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FLUOROX MOVING-BED PROCESS FOR PRODUCING UO_3, UF_4, AND UF_6: BIBLIOGRAPHY

J. E. Moore

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
UNION CARBIDE NUCLEAR COMPANY
A Division of Union Carbide and Carbon Corporation
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CHEMICAL TECHNOLOGY DIVISION

UNIT OPERATIONS SECTION

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AUG 6 1956

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Post Office Box P
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CONTENTS

1.0 ABSTRACT

A partial bibliography of reports on the Fluorox moving-bed process for producing UO_3, UF_4, and UF_6 is given.

2.0 INTRODUCTION

As an aid to other workers concerned with the Fluorox process for producing UO_3, UF_4, and UF_6 in moving-bed reactors, abstracts of the pertinent reports from the author's files are given. This compilation is not a complete bibliography on the subject; however, most of the additional related publications are referred to in the texts of the listed papers. The abstracts are arranged in groups, in chronological order. Although the Fluorox and Excer processes are two distinct processes, some of the discoveries that led to the Fluorox process were made during Excer process studies. Therefore the titles of some of the earlier reports overlap.

Work at ORNL each month is published in a feed materials monthly status report, available from the AEC Technical Information Service Extension, Oak Ridge. These reports are always No. 100 for the month in which they are published. Thus, the status report for May, 1956, the first in the series, is CF-56-5-100; the report for June is 56-6-100. Subsequent reports will be numbered similarly.

3.0 ORNL SUMMARY REPORTS

CF-54-2-130
Feb. 17, 1954

Moving-bed--Excer Cost Comparison, F. E. Harrington, J. E. Moore, J. T. Roberts

Compares Excer and moving-bed estimated costs and indicates that the moving-bed process should be cheaper for converting $UO_2(NO_3)_2$ to UF_4. Gives detailed estimated equipment, plant, and operating costs.

[redacted]

CF-54-6-208
June 3, 1954

Excer: Moving-bed Study for UF_4 Production, Program Statement, J. E. Moore

Describes several moving-bed processes for converting $UO_2(NO_3)_2$ and UO_2 to UF_4. Contains a comprehensive literature survey of the subject.

CF-54-10-144
Oct. 26, 1954

Moving-bed Study for UF_4 Production, Program Statement, F. E. Harrington, J. E. Moore

Gives Chemical Technology Division program for fiscal years 1955 and 1956.

CF-54-12-169
Dec. 9, 1954

Excer: Moving-bed Studies——A Literature Survey Concerning the One-step Production of UF_4 from UO_3, J. E. Moore

Gives 24 references and some original data on reduction-hydrofluorination of UO_3 to UF_4 with NH_3 and HF.

CF-55-5-176
May 26, 1955; also published as ORNL-1985

Interim Evaluation of Fluorox Process for UF_4 and UF_6 Manufacture, J. E. Moore

Gives status of Fluorox process as of publication date, including denitration of $UO_2(NO_3)_2$ to UO_3; pelleting of UO_3 with recycled UO_2F_2; reduction-hydrofluorination of UO_3 to UF_4; oxidation of UF_4 to UF_6 product and UO_2F_2, which is recycled.

CF-55-9-51
Sept. 14, 1955

Preliminary Economic Evaluation of the Fluorox Process for Manufacturing UF_4 and UF_6, J. E. Moore

Presents a process flow diagram, descriptions of the process equipment, and a preliminary economic evaluation of the Fluorox process for producing UF_4 and UF_6 from UO_3. Recommendations for a future experimental program are included.

CF-55-9-149
Sept. 1, 1955

Chemical Technology Information Meeting, Oct. 14, 1955: preprints of "Introduction to Feed Materials Program" and "Fluorox Process for UF_4 and UF_6 Manufacture," J. E. Moore

An introduction to the Fluorox and Excer processes and a summary of the potential technical and economic advantages of Fluorox.

