Date of Issue: OCT 31 1958

Report Number: KY-265

Subject Category: TECHNOLOGY OF
FEED MATERIALS
UC-47

AEC RESEARCH AND DEVELOPMENT REPORT

RECOVERY OF URANIUM HEXAFLUORIDE FROM A GAS STREAM BY ABSORPTION IN A FLUIDIZED BED OF URANIUM TETRAFLUORIDE

J. L. Powell, W. R. Foreshee, and S. Bernstein

This document is distributed in accordance with the category "Technology of Feed Materials", UC-47, as given in the "Distribution Lists for United States Atomic Energy Commission Nonclassified Research and Development Reports", TID-4500, October 1, 1958 (14th Edition Supplement).

UNION CARBIDE NUCLEAR COMPANY
Division of Union Carbide Corporation
PADUCAH PLANT
Paducah, Kentucky

DISCLAIMER

Report Number: KY-265

Subject Category: TECHNOLOGY OF
FEED MATERIALS
UC-47

Title: RECOVERY OF URANIUM HEXAFLUORIDE FROM A GAS STREAM BY ABSORPTION IN A FLUIDIZED BED OF URANIUM TETRAFLUORIDE

Authors: J. L. Powell
W. R. Foreshee
S. Bernstein

ABSTRACT

A unique absorption process for recovery of small quantities of uranium hexafluoride vapors from a highly reactive gas stream is discussed along with the design criteria that were developed as a result of laboratory and pilot plant tests. The chemistry of the absorption process is presented with a summary of the data collected during laboratory and pilot plant testing. A description is also given of the plant scale absorption system now in operation at the UF_6 manufacturing plant of the Union Carbide Nuclear Company at Paducah, Kentucky

The vent gases from the UF_6 manufacturing process at Paducah contain appreciable quantities of oxygen and nitrogen, some hydrofluoric acid and elemental fluorine, and small quantities of valuable uranium hexafluoride. To permit recovery of the UF_6, these vent gases are passed theough a fluidized bed of green salt (uranium tetrafluoride) where essentially all of the UF_6 and a portion of the F_2 react to from solid uranium fluoride intermediates. When operated at 400°F, as much as 0.38 pounds of UF_6 or its equivalent of F_2 can be absorbed per pound of green salt. The green salt containing the absorbed UF_6 and F_2 can either be returned to the UF_6 manufacturing plant or regenerated with hydrogen.

RECOVERY OF URANIUM HEXAFLUORIDE FROM A GAS STREAM BY ABSORPTION IN A FLUIDIZED BED OF URANIUM TETRAFLUORIDE

J. L. Powell, W. R. Foreshee, and S. Bernstein

The uranium hexafluoride (UF_6) used in the gaseous diffusion process for the separation of uranium isotopes is manufactured by high temperature techniques, wherein purified uranium tetrafluoride (UF_4) in the form of green salt is combined directly with elemental fluorine (F_2) in a flame reactor. The gaseous UF_6 product is condensed as a solid by cold trapping in two shell and tube heat exchangers in series at +10°F and -50°F. The vent gases leaving this process consist of appreciable quantities of oxygen and nitrogen, some hydrofluoric acid and fluorine, and small amounts of UF_6. Prior to venting, the gas temperature is reduced to approximately -50°F in the secondary cold traps where nearly all the UF_6 is removed; however, between 100 and 1000 ppm UF_6 remain in the gas phase because an appreciable vapor pressure of UF_6 exists over the solid phase at this cold trapping temperature. The value of this uranium, which would normally be lost, warrants the recovery of the small quantities present in these vent gases.

A unique technique has been developed where the UF_6 as well as a portion of the F_2 is recovered in a fluidized bed of UF_4. The products formed in the bed may be recycled back to the flame reactor for immediate reuse or may be regenerated with a reducing agent such as hydrogen. Conventional gas phase recovery methods such as spray towers, packed beds, low temperature condensation, or the gas phase reduction of the UF_6 to UF_4 have proven impractical because of the extreme reactivity of both F_2 and HF or because of the excessive costs involved. The use of a fluidized bed of UF_4 has proven to be a very satisfactory method of recovering small quantities of UF_6 from nearly any gas stream.

The use of a fluidized bed of UF_4 for recovering UF_6 was originally devised from a review of the known chemical behavior of UF_6 and was proven feasible by laboratory tests made at the Paducah Plant of the Union Carbide Nuclear Company. Pilot plant tests, made at the Oak Ridge Plant of the Union Carbide Nuclear Company, showed that the process would be quite feasible for plant scale use. The design criteria for a plant scale unit were established from these laboratory and pilot plant data, and a unit was installed for plant scale operation at the Paducah UF_6 manufacturing plant.

