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INTERIM EVALUATION OF THE FLUOROX PROCESS FOR UF_4 AND UF_6 MANUFACTURE

By
J. E. Moore

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Oak Ridge National Laboratory
Oak Ridge, Tennessee

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INTERIM EVALUATION OF THE FLUOROX PROCESS FOR UF_4 AND UF_6 MANUFACTURE

By

J. E. Moore

May 26, 1955

Work performed under Contract No. W-7405-Eng-26

OAK RIDGE NATIONAL LABORATORY
Operated By
CARBIDE AND CARBON CHEMICALS COMPANY
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

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The conversion of UNH to UF_4 and UF_6, utilizing moving-bed techniques, is being studied; sufficient progress has been made that an evaluation of the process is warranted. The procedures under study, the Fluorox Process, have three major advantages: (1) substitution of HF for high-cost fluorine, (2) considerable reduction in HF requirements, and (3) marked reduction in plant-size and mechanical complexity.

The process involves four major steps (see Fig. 1):

(1) Denitration of UNH to UO_3.

(2) Pelleting of UO_3 with recycled UO_2F_2.

(3) Reduction-hydrofluorination to UF_4.

(4) Oxidation of UF_4 to UF_6 product and UO_2F_2 intermediate.

Each of these steps has been successfully demonstrated and will now require increased effort to complete the program in a reasonable time.

Denitration. The feasibility of continuously denitrating UNH in a moving-bed reactor has been demonstrated in preliminary tests with 1-in. and 4-in. dia. moving-bed reactors. The pelleted feed can contain up to 10% nitrate, without caking in the reactor, representing a 40-60 weight ratio of UNH and UO_3, which requires that 75% of the UO_3 product be recycled for pellet preparation. The reactivity of the UO_3 produced in the moving-bed reactor is equal to or greater than that produced in the existing plants.

Heat for denitration may be supplied by wall-to-bed or gas-to-bed heat transfer. The latter method, utilizing heated, recycled product gases, is preferred. A 4-in. dia. denitration reactor, especially designed for gas-to-bed heat transfer has been fabricated; however, its installation and operation have been delayed pending an evaluation of alternate feed preparation methods.

Alternatives include (1) the development of a suitable, continuous denitration technique that avoids nitrate pelleting, since there is no advantage in producing UO_3 in pelleted form for the Fluorox Process; (2) the use of other compounds such as ammonium diurinate, which might be cheaper than UO_3 to prepare, not only from the nitrate but also from other starting materials; or (3) the feeding of high-grade ores and ore