TID-7501
January 1956

Active Process Development Activities for the Processing of Feed Materials

Part 1 is a compilation of papers presented at the feed materials meeting in Cincinnati, Ohio, on Jan. 12, 1956; Part 2 gives the subsequent discussions. Papers were on:

- New developments in the processing of uranium ores
- The Ion Exchange--Excer process for production of metal grade UF_4 from crude uranium sources
- Fluorox process for UF_4 to UF_6
- Fluidized-bed process for the production of UF_4 from uranyl nitrate solution
- Methods of improving the reactivity of UO_3 for the reduction-hydrofluorination process
- Densification of UF_4
- Applications of fluoride volatility process to feed materials

CF-56-1-182
Jan. 27, 1956
(See also supplement of March 28, 1956)

Feed Materials Information Meeting at ORNL, Jan. 27, 1956, F. E. Harrington, I. R. Higgins, J. E. Moore

Gives three papers which were presented at a feed materials meeting on Jan. 27, 1956, at ORNL. Flowsheets and cost estimates for the Excer and Fluorox processes are included. The Excer process is for producing metal-grade UF_4 from ore concentrate, and the Fluorox process produces UF_6 from the concentrate.

4.0 ORNL PERIODIC REPORTS

ORNL-1708
June 14, 1954

Chemical Technology Division Semiannual Progress Report for Period Ending March 31, 1954, Sec. 5.0, Excer Process

Compares moving-bed and Excer processes; shows economic advantage of moving-bed process and states that emphasis on development has been shifted from Excer to moving-bed work.

ORNL-1800
Dec. 28, 1954

Chemical Technology Division Semiannual Progress Report for Period Ending September 30, 1954, Sec. 4.0, Excer Program

Describes the moving-bed process for pelleting of $UO_2(NO_3)_2 \cdot 6H_2O$, denitration of $UO_2(NO_3)_2 \cdot 6H_2O$, pelleting of UO_3-H_2O, and reduction-hydrofluorination of the NO_3 with NH_3 and HF.

ORNL-1881
June 10, 1955

Chemical Technology Division Semiannual Progress Report for Period Ending March 31, 1955, Sec. 10.0, Fluorox Process

Gives a flowsheet of the Fluorox moving-bed process for producing UO_3, UF_4, and UF_6, starting with uranium solutions. Reviews feed preparation, reduction-hydrofluorination to UF_4, and oxidation to UF_6.

Ibid., Sec. 13.0, Excer Process

Reports further studies of the Excer process leading to reduced anode corrosion.

ORNL-2000
Jan. 10, 1956

Chemical Technology Division Semiannual Progress Report for Period Ending September 30, 1955, Sec. 9.0, Fluorox Process

Discusses feed preparation, reduction-hydrofluorination with starch and HF, and oxidation to UF_6, and gives economic evaluation of process.

Ibid., Sec. 10.0, Excer Process

Gives cost estimate, flow sheets, and decontamination data for Excer process.

CF-54-1-85
Jan. 19, 1954

Unit Operations Status Report for Week Ending 1/15/54, p. 2

Engineering evaluation drafted; bench-scale equipment being processed.

CF-54-1-86
Jan. 18, 1954

Unit Operations Status Report for Period Ending 1/8/54, p. 2

Cost estimate finished.

CF-54-1-150
Jan. 27, 1954

Unit Operations Status Report for Week Ending 1/22/54, p. 2

Pelleting of UO_3 started. Drawing of bench-scale moving-bed reactor finished.

CF-54-2-31
Feb. 2, 1954

Unit Operations Status Report for Week Ending 1/29/54, p. 2

Pelleting studies continued. Larger scale pelleting equipment being procured.

CF-54-2-111
Feb. 2, 1954

Unit Operations Status Report for Week Ending 2/5/54, p. 2

Pelleting of UO_3-$UO_2(NO_3)_2 \cdot 6H_2O$ started. Powder-conveying equipment procured.

CF-54-2-117
Feb. 17, 1954

Unit Operations Status Report for Week Ending 2/12/54, p. 3

Pelleting continued. Equipment design and procurement continued.

