UF_6 absorber were temporarily modified for the pilot plant investigation. The pilot plant reactor was 27 inches in diameter with a bed height of 3.5 feet. A total of eight test runs were made during the investigation covering a fluorine concentration range of 5 to 30 percent and a temperature range of 600 to 900°F. Based on the results of this study, a small 18.5 inch diameter prototype reactor was installed and operated for a period of approximately one year. As a result of the successful performance of the prototype fluidized bed system, the small 18.5 inch diameter reactor was replaced with the current 27 inch diameter unit.

The fluidized bed fluorine cleanup reactor has proven to be a highly efficient process for the recovery of dilute fluorine. Fluorine recovery efficiencies have averaged greater than 95 percent and reactor on stream efficiency has averaged

approximately 90 percent. Reactor downtime has been primarily due to descaling operations. Equipment maintenance has been negligible. Resulting economies have justified the installation in accordance with established plant policies.

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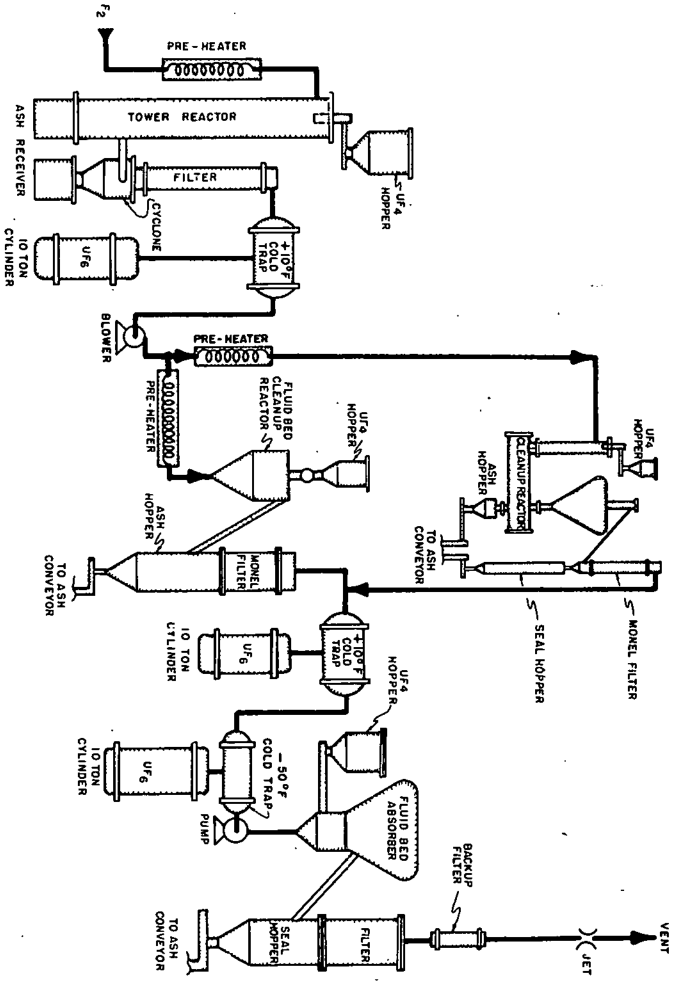
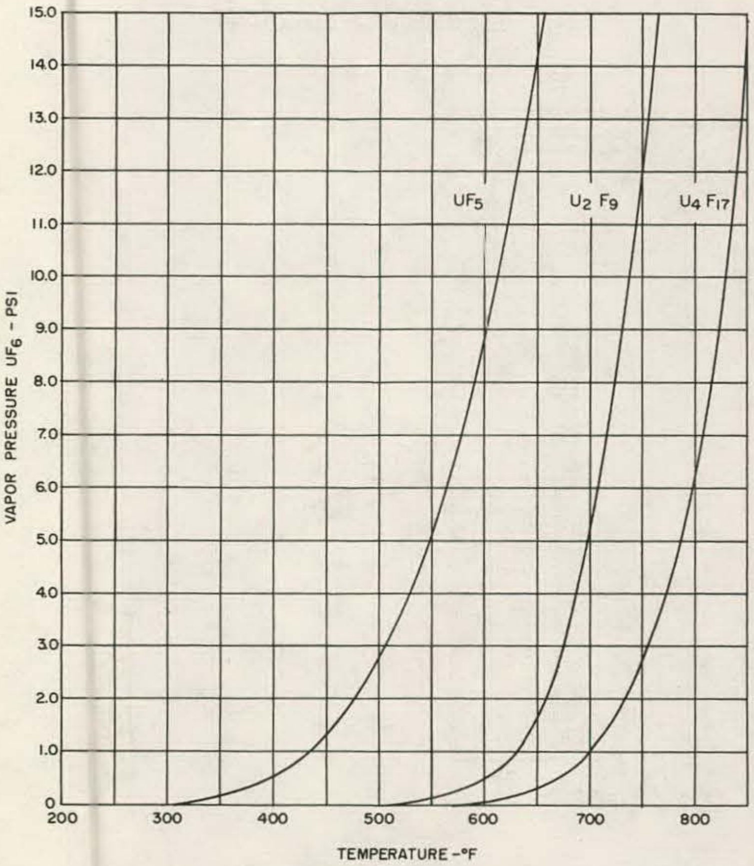


