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Uranium and Fission Product Fluorides

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1.0 Abstract

An all nickel fractionating column packed with 5/32" Fenske helices 8" deep has been designed and constructed for study of the separation of UF_6 from fission product fluorides.

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2.0 Summary

An all nickel distillation column, 11/16 inches inside diameter, packed 8 inches deep with 5/32 Fenske helices has been designed and constructed. The column was built to operate at 75°C and 1600 mm of Hg pressure for the purpose of purifying uranium from its fission products by fractionation of metal fluorides. Remote control and protective shielding are features of the design.

Operation of this column with fission product contaminated uranium hexafluoride should permit evaluation of relative volatilities, the degree of fluoride deterioration, and techniques of handling the distillation. From these data it is hoped that a pilot plant, consisting of two major columns and two small supplementary columns can be rationally designed for continuous production of UF₆.

3.0 Object

The metal fluorides are in many cases volatile at reasonable temperatures. It is expected that differences in the volatility of these fluorides will make possible the separation of uranium hexafluoride from fission product fluorides by distillation. It is the purpose of this work to determine the feasibility of such a procedure and to indicate the method of development of a workable project.

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4.0 Nature of the Problem:

As ejected from the ORNL pile, a slug material consisting of about 99.97% uranium and 0.03 mole % fission products and plutonium is obtained. Conversion to the fluorides will result in a mixture, having essentially the properties of uranium hexafluoride. Below a pressure of 1161 mm of Hg, the UF_6 does not form a liquid phase. Since distillation requires a liquid phase, operation of a column will require a pressure greater than 1161 mm of Hg. The melting point of UF_6 is $65^\circ C$. At $75^\circ C$ the vapor pressure of UF_6 is 1560 mm of Hg, at which temperature and pressure operation of the column is contemplated.

A listing of the pertinent properties of the fluorides is presented in Table I. The vapor pressure at $75^\circ C$ has been obtained from various vapor pressure data and the use of the Clausius-Clapeyron equation. Relative volatilities have been calculated assuming Raoult's law. This law is probably not valid (Henry's law range), but no data are available. From Table I it is seen that Kr, TeF_6 , IF_7 , and MoF_6 are more volatile than UF_6 , while the other fluorides are less volatile. Further, those fluorides beginning with BaF_2 and proceeding down the table are non-volatile and will not appear in the distillation apparatus, unless carried into it by entrainment. It is questionable as to whether Rh, Sn, or C_s will appear. Of those left, only Te, Cb, Ru, and Zr are present in appreciable quantities. PuF_6 will also be present, but it is assumed that its volatility will be sufficiently similar to UF_6 to prevent separation by distillation. PuF_6 will necessarily have to be removed by some other scheme.

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Nature of the Problem (continued)

Observation of the relative volatilities of the fission products shows that only a few of the fission product fluorides have a vapor pressure comparable to UF_6 , and hence it appears that distillation is a highly feasible process. Some difficulty is possible with Mo, Sb, and Cb, but the others should separate readily. Since these relative volatilities are approximate, it is necessary to experimentally determine the value of the volatility of IF_7 , MoF_6 , SbF_5 , CbF_5 and PuF_6 . This will permit accurate evaluation of the column height requirements.

The immediate answers required are thus: (1) the evaluation of the pertinent relative volatilities, (2) the methods of handling the distillation from a technique and apparatus point of view, and (3) the possibility of unpredicted oddities. In this latter respect, the dissociation of the fluorides, adsorption on the packing, or exchange phenomena are possibilities.

5.0 Description of the Apparatus

In order to obtain relative volatilities it is necessary that both overhead and bottoms analyses are available. For this reason, a short column was designed so that fractionation beyond the limit of analysis would not occur. Figure 1 shows the design of the fractionating column, packed with an 8 inch deep bed of 5/32 inch nickel Fenske helices. All equipment is nickel with the seals made of silver solder. Originally, these seals were made by nickel welding but it was found that pin holes developed in

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Description of the Apparatus (continued)

the welds, and it was necessary to seal over the welds with the silver solder. The inside diameter of the column is 11/16 inches. Roughly, the column is vacuum jacketed, and surrounded by magnesia pipe lagging. The condenser for the column is shown, along with other details, in the general assembly on Figure 1. The still is shown on Figure 2, and indicates the method of determining liquid level and pressure drop across the column. The float occupies considerable space in the still, and helps reduce the amount of liquid needed for the distillation studies. On Figure 3 is shown the twin upper condensers. Only one condenser at a time is to be connected to the pressurizing system. The condenser so connected will be cooled with refrigerated acetone. The temperature of the refrigerant can be regulated so that adequate trapping of the UF_6 vapors will exist. As this condenser is placed on stream, solid UF_6 will collect and gradually plug the condenser. When this occurs, operation will be transferred to the second condenser. The first condenser will be heated to melt out the UF_6 . On Figure 4 is shown the column head. The temperature of the vapor will be measured by use of the thermocouple well. The return of reflux through the column is by two paths, (1) directly, and (2) through a very small flowmeter (not shown). The valves shown are special plug valves developed by C. D. Watson and have a teflon plug with nickel body. Three of these are used, two as shown, and one as a sampler for the bottoms liquid. The line through the flowmeter will be used to calibrate the apparatus, using cold UF_6 . In operation with radioactive material, the reflux will pass only by the direct path back to the column.