CF-54-2-164 Feb. 2, 1954	Unit Operations Status Report for Week Ending 2/19/54, p. 2 Pelleting of UO_3-H_2O and UO_3-$UO_2(NO_3)_2 \cdot 6H_2O$ mixtures continued.
CF-54-3-13 March 3, 1954	Unit Operations Status Report for Week Ending 2/26/54, p. 2 1-in.-dia glass denitration moving-bed reactor designed. Design of 4-in.-dia moving-bed reactor facility completed.
CF-54-3-92 March 17, 1954	Unit Operations Status Report for Week Ending 3/5/54, p. 2 Glass denitration reactor fabricated. Moving-bed reactor work delayed by lack of priority. Conference held with Y-12.
CF-54-3-98 March 18, 1954	Unit Operations Status Report for Week Ending 3/12/54, p. 2 Stokes granulator received. Conferences with Feed Materials Production Center (FMPC).
CF-54-3-183 March 31, 1954	Unit Operations Status Report for Week Ending 3/26/54, p. 5 Met with FMPC people and recommended modification to FMPC moving-bed reactor equipment.
CF-54-4-28 April 6, 1954	Unit Operations Status Report for Week Ending 4/2/54, p. 2 UO_3-$UO_2(NO_3)_2 \cdot 6H_2O$ pellets denitrated and reduced in batch reactor.
CF-54-4-139 April 20, 1954	Unit Operations Status Report for Week Ending 4/9/54, p. 2 Denitration of UO_3-UNH pellets in 1-in.-dia reactor successful. Trip to New Brunswick Laboratory.
CF-54-4-193 April 28, 1954	Unit Operations Status Report for Week Ending 4/16/54, pp. 3,4 Operation of 1-in.-dia denitration reactor continued.
CF-54-5-39 May 3, 1954	Unit Operations Status Report for Week Ending 4/23/54, p. 2 Testing of the Fitzpatrick hammermill started.
CF-54-5-53 May 5, 1954	Unit Operations Status Report for Week Ending 4/30/54, p. 2 Reactivity of denitrated UO_3 determined.
CF-54-5-66 May 14, 1954	Unit Operations Status Report for Week Ending 5/7/54, p. 2 2000 lb of UO_3 processed in large-scale pelleting equipment.
CF-54-6-50 June 4, 1954	Unit Operations Status Report for Week Ending 5/28/54, p. 4 Two shakedown runs were carried out in 4-in.-dia reduction-hydrofluorination reactor with NH_3 and HF. Reactivity of UO_3 measured.

CF-54-6-170
June 21, 1954

Unit Operations Status Report for Week Ending 6/11/54, p. 4

Third run in 4-in.-dia reduction-hydrofluorination reactor. Pelleting studies continued.

CF-54-7-30
July 2, 1954

Unit Operations Status Report for Week Ending 7/2/54, pp. 8,9

Solids retention time was 5 hr with 180 and 145% stoichiometric NH_3 and HF. Startup procedure was improved. Time to attain desired temperature gradient was reduced. First product was 65% reduced and 80% hydrofluorinated.

CF-54-7-153
July 16, 1954

Unit Operations Status Report for Week Ending 7/16/54, p. 3

Shakedown run 6 on moving-bed reactor was made with 1/4-in.-dia UO_3 hydrate pellets. They flowed at a uniform rate. Product rate was 10.3 lb/hr with 4.4 hr retention time. The NH_3 was 0.6 lb/hr, and HF was 3.6 lb/hr, or 170 and 130% stoichiometric, respectively. Steam was used to reduce temperature and prevent formation of U_3O_8 in upper 20% of reactor. Did not prevent formation at 550°C.

CF-54-8-164
August 20, 1954

Unit Operations Status Report for Week Ending 8/20/54, p. 3

Pelleting equipment is being installed and cost estimate has been made.

CF-54-8-113
August 13, 1954

Unit Operations Status Report for Week Ending 8/13/54, pp. 5,6

Moving-bed reactor run 7 was made. Maximum reduction efficiency was 80%. UO_3 hydrate pellets used were 1/8 and 1/4 in. dia. Production rate was 8 lb/hr with 6.5 hr retention time. NH_3 and HF were 118 and 113% of stoichiometric, respectively. 1200 lb of pellets was made.

CF-54-9-126
Sept. 17, 1954

Unit Operations Status Report for Week Ending 9/17/54, pp. 3,4

Moving-bed reactor run 8 was made. It was a 58-hr run in which 400 lb of UO_3 hydrate was used; 167 and 214% stoichiometric NH_3 and HF were used; 95% reduction because bed temperature was 700°C. Inconel appears to be a suitable material for construction. Feed material contained 15 ppm of Ni and product contained 170 ppm.

CF-54-10-14
Oct. 1, 1954

Unit Operations Status Report for Week Ending 10/1/54, p. 2

Reactor heating jacket has been rebuilt so that heating elements are adjacent to reactor wall.

