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REMOVAL OF URANIUM HEXAFLUORIDE FROM GAS STREAMS

BY SODIUM FLUORIDE PELLETS*

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REMOVAL OF URANIUM HEXAFLUORIDE FROM GAS STREAMS

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ABSTRACT

The removal of uranium hexafluoride from a gas stream containing uranium hexafluoride and nitrogen by a single layer of sodium fluoride pellets was investigated. Experimental data on the rate and extent of sorption were obtained in the temperature range 29 to 225°C and uranium hexafluoride concentration range 0.57 to 10.9 mole per cent uranium hexafluoride.

The results of this study indicate that the rate controlling mechanisms are: transfer of uranium hexafluoride across a stagnant gas film surrounding the pellet, diffusion of gaseous uranium hexafluoride in the pores of the pellet, and diffusion of uranium hexafluoride through a layer of uranium hexafluoride-sodium fluoride complex covering the unreacted sodium fluoride in the interior of the pellet. The crystalline density of the complex, $\text{UF}_6 \cdot 2\text{NaF}$, was determined to be 4.13 grams per cubic centimeter which indicates that incomplete reaction of the sodium fluoride will occur for pellets in which the initial volume void fraction is less than 0.807.

A useful model was devised to represent the sorption of uranium hexafluoride by a single pellet of sodium fluoride. The experimental data were correlated on the basis of the model with a root-mean-square error of 12.0 per cent for all points.

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This paper is concerned with the determination of the rate controlling mechanisms for the removal of uranium hexafluoride from flowing streams of uranium hexafluoride in nitrogen by cylindrical pellets (one-eighth-inch right circular) of sodium fluoride.

As reported in the previous paper, uranium hexafluoride reacts reversibly with sodium fluoride to form a solid complex $UF_6 \cdot 2NaF$. The reversible character of the reaction makes it attractive as a means for separating uranium hexafluoride from other gases and/or as an alternative to low-temperature cold trapping for collecting uranium hexafluoride. Differences in the decomposition pressures of the fluorides that form sodium fluoride complexes are exploited during alternate sorption and desorption of the uranium hexafluoride in fixed beds of sodium fluoride to produce a uranium hexafluoride product of high purity.

Information on the effects of various system parameters on the rate of sorption is needed so that sodium fluoride sorbers may be designed for a wide range of operating conditions.

In this study, a determination was made of the rate-controlling steps in the sorption of uranium hexafluoride from a stream of uranium hexafluoride and nitrogen by sodium fluoride in the form of one-eighth-inch right circular cylindrical pellets at atmospheric pressure. The temperature range covered was 29 to 225°C, ^{and} the uranium hexafluoride concentration range was 0.57 to 10.9 mole per cent.

The experimental phase of the study consisted mainly of the determination of the loading of uranium hexafluoride on single layers of sodium fluoride pellets during a prescribed time interval under a given set of conditions. Some work was necessary for preparation of samples of the uranium hexafluoride-sodium fluoride complex for determination for crystalline density.

A flow diagram for the equipment used in this study is shown in Figure 1. Basically, the equipment provided means for preparing gas mixtures of the desired composition at a controlled flow rate, means for controlling the temperature of the gas mixture and the sorption vessel, and means for a second determination of the flow rate of the two gases used.

The flow rate of uranium hexafluoride was set by maintaining a controlled pressure drop across a calibrated capillary. The nitrogen was metered through a rotameter from a constant-pressure nitrogen supply. The two gases were introduced into a common line that led to a gas preheater. The preheated gas then flowed through the sorption vessel and through a sodium fluoride trap for removal of uranium hexafluoride which passed through the sorption vessel. Both the gas preheater and the sorption vessel were placed in a constant-temperature bath in which the temperature was controlled to within 0.5°C of the desired operating temperature. After removal of the uranium hexafluoride, the nitrogen was metered by a wet test meter.

A bypass around the sorption vessel and the sodium fluoride trap was provided so that the gases did not flow through the sorption vessel during startup and shutdown of the metering system.

The single layer runs were made by using one layer of sodium fluoride pellets placed between two four-and-one-fourth-inch sections of three-millimeter glass or Monel beads used as entrance and exit sections. As shown in Figure 2, the bed was constructed from one-and-one-half-inch diameter schedule-forty nickel pipe. The glass or Monel beads were conditioned before use by exposure to fluorine at 400°C for one hour.