CHEMISTRY OF THE ABSORPTION AND REGENERATION PROCESSES

The most stable forms of uranium fluorides exist in the tetravalent state as UF_4 and in the hexavalent state as UF_6. The pentavalent and other intermediate states such as U_2F_9 and U_4F_{17} are known to exist and to have volatilities which are a function of the temperature and the ratio of UF_6 to UF_4. Upon heating, all these intermediates decompose at varying rates to form UF_4 and UF_6. The following reactions occur to various degrees to form uranium fluoride intermediates which are essentially stable at room temperature:

$$UF_6 + 7UF_4 \rightleftharpoons 2U_4F_{17} \qquad (1)$$

$$2UF_6 + 3U_4F_{17} \rightleftharpoons 7U_2F_9 \qquad (2)$$

$$UF_6 + U_2F_9 \rightleftharpoons 3UF_5 \qquad (3)$$

The equilibrium vapor pressure of UF_6 over these intermediates at 400°F are given by Katz and Rabinowitch(1) as 30 mm Hg for α UF_5, 99 mm Hg for β UF_5, 0.024 mm Hg for U_2F_9, and 0.0064 mm Hg for U_4F_{17}.

At temperatures less than about 650°F, UF_4 reacts with F_2 to produce the same uranium fluoride intermediates possibly by the following reactions:

$$2UF_4 + F_2 \rightarrow 2UF_5 \qquad (4)$$

$$4UF_4 + F_2 \rightarrow 2U_2F_9 \qquad (5)$$

$$8UF_4 + F_2 \rightarrow 2U_4F_{17} \qquad (6)$$

These reactions also take place at elevated temperatures, but the intermediates formed are completely oxidized by F_2 to the hexavalent state.

Since all of these intermediates are solids with fairly low vapor pressures of UF_6, it is apparent that both UF_6 and F_2 could be absorbed by UF_4, if the temperature employed is low enough to prevent the F_2 from completely oxidizing the uranium fluorides to the gaseous hexavalent state. The temperature must be high enough, however, to permit completion of the reaction between UF_4 and UF_6, if complete recovery of the UF_6 is to be obtained. Pilot plant data has indicated that greater than 99% of the UF_6 can be absorbed by UF_4 at 400°F, when the inlet gases contain as much as 16% UF_6 and 12% F_2. The degree of reaction of UF_4 and F_2 to form UF_6 above this temperature is apparently dependant on the temperature.

Regeneration of the UF_4 containing absorbed UF_6 and F_2 by reduction of the various uranium fluoride intermediates has been shown to occur at 400°F with hydrogen as the reducing agent. The reaction products include UF_4 and HF probably formed according to the following reactions:

$$2UF_5 + H_2 \rightarrow 2UF_4 + 2HF \qquad (7)$$

$$2U_2F_9 + H_2 \rightarrow 4UF_4 + 2HF \qquad (8)$$

$$2U_4F_{17} + H_2 \rightarrow 8UF_4 + 2HF \qquad (9)$$

The net reactions for the absorption and regeneration processes would, therefore, be as follows:

$$UF_6 + H_2 \rightarrow UF_4 + 2HF \qquad (10)$$

$$F_2 + H_2 \rightarrow 2HF \qquad (11)$$

The recovery of the UF_6 by the direct reaction of the UF_6 and F_2 with hydrogen might be possible but would be hazardous, since the F_2 as well as the oxygen present in the vent gases might react explosively. The reaction in equation 10 is utilized to produce UF_4 as an intermediate step in the production of uranium metal. However, this reaction is carried out at elevated temperatures using high concentrations of UF_6. Oxidizing agents such as F_2 and O_2 are not present in this process.

If sufficient quantities of UF_4 are available, as they are in the UF_6 manufacturing plants, regeneration of the absorption bed is not necessary. However, if sufficient quantities are not available, the absorption bed could be regenerated with hydrogen or other gaseous reducing agents. Regeneration has an economic disadvantage in the UF_6 manufacturing process, since the partial conversion of UF_4 to UF_6 by F_2 in the absorption processes would be lost and would require the generation of additional F_2. For this reason, as well as the advantages realized from the recovery of elemental F_2, the regeneration process was discarded in favor of a continuous feed and withdrawal process.

FLUIDIZED BED TECHNIQUE

Once it was concluded that UF_6 might be absorbed by UF_4, a process for bringing the vent gases into intimate contact with the UF_4 or green salt powder had to be selected. Since green salt of approximately -200 mesh or smaller is available in quantities at the UF_6 manufacturing facilities, it was deemed desirable to use a process that would utilize this material directly without additional processing. A fluidized bed of the powder appeared ideally suited to an absorption process because this technique would provide excellent contact between solids and gases as well as optimum temperature control.