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Description of the Apparatus (continued)

On Figure 5 is shown the sampling device for taking off portions of the UF_6 . The actual sample bottle is made of fluorothene. Before the sample is taken, the whole device will be heated to 65 - 75°C. At this temperature, fluorothene has a degree of softness, and on forcing the fluorothene bottle against the sharp ring a seal can be effected. The sampling region will then be evacuated, the bottom of the sample bottle chilled with solid CO_2 , vacuum line closed, and the sampling valve connected so that liquid can flow into the bottle and solidify. In this way, a uniform solid sample of material may be obtained. This sample will then be dropped into a beaker containing water, and the UF_6 hydrolyzed for analysis.

The entire distilling column is enclosed in a box maintained thermostatically at 65°C by means of electrical heaters. Around the box is placed a 1/2 inch thick layer insulation (magnesia, rock wool), around which has been placed a two inch thickness of lead brick. Controls are all remote type, except for those which measure or use non-radioactive material only. Additional lead brick shielding will be used at critical points. Heating coils are placed around the sampling leads to prevent freezing of the UF_6 . Wherever a possible egress of the gas in the column could occur, it is well trapped.

6.0 Treatment of the Data

The first step is to calibrate the column. This can be done by distilling

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Treatment of the Data (continued)

a mixture of carbon tetrachloride and toluene. Let

n = number of theoretical plates in the column

D = subscript, refers to overhead

W = subscript, refers to bottoms

y = mole fraction of $C Cl_4$

Then

$$n + 1 = \frac{\log \frac{y_D}{y_W} \frac{1 - y_W}{1 - y_D}}{\log 2.5}$$

It is necessary to plot n as a function of the volume reflux rate. In this way, a calibration of the column in terms of this substance may be done.

It is desirable to calibrate the column in terms of UF_6 . This may be done by considering the liquid viscosity to be the major constituent affecting the column efficiency. (3)

$$HTU \propto \left(\frac{\mu}{\rho D} \right)^{1/2}, \text{ where}$$

μ = liquid viscosity

ρ = liquid density

D = diffusivity

An alternative method to be used as a check is as follows: (4)

$$\frac{n_1}{n_2} = \frac{.17 - .62 \mu_1}{.17 - .62 \mu_2}$$

In this way, the values of n can be obtained which pertain to UF_6 . The difference from that obtained for n with CCl_4 and toluene should be small.

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Treatment of the Data (continued)

After calibration of the column, it should be scrupulously cleaned, saturated with nitrogen-fluorine mixtures, and then tested out with cold UF_6 . Using the rotameter, establish the heating rate to the still as a function of rate of refluxing. After thoroughly testing the column, it should be ready for the radioactive material.

With radioactive material, the column should be operated at total reflux for an extended period, say 4 hours. A sample of the original feed should be taken. After the 4 hours distillation, samples of tops and bottoms should be taken. The data sheet should be as follows:

Starting time for distillation

Time of taking samples

Reflux rate, cc/min.

Vapor temperature, °C

Column pressure, lb/in²

Analytical Results

Material	Feed c/min	Tops c/min	Bottoms c/min
U			
Pu			
Gross β			
Te			
I			
Cb			
Ru			
Zr			
TRE			

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Treatment of the Data (continued)

The relative volatility of each of the substances can be computed by the equation:

$$\log \alpha = \frac{\log \frac{C_D}{C_W}}{n + 1}$$

where $C_D = \frac{\text{counts in the overhead}}{\text{unit of uranium}}$

$C_W = \frac{\text{counts in the bottoms}}{\text{unit of uranium}}$

$\alpha = \text{relative volatility}$

A check should be ascertained as to whether a good deal of the radio-activity has been lost in the column, i.e., has been adsorbed on the packing.

Also, a large series of runs should be made to determine:

- a) Whether α is changing in value according to some definite trend.
- b) Whether the results obtained are consistent and reproducible.

It should be possible to use the column over and over without appreciable additions of feed until this first part of the study is made.

The second part of the study should investigate the effects, if any, of radically different feed compositions. This can be done in the same manner.

From these studies, should be known:

- a) The values of relative volatility.
- b) The degree to which adsorption, reduction at metal surfaces, or other processes take place.
- c) The details of handling the material.

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Treatment of the Data (continued)

From this, it should be readily possible to develop a pilot plant which will perform the desired job.