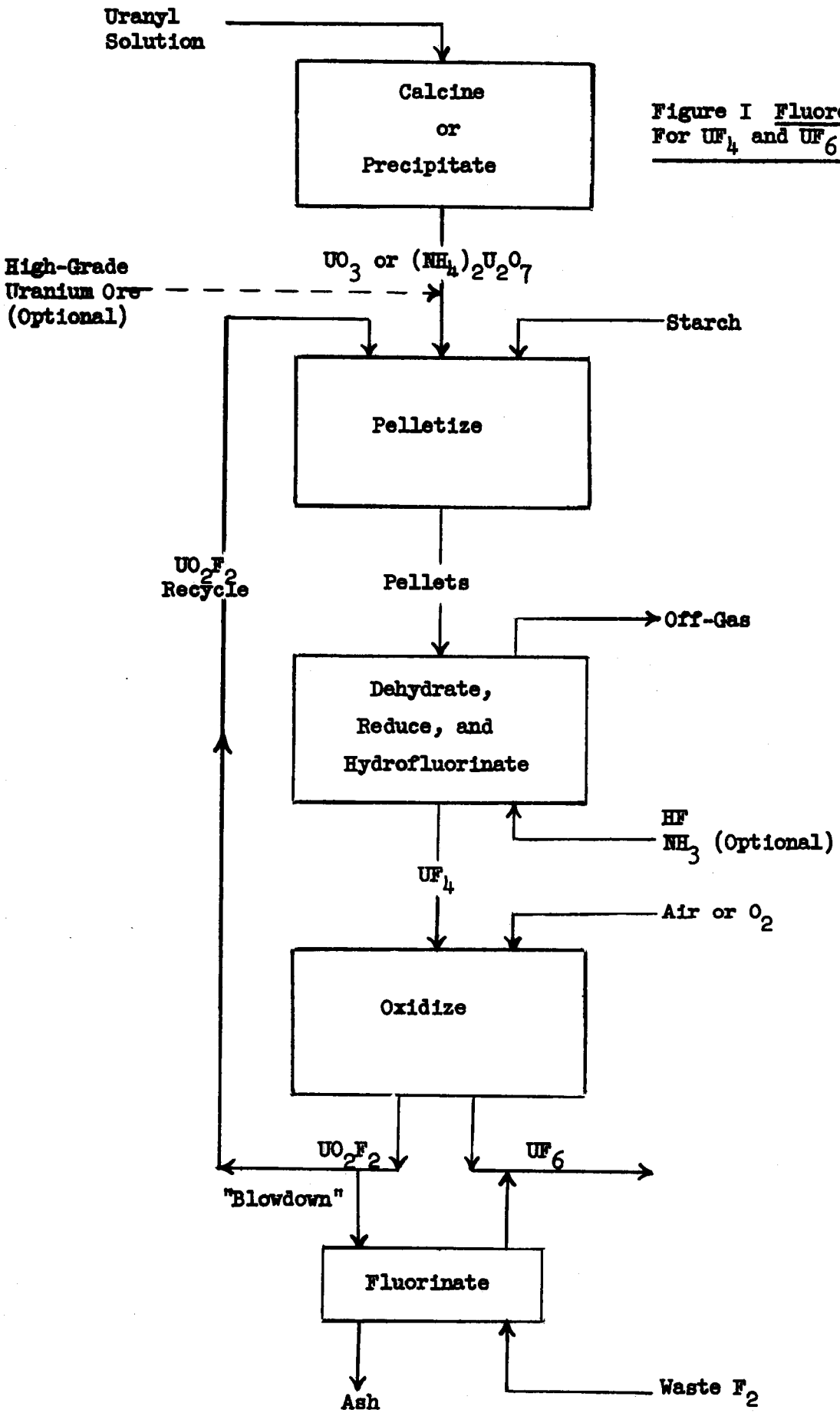

Figure I Fluorox Process For UF_4 and UF_6 Manufacture

concentrates directly.

Since no satisfactory, continuous full-scale method of preparing UO_3 has been developed, a continuing effort to select and perfect the most promising feed preparation technique is warranted; however, the reduction-hydrofluorination and oxidation steps offer much greater savings and therefore should receive the greatest immediate emphasis.

Pelleting. An automatically-controlled pelleting procedure has been developed and demonstrated with several feed materials in a totally-enclosed, integrated facility for 40-min periods at rates exceeding 1000 lbs/hr. Shorter tests at higher feed rates indicated that the unit has a much higher production capacity. The facility contains a special hammermill for mixing and extruding the feed and standard commercial units for conveying, milling and screening the pellets. Operator attention is minimized by an automatic controller, which regulates the pelleting operation by controlling the liquid feed to the hammermill.

The experiences in pelleting numerous feed materials by manual and mechanical techniques (see Table 1) indicate that it should be possible to produce satisfactory pelletized moving-bed reactor feed at high rates in commercial equipment from all of the prospective feed materials. Although the versatility of the pelleting equipment has been demonstrated, additional tests of longer duration and at higher rates will be required in order to (1) perfect operating techniques and (2) determine the maximum capacity of the equipment.