Although a fluidized bed reactor requires booster pumps to offset pressure losses, the savings in the floor space that would be required if a tray or screw type reactor were used more than justifies the fluidized bed type reactor. The fluidized bed reactor, consisting basically of a cylindrical shell with a diffusion plate at the bottom, can often be fabricated and installed for less capital investment than other types of solid-gas contactors.

Because of the advantages offered by a fluid bed reactor, all experimental work on the absorption process was performed utilizing this technique.

LABORATORY TESTS

To determine if relatively small quantities of UF_6 could be efficiently removed from a gas stream containing mostly inert gases with some F_2 and HF present, a batch type reactor was constructed from a 2-inch Monel pipe. Gaseous mixtures of air, F_2 and UF_6 were fed to the bed at various rates. The feasibility of the absorption process was determined as well as the optimum temperature, fluidizing velocity, and the bed loading that might be expected at exhaustion. It was indicated that a temperature of 400°F would be quite satisfactory as shown by the data given in Table I.

The preliminary results also indicated that a gas velocity of 0.4 to 0.5 fps was sufficient to fluidize the UF_4. A pressure drop of about 1 psi was experienced per foot of fluidized bed.

TABLE I

EFFECT OF TEMPERATURE ON UF_6 AND F_2 ABSORPTION

Temperature, °F	UF_6 Absorbed, %	F_2 Absorbed, %
100	91	30
200	90	33
400	> 98	50
455	> 98	37
505	95	38
550	89	48
600	85	64

Uranium tetrafluoride is usually available as green salt which consists of mostly UF_4 along with other uranium fluorides and oxyfluorides in either the tetravalent or hexavalent state. The forms usually found are uranium tetrafluoride (UF_4), uranyl fluoride (UO_2F_2), and uranium dioxide (UO_2). To determine if the quality of the green salt would affect the capacity of the absorption process, tests were made with green salts of both high and low UF_4 contents. The physical characteristics of each type green salt tested are given in Table II.

TABLE II

GREEN SALT QUALITY

	Analysis, %			Density, g/cc	
Type Green Salt	UF_4	UO_2F_2	UO_2	Free Flow	Packed
High Quality	99	0.2	1.0	3.0	4.2
Low Quality	78.1	10.4	11.5	2.8	3.6

Additional laboratory tests were made to determine the effect of bed loading and UF_6 concentration on the efficiency of the fluid bed of UF_4 for absorbing F_2 and UF_6. Concentrations in the range of 100 to 4000 ppm UF_6, and 2 to 3% F_2 were studied in particular. Some of the data collected are given in Figures 1 and 2, and Tables III and IV.