7.0 Design of a Pilot Plant

Either a batch or a continuous type distillation process may be considered. Although a batch process is simpler to build it suffers from three bad features, namely, (1) it does not have the capacity of a column of equal size operated continuously, (2) it requires closer control, and (3) the danger of cross contamination is present. A continuous process is indicated, especially since the fission products are believed to have a tendency to plate out on the metal surfaces.

The simplest type of continuous system would consist of two columns, the first being shorter than the second. In the first column light fission products, i.e., Kr, IF_7 , TeF_6 are removed. In the second column UF_6 is removed from the heavy fission products. In this way, pure UF_6 is removed as overhead from the second column.

Operation of the first column poses certain problems. To operate a column there must be reflux. On a molal basis, the light fission product content of the feed is negligible. Hence, the reflux for the first column cannot consist only of the light fission product fluorides, as this would be an extremely small flow. The bulk of this reflux must be UF_6 . Hence, with this simple system of two columns, some of the UF_6 will be lost with the light fission

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Design of a Pilot Plant (continued)

products. It is estimated that this would be about 2% of the UF_6 fed to the column. A number of solutions present themselves and these will now be discussed.

(1) The overhead can merely be discarded, taking the loss of uranium. Since this would amount to throwing away almost pure uranium, it is not a desirable solution.

(2) The overhead can be converted into the nitrates, and run through the Purex process. Again, this is not particularly desirable, as it requires that the dry fluoride process depend on another process.

(3) The half lives of the light fission products are as follows, for Te they are 32d, 72m, 9.3 hr., 90 d; for I 80 days, and for Mo 67 hrs. All of these half lives are quite short. By waiting sufficient time for this material to cool, the mixture can then be further treated for purification. The Te goes to stable I, the iodine to stable Xe, and the Mo to stable Ru. I and Xe belong to the light fission product fluoride class, the Ru belongs to the heavy class. The same problem thus exists as before, except that now the mixture is non-radioactive, and the fission products could be removed by an easily constructed small set of columns. This does not appear to be a good solution.

(4) A possibility for reducing UF_6 content of the overhead is to allow the light fission product content to build up to a high level in the 1st column. This suffers from the disadvantage that the radioactivity level

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Design of a Pilot Plant (continued)

will get extremely high and increases the possibility of contamination of bottoms from the first column with light fission products.

(5) A fluxing agent may be used. The problem here is to choose the agent, realizing that the fluxing agent must be discarded to waste unless a recovery system is used.

Fluxing agents that could be considered are the completely fluorinated fluorocarbons, which are extremely expensive. If the fission products in the overhead can be easily reduced to Te, I, Mo, etc., the fluorocarbon can be readily removed by use of an additional distillation column.

(6) The use of a small supplementary distillation column for treating the light fraction can be considered. Even here there will of necessity be some UF_6 lost in the overhead, but it should be quite small. This system has a number of advantages (a) the fission product fluorides are obtained in a highly concentrated form, (b) there is no waste disposal problem or fluxing agent considerations. It is probable that one additional column will be adequate, but the procedure can obviously be pyramided. At the present, this procedure seems the most likely, reducing the UF_6 loss down to an estimated 0.1% of the total UF_6 in the initial feed. It may be possible to include some of the advantages of the others as method (4).

An additional problem is the disposal of radioactive krypton. This will not dissolve in the reflux stream. The practicable solution is to pass it into the atmosphere out a high stack.

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Design of a Pilot Plant (continued)

The second column will not have these problems. The contamination of bottoms by UF_6 can be made quite small. A supplementary small stripping column can be used if necessary or desirable. This will probably be the case.

A sketch of the recommended type of apparatus is shown on Figure VIII, showing the two main fractionating columns and the two very thin supplementary columns.

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Table I

Properties of Fluoride Feed Mixture Components

Component	B. P. °C	Vapor Pressure at 75°C	Relative Volatility Referred to UF ₆
Kr	- 153	Very high	300?
TaF ₆	- 39	84,000	54
IF ₇	4	19,800	12.7
MoF ₆	35	2,380	1.52
UF ₆	75	1,560	1.00
PuF ₆	75?	--	1.0
SbF ₅	150	663	.43
CbF ₅	225	470	.30
RuF ₅	272	408	.26
ZrF ₄	577	15	.006
RhF ₃	597	Negligible	Negligible
SnF ₄	705		
CsF	1251		
BaF ₂	2220		
YF ₃	2230		
CeF ₃	2330		
LaF ₃	2330		
NdF ₃	2330		
PrF ₃	2330		
EuF ₃	2330		
SrF ₂	2510		

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FIGURE 1
COLUMN ASSEMBLY

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FIGURE 2
STILL POT

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FIGURE 3

UPPER CONDENSER

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FIGURE 4
COLUMN HEAD

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SAMPLE STATION ASSEMBLY

143 022