Reduction-Hydrofluorination. The Fluorox Process requires that UF_4 be produced by simultaneous reduction-hydrofluorination of UO_2F_2, UO_3, or other uranium source; consequently, this step has received the greatest amount of effort and therefore is in the most advanced state of development. Of the two reducing agents tested, starch and ammonia, starch is by far the better; however, in the event that carbon-free UF_4 is desired, NH_3 might be used to replace part of the starch. A 4-in. dia. x 5-ft high moving-bed reactor has been employed in 14 tests with NH_3 and in four tests with starch. Variables studied include starch, NH_3, and HF requirements, reactor capacity, bed temperature effect and control, and pellet characteristics.

Table 1

Summary of Experience in Pelleting Moving-Bed Reactor Feed Materials

Feed Mixture		Pelleting Conditions	Results and Conclusions
Materials	App wt. %		
UO_3 H_2O	87 13	Hammermill and associated equipment employed at a rate of 1000 lbs/hr for up to 40-min periods in producing more than a ton of pellets.	Feasibility of continuous large-scale production of hard, porous pellets demonstrated; suitability of equipment determined; automatic control system developed and demonstrated.
UO_3 Starch H_2O	80 7 13	Hammermill and associated equipment tested for 15-min period at rate of 800 lbs/hr.	Suitability of pelleting procedure for this mixture indicated; however, additional tests required to improve technique.
UO_3 UNH	70 30	Molten UNH pumped and UO_3 screw-fed at manually-controlled rates to Hammermill at 1200 lbs/hr for up to 45 minutes.	Feasibility of continuous, large-scale production of UNH-UO_3 pellets demonstrated. Uranyl nitrate solutions containing 50% or more of U can be used.
UO_3 UNH Fines	50 20 30	Recycled, minus 8 mesh fines and UO_3 fed with molten UNH to the Hammermill at 1200 lbs/hr.	Feasibility of recycling all of the fines from the pelleting and milling operations demonstrated.
UO_3 UO_2F_2 H_2O	40 40 20	Small batches manually mixed and pelleted by forcing through a screen.[a]	Hard stable pellets resulted from setting action. Similarity to UO_3-H_2O characteristics indicated automatically-controlled pelleting equipment should be suitable.
$(NH_4)_2U_2O_7$ UO_2F_2 H_2O	40 40 20	Small batches manually mixed and pelleted by forcing through a screen.[a]	Hard, stable pellets resulted after drying at 100°C. Hammermill and associated equipment, plus a drier, should be suitable.

[a]This work done by the Chemical Development Section.

The tests with starch were most successful, with 1300 lbs of UF_4 being produced from UO_3 in 96 hrs of operation. At the peak rate tested, 29 lbs UF_4/hr was produced, with 10% excess HF, with a starch-to-UO_3 weight ratio of 0.080, and with a hydrofluorination efficiency of 99%. This is equivalent to a production rate of 50 lbs of uranium/lb/cu ft of reactor volume, or 7.3 tons of uranium/day in the 15-in. dia. by 10-ft high FMPC pilot plant moving-bed reactor, or 91 tons of uranium/day in the 4.5 ft dia. by 9.5 ft high K-25 "vertical hydrofluorinator" (if adapted for moving-bed operation). In comparison, the present nominal capacity of the K-25 reactor is 3.5 tons of uranium/day in the production of UF_4 from UO_2 powder. Standard reactivity tests, performed at K-25, indicate that the UO_3-starch pellets are highly reactive in conversion to UF_4, with the reactivity equal to that of "activated" UO_3 prepared by the K-25 "hot slurry" process.

The bed temperature profile had a greater effect on the reduction and hydrofluorination efficiencies, with both starch and NH_3, than any other known factor. The reactions started and proceeded spontaneously, rapidly, and with the evolution of heat. A technique was developed for utilizing part of the cooling effect of the HF to compensate for this heat and to maintain the desired bed temperature gradient in the 4-in. dia. adiabatically-controlled reactor. The conditions under which complete conversion to UF_4 was obtained are summarized in Fig. II. The cooling effect of the HF was so great and the reactor was so nearly adiabatic, in the tests, that bed temperature control in a large-diameter reactor is assured.