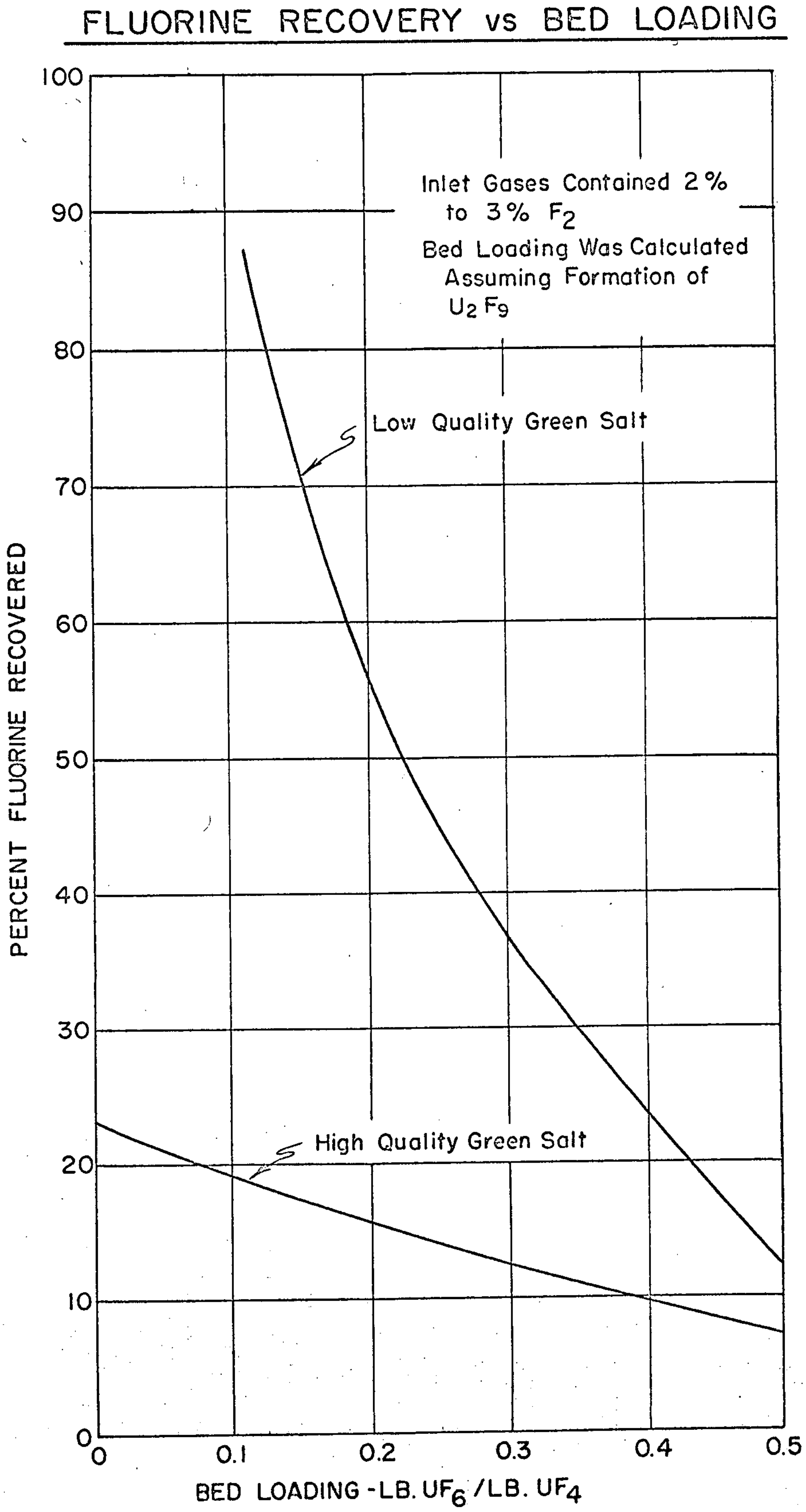
FLUORINE RECOVERY vs BED LOADING
Inlet Gases Contained 2% to 3% F_2
Bed Loading Was Calculated Assuming Formation of U_2F_9
Low Quality Green Salt
High Quality Green Salt
PERCENT FLUORINE RECOVERED
100
90
80
70
60
50
40
30
20
10
0
0
0.1
0.2
0.3
0.4
0.5
BED LOADING - LB. UF_6 / LB. UF_4

FIGURE 1

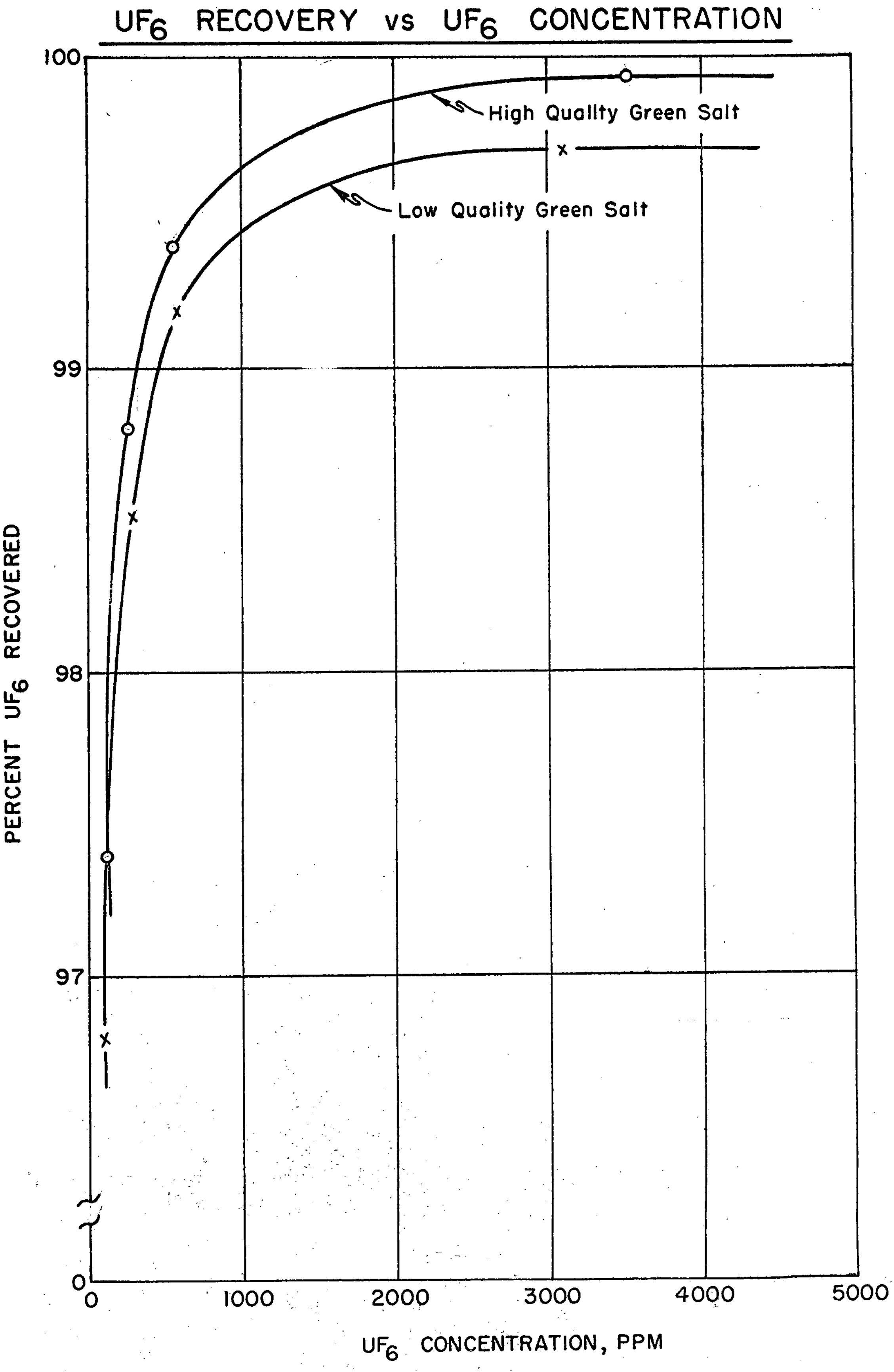
UF$_6$ RECOVERY vs UF$_6$ CONCENTRATION
High Quality Green Salt
Low Quality Green Salt
PERCENT UF$_6$ RECOVERED
100
99
98
97
0
0
1000
2000
3000
4000
5000
UF$_6$ CONCENTRATION, PPM