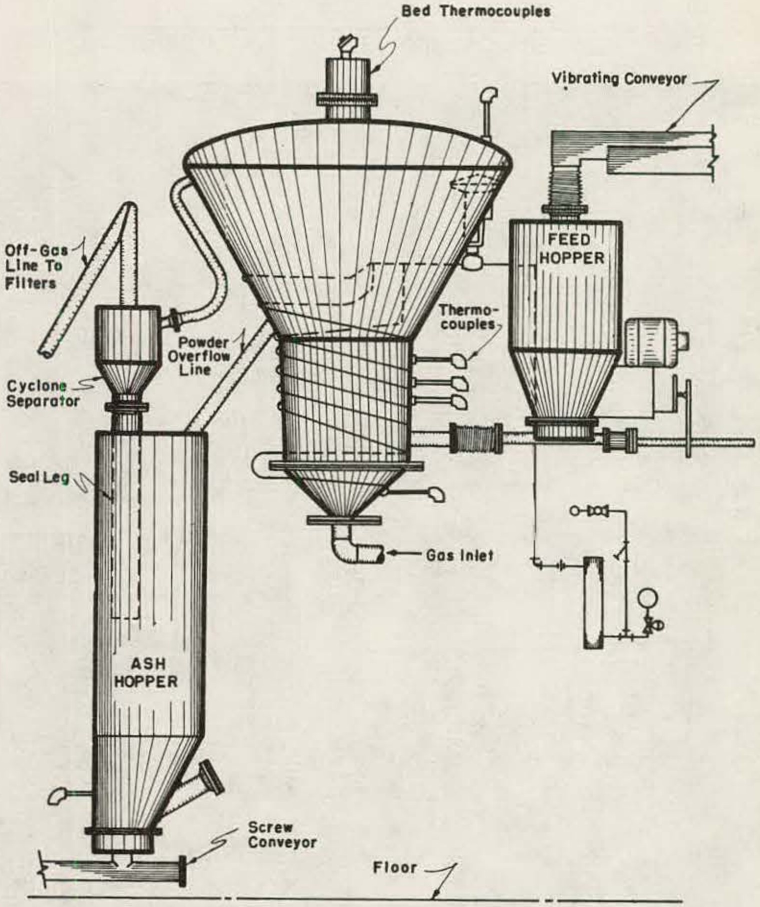
FLUORINATION SYSTEM FLOW DIAGRAM

Figure 1



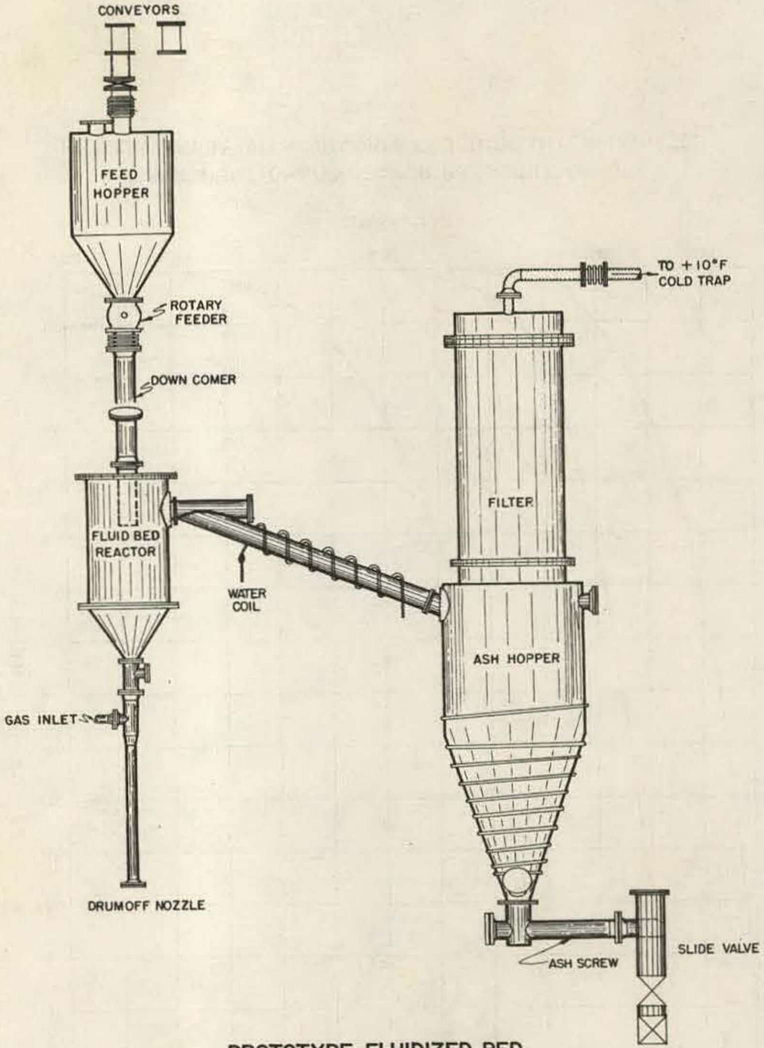
DISPROPORTIONATION VAPOR PRESSURE OF UF_6 IN EQUILIBRIUM WITH URANIUM FLUORIDE INTERMEDIATES