The results of the ORNL tests with starch and HF in the one-step production of UF_4 from UO_3 have been transmitted to National Lead of Ohio personnel, who plan to conduct a larger-scale test of the process in the 15-in. dia. moving-bed hydrofluorination reactor at the Feed Materials Production Center. Additional moving-bed tests of the process at ORNL are contemplated to:

(1) Test the pellets prepared at the FMPC,

(2) Develop techniques for eliminating traces of carbon in the UF_4 product.

(3) Confirm batch tests, which indicate that UO_3-UO_2F_2 mixtures can be converted readily to UF_4 with starch and HF.

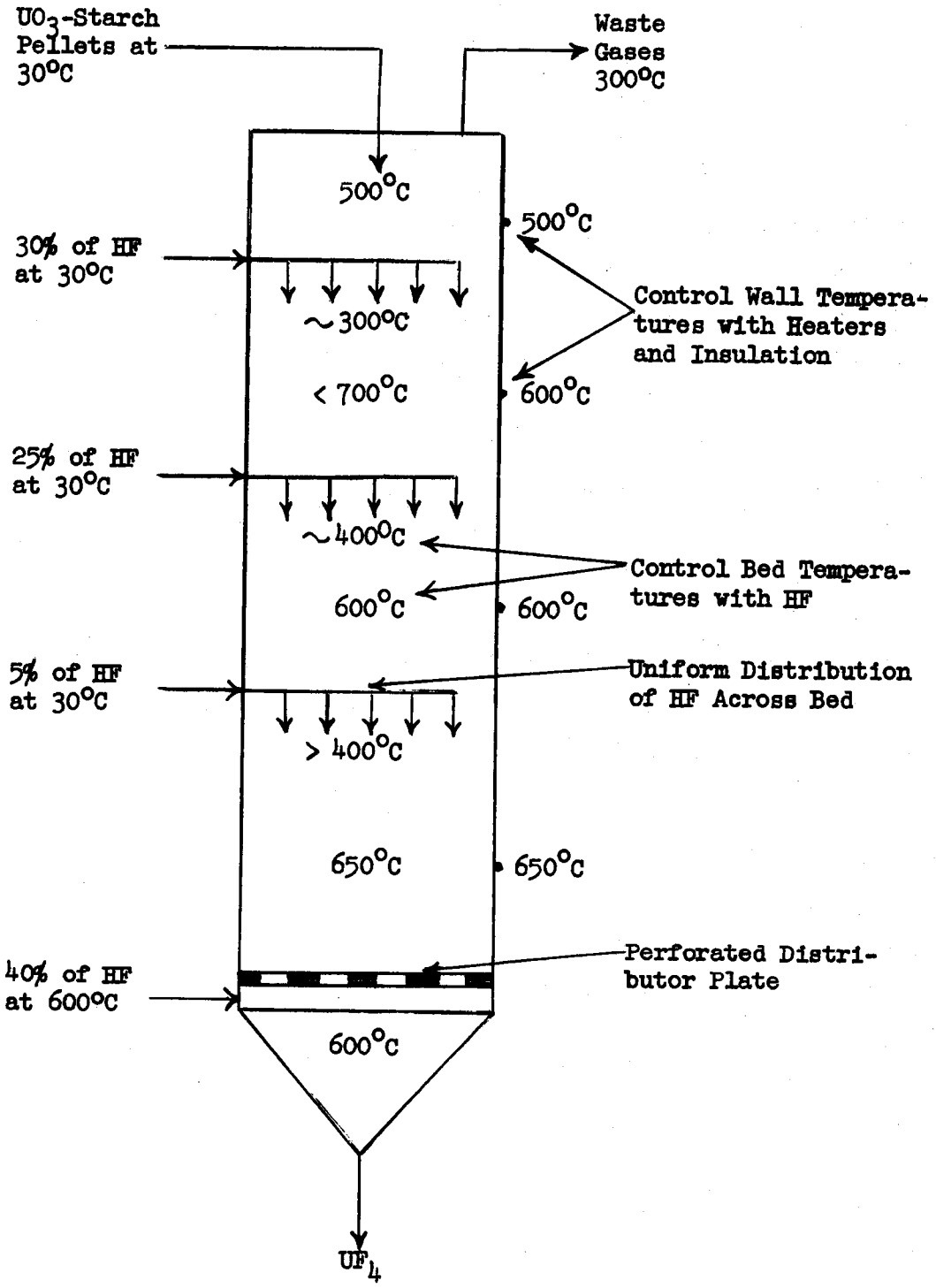

Figure II Operating Conditions For Reduction-Hydrofluorination Reactor

(4) Investigate by the new technique the production of UF_4 from $(NH_4)_2U_2O_7$ mixtures and other feed materials.

Oxidation. The chemical feasibility of converting UF_4 to UF_6 by reaction with oxygen,

$$2UF_4 + O_2 \longrightarrow UO_2F_2 + UF_6$$

instead of elemental fluorine has been demonstrated in a 1-in. dia. x 11-in. long reactor.[a] Pellets of UF_4, produced in the reduction-hydrofluorination reactor, and dry air were passed cocurrently down the reactor. When the bed temperature reached 800°C, from external heating, the UF_4 pellets reacted rapidly to form dimentionally-stable, porous, yellow UO_2F_2 pellets and UF_6 gas. The sharp interface between pellets being fed and the essentially pure UO_2F_2 pellets being produced, which was observed when the bed was withdrawn at the end of the run, indicated that the reaction proceeded rapidly to completion.

The main experimental difficulty was caused by the reaction of UF_6 with a few UF_4 pellets that had passed through the reaction zone before operating temperatures were attained. The intermediates, U_2F_9 and U_4F_{17}, that were formed, caused bridging in the bed. This start-up difficulty can be avoided by filling the reactor with uranyl fluoride pellets initially and feeding UF_4 pellets only when the bed is at 800°C.

Tests of this step of the Fluorox process in the 4-in. dia. reactor are planned in order to investigate on a larger scale (1) reactor capacity, (2) conversion efficiency, and (3) amount of intermediate formation and dust carry-over. A 12-in. dia. reactor has been designed (see Fig. III) for corrosion tests. In this reactor, the walls would be protected from corrosion by external cooling and by an internal, static layer of solid reactants. Only the small, replaceable gas inlet tube would be exposed to the high-temperature, oxidizing conditions.

Future Work. The demonstrated and potential advantages of the Fluorox Process over existing processes for making UF_4 and UF_6 are so great than an increased effort to complete its development is recommended. Potentially, the Fluorox Process should be capable of producing in one operating unit all of the UF_4 now scheduled for production in many sets of equipment in several plants. A second reactor should be able to

[a] Work done by the Chemical Development Section.