FIGURE 2

TABLE III

BED LOADING AT EXHAUSTION FOR THE ABSORPTION OF UF_6 AND F_2 AT 400°F

Powder Quality	Gas	Bed Loading per Pound Green Salt Pound UF_6	 Pound F_2
High*	UF_6, F_2, air	0.085	0.011
High*	UF_6, air	0.15	-----
Low*	UF_6, F_2, air	0.077	0.023
Low*	UF_6, air	0.38	-----
Low**	F_2, air	-----	0.041

*Exhaustion taken as less than 95% recovery of UF_6.

**Exhaustion taken as greater than 10 ppm UF_6 leaving the bed.

TABLE IV

ANALYSIS OF GREEN SALT AFTER ABSORPTION OF UF_6 AND F_2 AT 400°F

		Analysis, %			
Powder Quality	Gas	U_{total}	U^{+4}	F	Water Soluble
High	Before exposure	75.8	75.8	----	0.9
	UF_6, F_2, air	74.7	66.9	----	16.4
Low	Before exposure	77.1	69.1	20.2	----
	UF_6, F_2, air	73.0	56.8	22.5	----
	F_2, air	71.3	53.9	22.0	----
	UF_6, air	72.3	48.4	25.3	----

UF_6 Recovery Efficiency versus Bed Loading

Prior to exhaustion of the bed, at least 98% recovery of the UF_6 was obtained with UF_6 concentrations greater than 100 ppm when using the high quality green salt as the absorbing medium. The same good recovery efficiency was obtained with UF_6 concentrations greater than 300 ppm UF_6 with the low quality green salt mentioned previously. These data were obtained with 2 to 3% F_2 in the gas.

The recovery efficiency for UF_6 was essentially unaffected by the quality of the green salt used. However, as shown in Figure 1, the absorption efficiency for F_2 was strongly a function of the green salt quality. The higher the green salt quality, the lower the efficiency for F_2 recovery. The presence of uranium oxides in the lower quality green salt undoubtedly accounts for the increased absorption efficiency for F_2. Fluorine reacts rapidly with uranium dioxide (UO_2) and uranium trioxide (UO_3) at 400°F according to the following reactions:

$$UO_2 + 2F_2 \rightarrow UF_4 + O_2 \tag{12}$$

$$2UO_3 + 2F_2 \rightarrow 2UO_2F_2 + O_2 \tag{13}$$

UF_6 Recovery versus UF_6 Concentration

The effect of UF_6 concentration on the recovery efficiency for UF_6 is shown in Figure 2. It was found that the UF_6 concentration was reduced to less than 10 ppm UF_6 regardless of inlet concentration as long as the bed was not near exhaustion. This fact suggests that the outlet concentration is only a function of the vapor pressure of UF_6 over the intermediates formed, if the gas has sufficient retention time in the fluidized bed.