CF-54-10-88
Oct. 15, 1954

Unit Operations Status Report for Week Ending 10/15/54, p. 2

Installation of pelleting equipment has been started. Heat losses in 4-in.-dia moving-bed reactor are being measured. The reactor was filled with alundum pellets. The effectiveness of cooling of HF can be evaluated with these measurements.

CF-54-11-52
Nov. 5, 1954

Unit Operations Status Report for Week Ending 11/5/54, pp. 2-4

A review of the system and reactions is presented; operating criteria have been well developed. Included is a report of a trip to the FMPC pilot plant. Their difficulties are listed. Among them were the decreased stability of UO_3 pellets when U_3O_8 was present. Reactor could not be satisfactorily preheated with steam; water condensed in reactor.

CF-54-11-86
Nov. 12, 1954

Unit Operations Status Report for Week Ending 11/12/54, pp. 2-4

Pelleting equipment is complete. Study of heat transfer in bed has been expanded for denitration of uranyl nitrate. Operating conditions for the reactor are tabulated, including the power required.

CF-54-11-146
Nov. 19, 1954

Unit Operations Status Report for Week Ending 11/19/54, p. 3

A rough draft of a report (CF-54-12-169) on a survey of project literature on the one-step production of UF_4 from UO_3 has been completed. The pelleting machine was tested and found satisfactory. A conference was held with the Design Section and the Engineering and Maintenance Division to prepare a construction request for a moving-bed reactor pilot plant at the metal recovery building. The Engineering and Maintenance Division has started on a design.

CF-55-1-62
Jan. 6, 1955

Unit Operations Status Report for December, 1954 (Part II), pp. 26-28

Pellets of UO_3 hydrate were produced successfully at a minimum rate of 700 lb/hr in commercial-scale equipment in which the consistency of the pellets was controlled automatically. The same equipment was adapted and used to produce pellets containing the equivalent of 80 mole % of the uranium as UO_3 and 20 mole % as $UO_2(NO_3)_2 \cdot 6H_2O$, plus 4 wt % H_2O. The longest period of continuous operation was limited to 40 min because of limited availability of UO_3. More extensive tests will be required to assure satisfactory continuous plant-scale use of the pelleting process.

In small-scale batch-denitration tests with pellets containing 40 parts of $UO_2(NO_3)_2 \cdot 6H_2O$ to 60 parts of UO_3, about 50% of the water was removed with only 10% of the nitrate at temperatures below 200°C, and concentrated nitric acid was condensed from the gases evolved at temperatures above 200°C.

The 4-in.-dia moving-bed reactor has been modified for dehydration and denitration tests by use of a wall-to-bed heat transfer mechanism. More extensive modifications will be required for effective testing of the gas-to-bed heat transfer mechanism, which calculations show to be far preferable.

CF-55-1-94
Jan. 28, 1955

Unit Operations Status Report for January, 1955, pp. 16-27

In a second pelleting run, with molten uranyl nitrate and pulverized UO_3, 415 lb of pellets was produced at a rate of about 1200 lb/hr. Satisfactory, uniform operation of the pelleting equipment was maintained throughout the 20-min period. The pellets contained 19 mole % of the uranium as uranyl nitrate and 81 mole % as UO_3.

A 100-lb lot of -3 to +8 mesh pellets, containing nitrate, was continuously denitrated in the 4-in.-dia vertical moving-bed reactor at a rate of 25 lb/hr. Wall-to-bed heating was employed to attain an outlet bed temperature of 355°C. The 4-hr run was satisfactory, uniform flow of the bed was maintained, and equilibrium conditions were established. Fifty per cent of the acid was recovered from the off-gases as 5.4 $\underline{N}$ HNO_3. Theoretical considerations and semiquantitative results from small batch denitrations in the laboratory indicate that over 90% acid recovery as 14 $\underline{N}$ HNO_3 may be feasible if weak acid vapors produced in the top part of the reactor and the more concentrated acid vapors produced at higher temperatures in the lower section of the reactor are removed separately.