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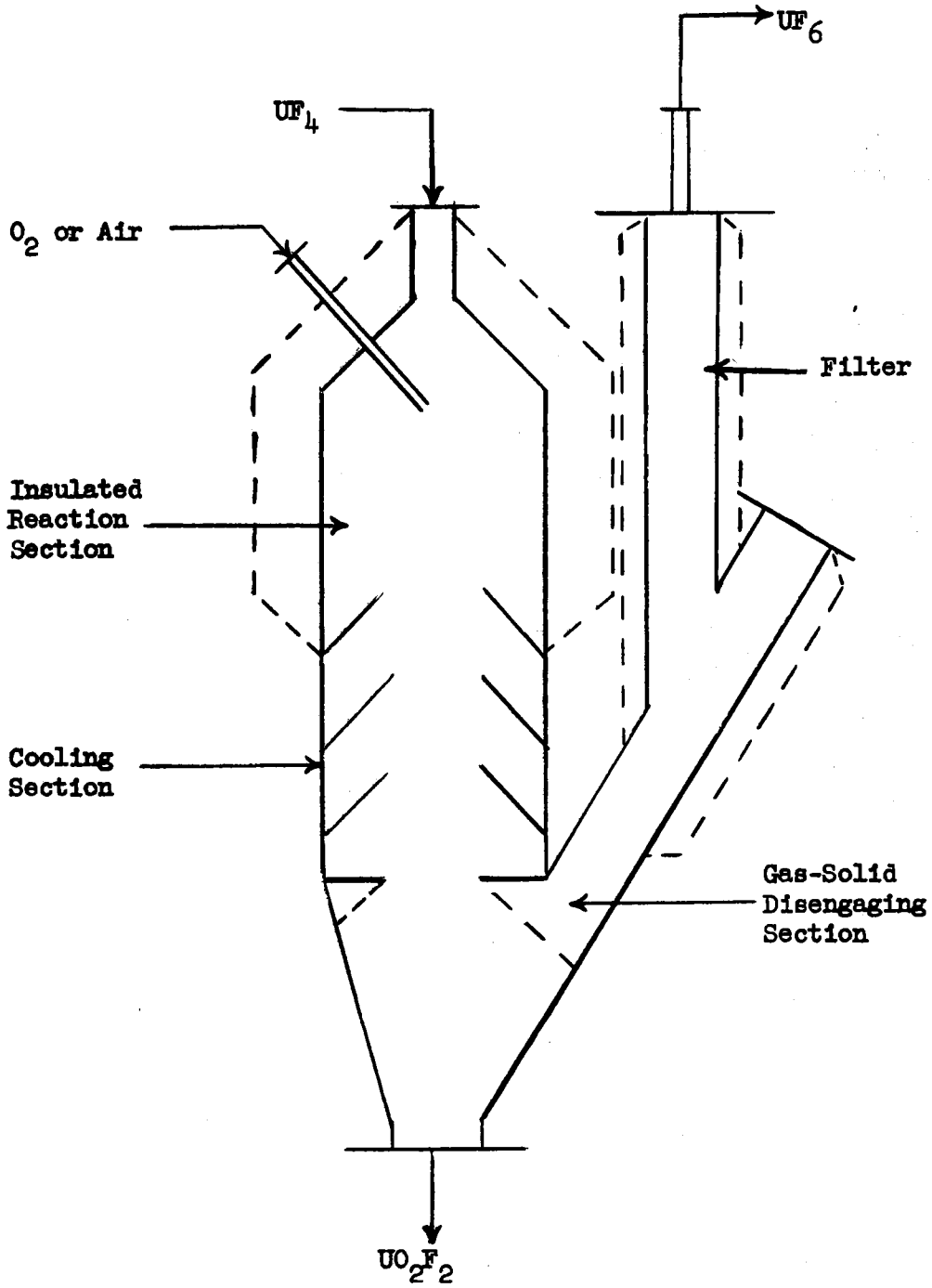

Figure III Preliminary Design of 12-in.-o.d. Oxidation Reactor (4-in. dia. Reaction Zone)

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handle all of the UF_6 production, thereby eliminating the need for large-scale production of high-cost fluorine. These moving-bed reactors would be small in comparison with similar units now being used in the petroleum industry. Undoubtedly, the cost of installing the Fluorox Process could be quickly repaid with savings[1] resulting from reduced production costs.

Most of the problems requiring further study have been mentioned. After the unit operations have been investigated separately, all of the operations required for UF_6 production should be studied in an integrated system, since a UO_2F_2 recycle stream is involved. The extent to which solid impurities can be permitted to accumulate in the UO_2F_2 recycle stream and the size of the UO_2F_2 "blow-down" stream, which should be less than 1% with the present feed materials, need to be determined. Also, the available methods for recovering the uranium from the "blow-down" stream should be evaluated. The Unit Operations Section's participation in the proposed program is estimated as follows:

Fiscal Year	Manpower	Budget
1956	4 MY	$150,000
1957	3 MY	$ 90,000

[1] A comparison of estimated investment and operating costs for the Fluorox Process and present costs in existing plants has been started and will be issued at a later date.

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