Bed Loading at Exhaustion

The quantities of UF_6 and F_2 that could be absorbed by the high and low quality green salts described in Table II were determined by operating a batch-wise fluid bed until breakthrough of UF_6 occurred. The results obtained from these tests are given in Table III. Results of analyses of the green salts after exhaustion are given in Table IV.

These data indicate that as much as 0.38 lb UF_6/lb green salt or 0.041 lb F_2/lb green salt can be recovered at 400°F if low quality green salt is used. Recovery of UF_6 from a gas containing 2 to 3% F_2 can be efficiently accomplished up to a bed loading of 0.085 lb UF_6/lb green salt with the high quality green salt and 0.077 lb UF_6/lb green salt with the low quality green salt.

PILOT PLANT TESTS

To scale-up the laboratory tests to permit better evaluation of the absorption process, and to provide plant scale design criteria, a pilot plant consisting of a 6" diameter reactor with a 24" bed was operated at the Oak Ridge Plant of the Union Carbide Nuclear Company. These tests consisted of verifying the previous laboratory tests and studying the use of a continuous powder feed and withdrawal system rather than a batchwise process. The effect of surges of F_2, HF, and UF_6 were also studied to determine if temperature control might be lost, permitting formation of UF_6 by direct reaction between F_2 and the UF_4 or intermediates.

These pilot plant tests indicated the feasibility of continuous powder feed and withdrawal, and showed that regeneration of the exhausted bed with hydrogen would not be necessary if sufficient green salt is available. The capacity of the bed was unaffected by HF content of 10½% in the inlet gas and the bed temperature was easily controlled at 400 ±15°F when the F_2 concentration averaged as high as 17% for a two and one-half hour period. In no case at a bed temperature of 400°F was the concentration of UF_6 leaving the bed greater than that entering. Better than 99% recovery of UF_6 was effected from a gas mixture containing approximately 16% UF_6 and 12% F_2.

The fluid bed technique provided excellent temperature control of the fluidized powder. Steam cooling and electrical heating gave satisfactory performance. A bed temperature of 400°F proved to be the optimum from the standpoint of UF_6 recovery. At temperatures above approximately 500°F, the UF_6 in the outlet gas increased appreciably. At temperatures below 400°F, the absorption efficiency for F_2 decreased.

Satisfactory fluidization of the green salt was obtained with superficial gas velocities betweem 0.15 and 0.75 fps. Powder retention times between

1.6 and 4.2 hours and a bed depth of approximately two feet gave satisfactory recovery of both F_2 and UF_6. No caking occurred in the fluidized bed reactor.

PLANT SCALE APPLICATION

As a result of the experimental work previously described, a plant scale fluidized bed absorber was installed at the UF_6 manufacturing plant at Paducah, Kentucky, during July 1958. This reactor, as shown in Figure 3, operates at 400 ±25°F, between 14 and 16 psia, and is capable of handling between 25 and 95 scfm of vent gas. The temperature of the bed is maintained electrically during operation and steam coils are provided for cooling. A schematic diagram of the recovery system is shown in Figure 4.

Green salt ranging between 75 and 99% UF_4 is conveyed on a vibrating conveyor to a feed hopper. The green salt is fed from the feed hopper into the bottom of the fluidized bed by a 2½ inch screw conveyor. Fluidized powder overflows from the reactor three feet above the diffusion plate and falls by gravity along with the unreacted gases through an inclined pipe into a cyclone separator. A powder seal is provided at the bottom of the cyclone separator to prevent leakage of gas. The green salt containing the absorbed UF_6 and F_2 is removed from this seal leg by a screw conveyor and is fed into a product hopper which in turn feeds a take-off conveyor. A take-off conveyor routes the powder to the flame reactors in the UF_6 manufacturing area.

The vent gases are compressed from 11 to 16 psia by a Root's type compressor before entering the reactor. The gases enter the bed of green salt through a drilled diffusion plate and maintain the bed in a semi-fluidized condition. The unreacted gases leave the reactor through a cyclone separator where the major protion of the dust burden is removed. After leaving the cyclone separator, the gases pass first through a primary filter and then a back-up filter, both of which utilize porous metal filter elements. These filters are blown back periodically with dry air or nitrogen.

