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SEPARATION OF TECHNETIUM-99 FROM URANIUM HEXAFLUORIDE

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SEPARATION OF TECHNETIUM-99 FROM URANIUM HEXAFLUORIDE

The discovery of technetium, element number 43, is credited to Perrier and Segré, who in 1937, artificially produced the element by the deuteron bombardment of metallic molybdenum in the Berkeley cyclotron^{1/}. Technetium is not found in the earth's crust and the most abundant source is that produced in nuclear reactors by the fission of uranium or plutonium. It was from this source that Parker et al.^{2/} in 1946 and later Boyd et al.^{3/} isolated milligram quantities of technetium-99. Technetium in kilogram quantities, at approximately 99 percent purity, was isolated in 1960, by an anion exchange process at the Paducah Plant^{4/}. Final purification and preparation of technetium compounds with this material have been performed at the Oak Ridge National Laboratory^{5/}.

Due to the solvent extraction characteristics of technetium, some of the element produced in nuclear reactors accompanies uranium during the fission product purification process and is found as a contaminant in the uranium trioxide produced. This uranium trioxide, UO_3 , is converted into UF_6 and used as feed to gaseous diffusion cascades for U^{235} enrichment^{6/}.

At the Paducah, Kentucky Gaseous Diffusion Plant, operated by Union Carbide Nuclear Company for the Atomic Energy Commission, we receive from Hanford, Washington UO_3 which has been produced from spent nuclear fuel elements. This UO_3 contains a small amount of technetium-99. Our process for producing UF_6 from this material (figure 1) is to reduce the UO_3 with hydrogen to UO_2 and then to hydrofluorinate the UO_2 to UF_4 with anhydrous HF . The technetium accompanies the uranium quantitatively through these two steps. The UF_4 produced is fluorinated to UF_6 with elemental fluorine in a tower reactor and the nonvolatile metallic impurities along with some unfluorinated UF_4 is collected as a residue. The UF_6 is condensed in cold traps and drained into cylinders. The material is vaporized into the cascade from the cylinders by heating with steam. In this part of the system, technetium predominantly accompanies the uranium, but some of the technetium is contained and concentrated in the nonvolatile metallic fluoride residues. This behavior of

technetium suggested that the material could be recovered by exposing the UF_6 stream to an inorganic fluoride. The first part of the investigation was concerned with finding an inorganic fluoride which had an appreciable affinity for the technetium in the UF_6 stream. We have not identified the technetium compound present in the system although we believe it is ^{either} the hexafluoride, TcF_6 ^{or TcO_3F_2} . Since the compound had not been identified and the major source of technetium for study was in plant-produced UF_6 , a test was designed to use this material. From the standpoint of the plant fluorination process, a sorption column located in the UF_6 gas stream between the fluorination towers and the cold traps was preferred; thus, the scope of testing was limited to plant conditions prevailing at this location (i.e. 200°F , near atmospheric pressure, and a maximum of 1-pound pressure drop across the column).

Preliminary investigations were made by placing various test materials in a 7/8-inch diameter Monel tube, figure 2, and passing 500 grams of UF_6 containing technetium through the powder over a 2-hour period. The temperature was regulated at 200°F and atmospheric pressure was used. The fluorides of nickel, copper, barium, aluminum, magnesium and lithium gave satisfactory results while the fluorides of calcium, sodium and iron and the compounds alumina, uranyl fluoride, and uranium tetrafluoride were not suitable (table 1). Although several of the materials tested compared favorably as to the percentage of technetium recovered, magnesium fluoride was chosen for further study since it is practically insoluble in water, is available as a high surface area powder, has a low uranium adsorption, and is cheaper than other fluoride compounds with these characteristics.

Before magnesium fluoride could be considered further, it was necessary to obtain this salt in a pelletized form. It was found that magnesium fluoride could be pelletized with a commercially available 39-inch pelletizing disc¹ using water as a binder. The size of the pellets could be varied by adjusting the unit, and for test purposes pellets sized from - 1/4 inch to + 1/8 inch were produced. The water was removed from the pellets by air drying and purging with fluorine. The pellets had a 111 M^2/g surface area as determined by the BET method.

Preliminary information indicated that magnesium fluoride would sorb technetium from uranium hexafluoride, but little was known about the retention time necessary to accomplish a high recovery efficiency. The proposed plant location fixed the column temperature, pressure and pressure drop. With these conditions, the only variable to investigate was the effect of gas velocity. A system shown in figure 3 was assembled to investigate the effect of gas velocity in the reactor. UF_6 containing technetium was vaporized through a porous Monel filter and the flow was measured and controlled by a Differential Blind Multiplier across a 0.125-inch orifice. Magnesium fluoride pellets ($-1/4$ inch to $+1/8$ -inch) were contained in a 2-1/2-inch dia. reactor with a bed height of 30 inches. The UF_6 passed through the bed and was trapped in a cylinder cooled in a dry-ice bath. Valves were provided to control the pressure in the bed and to supply nitrogen and vacuum for purging operations.