Prior to a run, the sorption vessel was loaded and placed in the constant-temperature bath. At least one hour was allowed for the bed temperature to reach that of the bath, since it was calculated that after 0.45 hour the difference between the center-line temperature of the bed and the bath temperature would

Slide 1. Flow Diagram for Equipment Used in the Study of Sorption of Uranium Hexafluoride by Sodium Fluoride.

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Slide 2. Sorption Vessel Used in Differential-Bed Studies.

be less than two per cent of the original temperature difference. Prior to starting a run, the uranium hexafluoride and nitrogen flow rates were set, and the stream was allowed to flow through the preheater coil for at least five minutes in order to establish a constant concentration in the coil. During this period, the stream was bypassed around the sorption vessel and the sodium fluoride bed. A run was started by diverting the stream through the differential-bed. Gas was passed through the bed for a predetermined length of time, after which the stream was diverted into the bypass. About ten seconds were required for effecting the valving changes necessary for diverting the gas stream. The uranium hexafluoride flow was stopped and the nitrogen flow was continued through the preheater coil for two minutes to free the coil of uranium hexafluoride. The nitrogen flow was then diverted through the sorption vessel for one minute to free the bed of unreacted uranium hexafluoride. The bed was then sealed, removed from the constant-temperature bath, and allowed to cool in a dry box containing dry air. The sodium fluoride was removed from the reaction vessel in the dry box and placed in a sealed container for weighing on an analytical balance. The sodium fluoride trap was treated similarly.

For determination of the crystalline density of the uranium hexafluoride-sodium fluoride complex, pellets of sodium fluoride that had been treated with fluorine for one hour at 400°C were ground with a mortar and pestle in a dry box. A half-inch layer of the powder in a nickel dish was exposed to a stream of dilute gaseous uranium hexafluoride (five to ten mole per cent uranium hexafluoride in nitrogen) at 100°C, after which the resultant material was again ground with a mortar and pestle in a dry box. The material was repeatedly exposed to uranium hexafluoride and ground until the desired weight gain had occurred. Samples of the material and of the original sodium fluoride were then

submitted for crystalline density determination by toluene immersion. The crystalline density of the complex was determined to be 4.13 g/cm^3 at 26°C .

The partially reacted pellets from a number of runs were sectioned for determination of the distribution of sorbed uranium hexafluoride. The contrast between the pale yellow color of the complex and the white color of sodium fluoride allowed qualitative determination of the distribution of the uranium hexafluoride in a pellet by microscopic and photographic means. Partially reacted pellets, which have been sectioned axially, are shown in Figure 3. By use of the proper filter, the pale yellow of the complex was made to appear grey. The pellets in Figure 3 are from a run at 50°C and contain the maximum quantity of uranium hexafluoride which will be sorbed at that temperature. A considerable variation in penetration of uranium hexafluoride is observed not only between individual pellets but also between different areas of the same pellet. Of particular interest is the slight penetration near the corners of some pellets since this type of profile is not observed in the case of diffusion of a substance into a finite cylinder of constant properties. It is felt that the differences in penetration are due to variation in the density of different areas of the pellet. The method of manufacture of the pellets, compression of a powder, would be expected to produce variations in density, with high-density areas in the unreacted corners of the sectioned pellets. Profiles at other temperatures are similar to those at 50°C except that less penetration is observed at higher temperatures and more at lower temperatures.

The over-all process of removal of uranium hexafluoride from a flowing stream of uranium hexafluoride in nitrogen by a pellet of sodium fluoride is believed to involve the following processes:

1. The movement of uranium hexafluoride from the gas stream to the external surface of the pellet, which is commonly depicted as the

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Slide 3. Axially-Sectioned Sodium Fluoride Pellets Containing Uranium Hexafluoride Sorbed at 50°C.

transfer of uranium hexafluoride across a stagnant nitrogen film surrounding the pellet.

2. The diffusion of gaseous uranium hexafluoride through nitrogen in the pores of the pellet.
3. The diffusion of gaseous uranium hexafluoride through a layer of complex on the internal surfaces of the pellet.
4. The reaction of uranium hexafluoride with sodium fluoride below the complex layer.

Any model proposed to represent the over-all sorption process must take into account those steps whose rates are of the same order of magnitude as the rate of the over-all process. The model must also account for effects resulting from deposition of complex in the pores of the pellet.