FLUIDIZED BED REACTOR

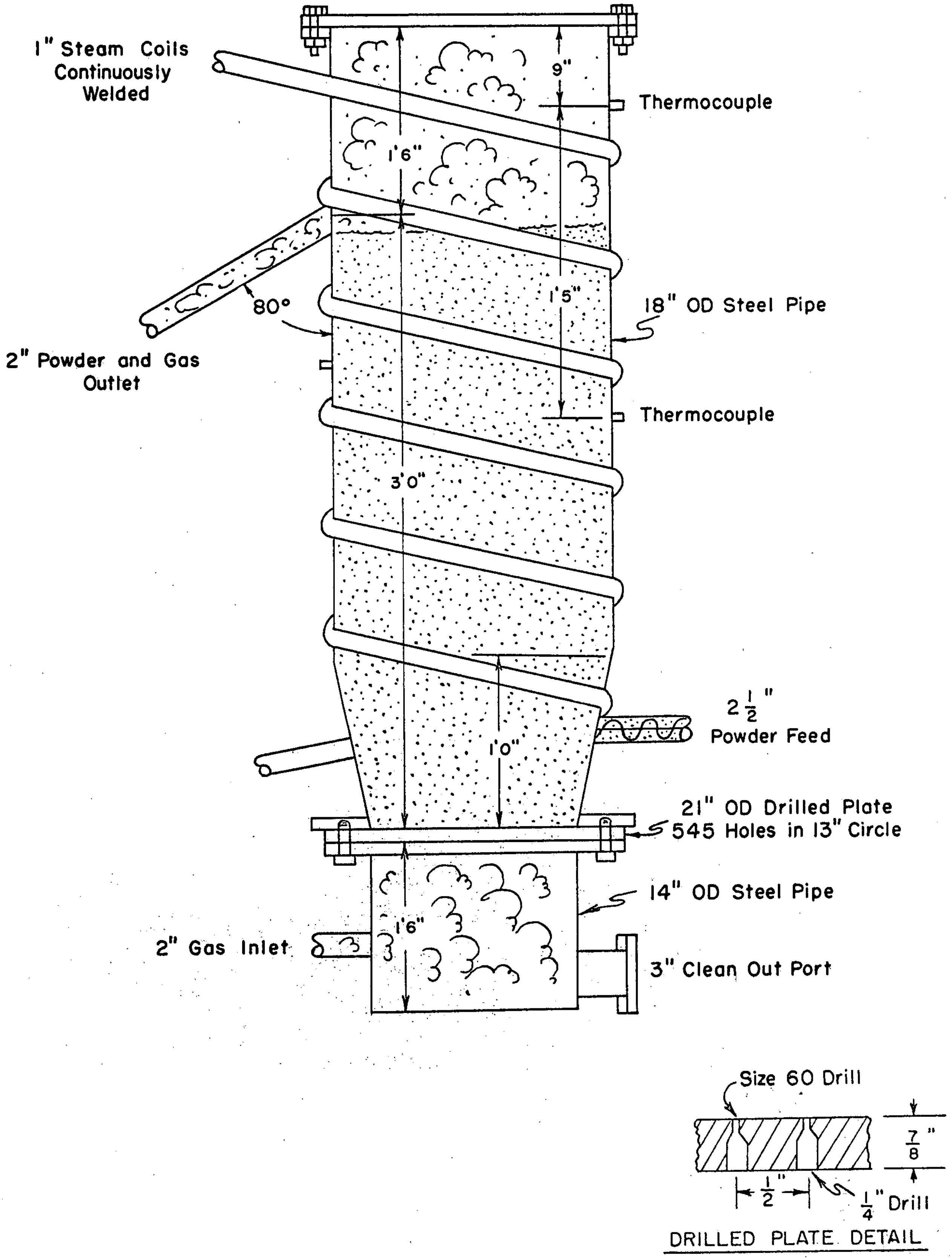

FIGURE 3

ABSORPTION SYSTEM FOR RECOVERY OF UF_6 AND F_2

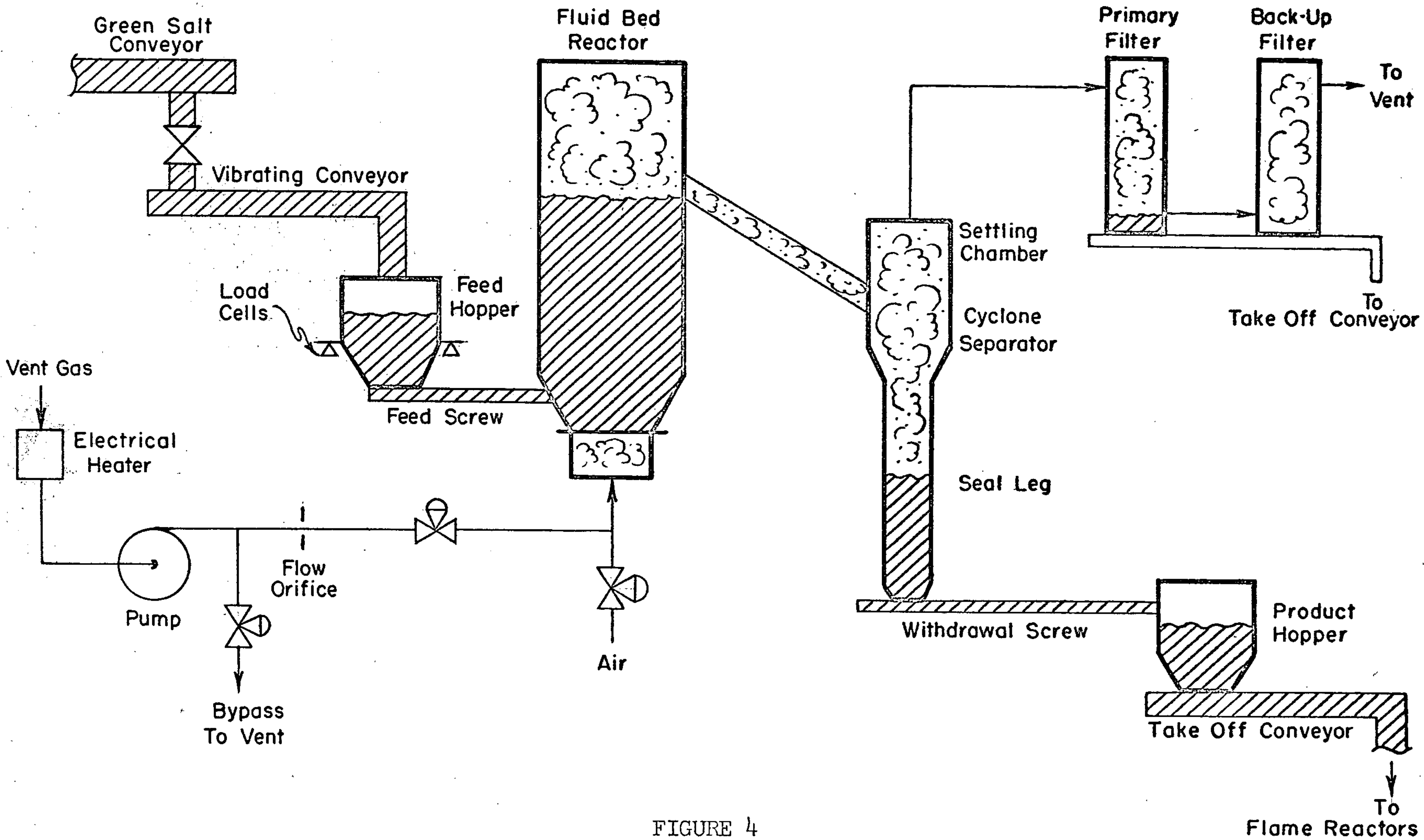

FIGURE 4

SUMMARY

It has been found that UF_6 at concentrations as low as 100 ppm can be economically and efficiently recovered from a gas stream by absorption in a fluidized bed of UF_4 or green salt at 400°F. The recovery efficiency for UF_6 is essentially unaffected by the presence of highly reactive gases such as F_2 and HF; however, a portion of the F_2 is absorbed and consequently decreases the maximum UF_6 bed loading that can be obtained. The recovery efficiency for UF_6 is only very slightly affected by the quality of the green salt used, although the portion of F_2 absorbed is markedly reduced by increased green salt quality.

Apparently both UF_6 and F_2 are absorbed by UF_4 because of the formation of solid uranium fluoride intermediates such as UF_5, U_2F_9, or U_4F_{17}. At temperatures above approximately 650°F these intermediates are oxidized by F_2 to UF_6. At temperatures less than 400°F, the absorption efficiency for both UF_6 and F_2 decreases because of the reduced reaction rate. Regeneration of the exhausted bed with H_2 has been shown to be effective and quite desirable when only small quantities of green salt are available.

The use of a fluidized bed, to bring the solid UF_4 or green salt into intimate contact with the gases containing UF_6, has proven to be a very satisfactory technique. Installation of an 18" diameter fluidized bed absorber with continuous powder feed and withdrawal, at the Paducah Plant of the Union Carbide Nuclear Company, has permitted essentially complete recovery of the small quantities of valuable UF_6 normally lost in the vent gases from the UF_6 manufacturing process.

ACKNOWLEDGEMENT

The authors wish to acknowledge the laboratory investigations performed and constructive criticism offered by Messrs. G. H. Conner, W. R. Golliher, T. J. Mayo, and W. R. Rossmassler of the Laboratory Division at the Paducah Plant of the Union Carbide Nuclear Company. Also, the most helpful pilot plant work done by Messrs. C. C. Littlefield, D. C. Brater, and J. H. Pashley of the Design and Development Section at the Oak Ridge Plant of the Union Carbide Nuclear Company is acknowledged.

REFERENCE

(1) Katz, J. J., and Rabinowitch, E., *The Chemistry of Uranium, Part I*, 1st ed., New York, McGraw-Hill, (1951), p. 382-392.