Heat transfer data from wall-to-bed heating of alundum balls, dehydration of UO_3 pellets, and denitration of $UO_2(NO_3)_2 \cdot 6H_2O$-UO_3 pellets in the 4-in.-dia reactor and from the New Brunswick Laboratory dehydration of UO_3 pellets in a 3-in.-dia reactor (NYO-2043) are in agreement with the conclusion, based on theoretical considerations, that the denitration capacities of 3 and 4-in.-dia tubes would be approximately the same in a wall-to-bed heat exchanger. A thermal conductivity of 0.10 $\pm$ 0.03 Btu/ft/hr/°F was determined for dehydration of UO_3 and denitration of $UO_2(NO_3)_2 \cdot 6H_2O$-UO_3 pellets.

CF-55-2-185
Feb. 24, 1955

Unit Operations Status Report for February, 1955, p. 18

Fabrication of the 4-in.-dia moving-bed denitration reactor and installation of the auxiliary equipment have been started. Four runs in the reduction-hydrofluorination of UO_3 to UF_4 were carried out in the existing 4-in.-dia reactor. Reduction and hydrofluorination efficiencies were 99 and 90%, respectively. The existing reactor was equipped with the appurtenances needed for conducting exploratory UF_4-to-UF_6 tests with oxygen.

CF-55-3-190

Unit Operations Status Report for March, 1955, pp. 17-19

Shop fabrication of the 4-in.dia stainless steel moving-bed denitration reactor was completed. The existing 4-in.-dia reduction-hydrofluorination reactor was operated in two runs in the one-step conversion of UO_3 to UF_4 with NH_3 and HF. The desired cooling effect of these gases, in compensating for heats of reaction, was much more pronounced with the gases injected directly into the bed instead of through annuli surrounding the reactor wall.

CF-55-4-164 Monthly Progress Report, April 1955, Unit Operations Section, Chemical Technology Division, pp. 17-23

Over 100 lb of UF_4, averaging 97% purity, was produced from UO_3 pellets in the 4-in.-dia moving-bed reactor during 11 hr operation. Starch, incorporated in the pellets, was used as the reducing agent. The amount of anhydrous HF gas needed was less than 110% of the stoichiometric requirement. The solids retention time averaged approximately 5 hr. The dissociative cooling capacity of the HF was used effectively to maintain the bed temperature below 700°C in the adiabatically controlled reactor. The moving-bed test was made after small-scale batch tests indicated that starch would be preferable to sugar or activated charcoal as the reducing agent. Cheaper reductants—butane, propane, and natural gas—are also being considered. CO_2 purge gas is being considered for removing, as CO, any residual carbon in order to obtain metal-grade UF_4. However, residual carbon probably would be desirable in UF_4 pellets to be converted to UF_6 by reaction with oxygen, since heat may have to be supplied for this reaction.

CF-55-5-179 Monthly Progress Report, May 1955, Unit Operations Section, Chemical Technology Division, pp. 11-19

By reaction of UO_3-starch pellets with HF, 1300 lb of UF_4 was produced in the 4-in.-dia moving-bed reactor. A starch/UO_3 ratio of 0.083 and 10% excess HF were adequate for 99% conversion. Under these conditions, the temperature gradient was the only factor that appreciably affected conversion efficiency. The desired bed temperature gradient was effectively maintained by controlling the HF feed temperature and distribution in the adiabatically controlled reactor. Metal-grade UF_4 (over 97%) was produced at a sustained rate of 43 lb/hr/cu ft of reactor volume and at a peak rate of 66 lb/hr/cu ft. The higher rate is equivalent to 7.3 tons of uranium per day in the FMPC pilot plant moving-bed reactor and to 91 tons of uranium per day in the K-25 "vertical hydrofluorinator" (if modified for moving-bed operation).

A 300-lb lot of the UF_4 product was shipped to FMPC for metal-reduction studies. The FMPC is also preparing to carry out a moving-bed pilot plant test in the production of UF_4 from UO_3-starch pellets.

CF-55-6-180 Chemical Technology Division, Unit Operations Section, Monthly Progress Report, June 1955, pp. 23-27

The pelleting facility was successfully operated in a 40-min run at a rate of 600 lb/hr to produce pellets of UO_3, starch, and water.

To demonstrate that the fines from the pelleting operation can be utilized, 33 wt % of -8 mesh fines from a previous run were incorporated in the pellets. The reactivity of these pellets is equal to that of the highly reactive "hot slurry" UO_3 hydrate, as determined in standard reactivity tests at K-25.