Figure 2



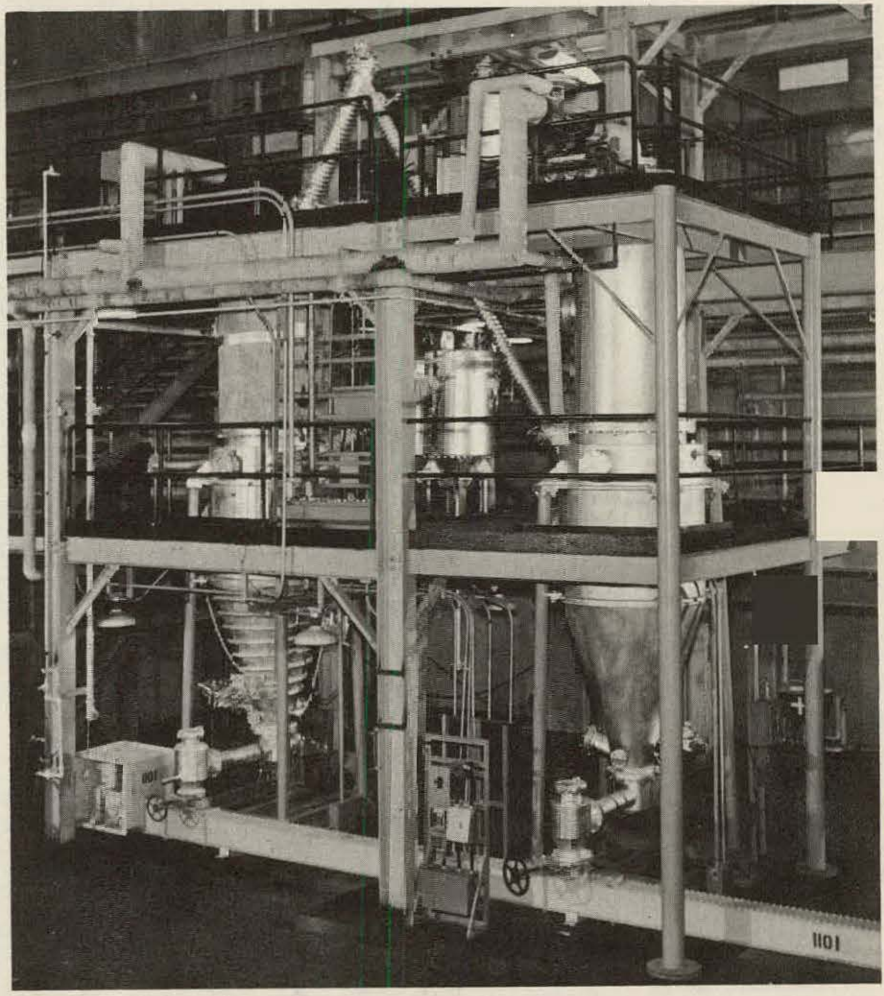
FLUIDIZED BED UF_6 ABSORBER
(PILOT PLANT REACTOR)

Figure 3



PROTOTYPE FLUIDIZED BED CLEANUP REACTOR

Figure 4



MODIFIED FLUIDIZED BED CLEANUP REACTOR

Figure 5