The most striking characteristic of the system under study is the effect of temperature on the rate and on the extent of reaction between uranium hexafluoride and sodium fluoride. For reaction between uranium hexafluoride and powdered sodium fluoride, an increase in temperature over the range 29 to 100°C results in an increase in the rate of reaction and the extent of reaction at a specific time. However, in the same temperature range, there is an inverse effect of temperature on the maximum extent of the reaction of the sodium fluoride pellets with uranium hexafluoride.

An explanation of this anomalous effect of temperature on the rate and extent of sorption for finely divided sodium fluoride and for sodium fluoride pellets is based on the combination of two ideas. The first idea is that the temperature dependence of most chemical reactions and of solid-phase diffusion is of the form $e^{-E/RT}$, whereas the temperature dependence of bulk diffusion of gases is of the form $T^{3/2}$. At some temperature, a given increase in temperature will increase the point reaction rate by a greater amount than the point

rate of bulk diffusion. The second idea is that, based on measurement of the crystalline density of the complex, the pores of a pellet will be closed with complex before complete reaction of the sodium fluoride can occur. (A maximum reaction of thirty-three per cent of the sodium fluoride was calculated for the typical NaF pellets.)

In order to test the hypotheses discussed above it is necessary to solve the equation for diffusion with chemical reaction allowing for variable diffusivity and variable reaction rate.

The assumptions shown in Figure 4 were made. Typical experimental data and calculated results for a typical series of runs are shown in Figures 5, 6, and 7. A total of 108 points were obtained in a set of 12 such series. The root-mean-square error for all points was 12.0 per cent.

The variation of pellet capacity for UF_6 with temperature is shown in Figure 8 for several values of initial pellet surface area.

The following conclusions can be drawn from the results of this study:

1. The apparent mechanisms controlling the rate of sorption of uranium hexafluoride by sodium fluoride pellets are transfer of uranium hexafluoride across a stagnant gas film surrounding the pellet, diffusion of gaseous uranium hexafluoride in the pore space of the pellet, and diffusion of uranium hexafluoride through a layer of uranium hexafluoride-sodium fluoride complex covering unreacted sodium fluoride.

2. Sorption of uranium hexafluoride at a point in a sodium fluoride pellet results in a decrease in the volume void fraction, the effective diffusivity of gaseous uranium hexafluoride, and the reaction rate at the point.

3. The maximum quantity of uranium hexafluoride that can be sorbed at a point in a pellet of sodium fluoride depends only on the initial void fraction of the pellet at the point. For void fraction values less than 0.807, incomplete reaction of the sodium fluoride will occur.

1. The pellet is a sphere having a volume equal to the one-eighth-inch right circular cylindrical pellets.
2. The pellet is homogeneous.
3. Radial symmetry.
4. The temperature variation in the pellet is negligible.
5. Radial transfer of UF_6 in the pellet is by diffusion of gaseous UF_6 through an inert gas in the pores of the pellet.
6. The local rate of reaction between gaseous UF_6 and unreacted NaF is of the form:

$$\frac{dq}{dt} = k_1 \frac{e^{-E/RT}}{k_2 + e^{-E/RT}} e^{-bq} (C - C^*)$$

where C^* is the decomposition pressure of the complex.

7. The local effective diffusivity for diffusion in the pores of the pellet is of the form:

$$D_e = D_{\text{UF}_6\text{-N}_2} \gamma \epsilon_0^2 (1 - q/q_{\text{max}})^2$$

Slide 4.

Slide 5. Comparison of Experimental and Model-Predicted Data Showing Variation of Pellet Loading with Time at 100°C and 0.57 Mole Per Cent Uranium Hexafluoride.

Slide 6. Comparison of Experimental and Model-Predicted Data Showing Variation of Pellet Loading with Time at 50°C and 2.35 Mole Per Cent Uranium Hexafluoride.

Slide 7. Comparison of Experimental and Model-Predicted Data Showing Variation of Pellet Loading with Time at 100°C and 8.51 Mole Per Cent Uranium Hexafluoride.

Slide 8. Calculated Values of Effective Pellet Capacity for Pellets having an Initial Void Fraction of 0.45 Showing Effect of Pellet Surface Area.

4. Cessation of sorption of uranium hexafluoride by pelleted sodium fluoride occurs when the pores at the external pellet surface have been filled with complex.

5. The density of the uranium hexafluoride-sodium fluoride complex $\text{UF}_6 \cdot 2\text{NaF}$ is 4.13 grams per cubic centimeter at 26°C.

6. Considerable variation in characteristics exist in individual pellets as well as between pellets of commercial sodium fluoride.