Starch-deficient UO_3-starch pellets were converted to UF_4 by simultaneous reaction with NH_3 and HF in an effort to produce a carbon-free product. However, the carbon content of the product was higher and the conversion to UF_4 was lower than when all the reductant was supplied as starch. The data indicated that carbon removal and UF_4 conversion should be considerably improved by elevating the bed temperatures, which can be accomplished by preheating the NH_3.

A series of exploratory batch and moving-bed tests to remove residual carbon from UF_4 pellets by preferential oxidation with O_2, air, or CO_2 was started.

CF-55-7-138 Chemical Technology Division, Unit Operations Section, Monthly Progress Report, July 1955, pp. 8,9

UO_3-starch pellets for moving-bed conversion to UF_4 were prepared manually and in the automatically controlled pelleting equipment. Although the pelleting unit has performed satisfactorily with mixtures containing no recycled fines, difficulties were encountered in pelleting mixtures containing no recycled material.

Batch and moving-bed tests were carried out in a study of factors affecting the carbon content of UF_4 produced from UO_3-starch pellets, and other tests were performed to study preferential removal of carbon from UF_4 by O_2, air, CO_2, and H_2. Results are incomplete.

CF-55-8-157 Chemical Technology Division, Unit Operations Section, Monthly Progress Report, August 1955, pp. 7-18

Small-scale tests indicated the feasibility of removing carbon from pellets with air, O_2, and CO_2. Excessive temperatures caused oxidation of the UF_4. For example, at 428°C, the carbon content was decreased from 0.6 to 0.19% by O_2 without oxidizing the UF_4; and at 565°C, the carbon content was reduced to 0.02% and approximately 2.5% of the uranium was oxidized. A small amount of oxidized uranium in UF_4 for metal production is beneficial. Hydrogen was ineffective in removing carbon.

Moving-bed reactor tests with starch-deficient UO_3 pellets and gaseous HF and H_2 showed that (1) substitution of hydrogen for

13% of the carbon failed to produce carbon-free UF_4, (2) increasing the bed temperature 2 in. below the off-gas level from 150 to 600°C reduced the carbon in the product from 0.5 to 0.12%, and (3) hydrogen shows promise as a reducing agent in the one-step production of UF_4 from UO_3 since 96% reduction was attained.

Small-scale studies with various starches in the reduction of UO_3 indicated that raw powdered corn starch was equal or superior to the other starches tested.

CF-55-9-150 Chemical Technology Division, Unit Operations Section, Monthly Progress Report, September 1955, pp. 8-16

A preliminary economic evaluation of the Fluorox process for producing UF_4 and UF_6 in moving-bed reactors showed that the potential savings are sufficient that the cost of replacing existing equipment with Fluorox units for converting UO_3 to UF_6 should be repaid in about a year.

A 4-in-dia moving-bed reactor was constructed for testing the conversion of UF_4 to UF_6 gas and UO_2F_2 by reaction with air or oxygen. The reactor was lined with refractory U_3O_8 blocks to protect the inconel shell from corrosion. A technique for manufacturing the hard, thermally stable U_3O_8 blocks for this purpose was developed. Tests showed the blocks to be resistant to thermal shock when subjected to rapid temperature changes in the range 20 to 1200°C.

CF-55-10-110 Chemical Technology Division, Unit Operations Section, Monthly Progress Report, October 1955, pp. 7-9

The 4-in.-i.d. moving-bed reduction-hydrofluorination reactor was made ready for additional tests in the one-step conversion of UO_3 to UF_4. A 300-lb lot of UO_3-starch pellets was received from FMPC for testing. The results will be compared with those obtained on the same material in the 14-in.-i.d. FMPC reactor. A 200-lb lot of UO_3-starch pellets, containing 35% of the stoichiometric amount of starch, and a 200-lb lot of UO_3 hydrate pellets, containing no starch, were prepared for testing the simultaneous reduction-hydrofluorination of UO_3 to UF_4 with hydrogen and HF gases.

Calculations indicate that it may be possible to develop a procedure for converting ore concentrates, containing 15% or more impurities, directly to UF_6 by the Fluorox process with little or no fluorine being required. A representative 30-gal shipment of the ore concentrate was requested for use in testing the scheme.