The data obtained with this system indicated that the sorption efficiency of magnesium fluoride for technetium is dependent on the gas velocity or gas retention time in the reactor. At a superficial gas velocity of 0.95 ft./sec., the recovery efficiency was a maximum of 83 percent at the beginning of the test and decreased rapidly to about 40 percent (figure 4). At a velocity of 0.27 ft./sec., the recovery efficiency was greater than 99 percent until 2.8 g of technetium had been fed to the bed (figure 5). This would correspond to 0.77 percent technetium. At this time, the efficiency started decreasing and after 4.4 g technetium had been fed, the efficiency was zero. These tests indicated that a column of MgF_2 would be a feasible method for removing technetium from UF_6 .

The second phase of the problem was to determine a method of recovering the technetium from the MgF_2 . Two general methods were investigated. One consisted of dissolving the technetium from the pellets in either water or nitric acid and the other was a dry chemical process involving F_2 , O_2 , N_2 or steam.

The technetium sorbed on the magnesium fluoride is not removed effectively by an oxygen, nitrogen or steam purge at 1000°F (table 2). A purge of fluorine is not satisfactory at 500°F, but at 1000°F, 97 percent of the technetium is removed in 5 minutes. A fluorine purge for technetium recovery from the magnesium fluoride has the disadvantages of requiring a relatively high temperature, a second trapping system and the technetium in the stream is contaminated with UF_6 and other volatile metallic fluorides.

Since magnesium fluoride is insoluble in water and dilute nitric acid, these liquids were tested for technetium removal. Both of these materials give good technetium recovery. Water at room temperature removes approximately 95 percent of the technetium while nitric acid shows slightly better results. The advantage of this system is that the magnesium fluoride can be reused by filtration and drying and the technetium in the water can be recovered by the existing anion exchange system at Paducah, Kentucky, or the solvent extraction process at the Oak Ridge National Laboratories.

As the result of this laboratory work, a plant system which consists of two traps in parallel has been installed and operated. The traps are 40 inches in diameter and 48 inches high, and each one contains 1100 pounds of MgF_2 pellets sized between $-1/4$ and $+1/8$ of an inch. The traps are placed in the UF_6 stream immediately after the fluorination towers (figure 6). During normal operation the pressure drop across the traps is less than 0.5 psi. In the first plant test UF_6 containing trace quantities of technetium was processed through the columns and approximately 96 percent of the technetium was retained on the MgF_2 . The traps were removed at this time to check the technetium recovery from MgF_2 . The MgF_2 pellets containing 0.45 percent technetium were leached by circulating 285 gallons of water at room temperature through each trap. Four and six-tenths kg of technetium (93%) were removed from the magnesium fluoride. The solution contained approximately 2.1 g Tc/l, 4 g F/l, 3 g U/l, and other metallic impurities. The MgF_2 pellets were dried by air and then with a fluorine purge and returned to the sorption cycle.

The system described for technetium recovery from UF_6 is currently in operation at the Paducah Plant and most of the technetium available in the United States today has been recovered by this system. Since the technetium in the UO_3 is relatively free from fission products and further purification is obtained in the recovery, the technetium product is extremely pure from other beta emitting materials. Although information is lacking on the mechanisms involved in the recovery system, the method provides excellent separation of the technetium compound from UF_6 and provides adequate technetium recovery.

TABLE 1
RECOVERY OF TECHNETIUM FROM UF_6

	Technetium Recovery, %
Calcium Fluoride	12
Sodium Fluoride	4
Alumina	19
Uranium Tetrafluoride	17
Nickel Fluoride	76
Ferric Fluoride	4
Cupric Fluoride	60
Barium Fluoride	90
Aluminum Fluoride	99
Magnesium Fluoride	99
Lithium Fluoride	89
Aluminum Fluoride (pellets)	48
Uranyl Fluoride	28

TABLE 2
RECOVERY OF TECHNETIUM FROM MAGNESIUM FLUORIDE

Recovery Agent	Type MgF_2	Temperature, $^{\circ}F$	Reaction Time, Minutes	Technetium Recovery, %
Fluorine	pellet	500	180	53
	pellet	1000	180	99.8
	pellet	1000	20	97
	pellet	1000	5	97
Oxygen	pellet	1000	180	26
Nitrogen	pellet	1000	180	18
Steam	pellet	1000	180	36
Water	ground	80	60	97
	ground	160	60	99.5
	pellet	212	10	95
4M HNO_3	pellet	80	60	95
	pellet	160	60	97

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FIGURE 1
 UF_6 PRODUCTION SYSTEM

Figure 2

APPARATUS FOR SCREENING TESTS

Figure 3

LABORATORY APPARATUS FOR DETERMINING T_c LOADING FACTOR

Figure 4
MILLIGRAMS TECHNETIUM⁹⁹ FED
vs
% REMOVED FROM UF_6 GAS STREAM

FIGURE 5

GRAMS TECHNETIUM⁹⁹ FED
VS
% REMOVED FROM UF₆ GAS STREAM

FIGURE 8
FLUORINATION SYSTEM