CF-55-11-176 Chemical Technology Division, Unit Operations Section, Monthly Progress Report, November 1955, pp. 5-10

Three lots of UO_3 pellets were tested in the 4-in.-i.d. moving-bed reduction-hydrofluorination reactor in the one-step conversion of UO_3 to UF_4. The 300-lb lot of UO_3-starch pellets prepared at FMPC was reacted with HF at three distinct reactor bed temperature gradients. With the low temperatures typical of those obtainable in the FMPC moving-bed reactor, 90% conversion to UF_4 was experienced. With the higher temperature gradient normally used in the ORNL reactor, 98% conversion was attained. With inadequate cooling from the HF, the conversion dropped to 88%. These data confirmed the temperature gradient previously specified for this reaction. The other two lots of UO_3, one with 35% of the stoichiometric amount of starch and one with no starch, were incompletely converted to UF_4 when reacted simultaneously with H_2 and HF gases.

The 4-in.-i.d. oxidation (UF_4 to UF_6) reactor was installed and tested in two inconclusive shakedown runs in which the desired temperatures (800-900°C) were not attained. It is planned to increase the carbon content of the UF_4 feed in order to obtain the added heat needed.

CF-55-12-154 Chemical Technology Division, Unit Operations Section, Monthly Progress Report, December 1955, pp. 8-11

Reactivity tests have confirmed the indications observed in moving-bed runs that the UO_3-starch pellets produced at FMPC were less reactive in conversion to UF_4 than those produced at ORNL. The reason for this difference has not been determined.

The 4-in.-dia oxidation reactor has been operated in four additional exploratory runs to determine the effect of temperature on conversion of UF_4 to UF_6 with oxygen. The preheating temperature and carbon content of the pellets were varied in an attempt to obtain the optimum operating temperature in the reactor. Preliminary indications were that the optimum temperature would be reached with UF_4 pellets containing 0.4% carbon when preheated to about 600°C. No appreciable intermediate formation or dust entrainment was encountered. When bed temperatures (probably over 900°C) were excessive, the bed fused. The fused material, containing about 12% fluoride, could not be remelted at 1100°C.

CF-56-1-175 Chemical Technology Division, Unit Operations Section, Monthly Progress Report, January 1956, pp. 10-14

Three additional exploratory runs were made in the 4-in.-i.d. moving-bed oxidation reactor in the conversion of UF_4 to UF_6 and UO_2F_2 with oxygen. Satisfactory operation was experienced throughout one run with UF_4 pellets containing o.4% carbon, preheated to 625°C. The conversion efficiency with 100% excess

oxygen, during a residence time of 1.5 hr, was calculated to be 90%. Negligible amounts of intermediates, dust, and fluorocarbons were formed.

CF-56-2-154 Chemical Technology Division, Unit Operations Section, Monthly Progress Report, February 1956, pp. 24-30

Small-scale pelleting and reduction-hydrofluorination studies were successful in producing UF_4 from Hanford screw-calcined UO_3, from ore concentrate, and from UO_2F_2-ore concentrate mixtures. Reactivity studies indicated that it should be possible to efficiently process all these materials to UF_4 in the first step of the Fluorox process.

Another in a series of exploratory runs was carried out in the 4-in.-i.d. moving-bed oxidation reactor in the conversion of UF_4 to UF_6 and UO_2F_2 with oxygen. The operating conditions found to be optimum last month were attained for 1.5 hr of steady operation.

CF-56-3-177 Chemical Technology Division, Unit Operations Section, Monthly Progress Report, March 1956, pp. 13-19 (same information reported in CF-56-5-100)

A 24-hr run in the 4-in.-i.d. moving-bed reductor-hydrofluorinator confirmed small-scale studies, which indicated that UO_3 produced in the Hanford continuous calciner can be readily converted to fluorination-grade UF_4 (over 95%) by reaction with starch and HF in a moving-bed reactor. Since the UF_4 contained 0.4% carbon, which would make it unsuitable for conversion to UF_6 by reaction with elemental fluorine, 400 lb of UF_4 was treated with oxygen to remove the carbon. Over 90% of the carbon was removed at 600 to 700°C, without loss of fluoride or uranium, and with less than 2.5% oxidation of the uranium to the hexavalent state.

CF-56-4-210 Chemical Technology Division, Unit Operations Section, Monthly Progress Report, April 1956, pp. 22-30 (same information reported in CF-56-6-100)

The 4-in.-i.d. reduction-hydrofluorination and oxidation reactors were modified to improve their operability. The modified oxidation reactor was tested in two exploratory runs, in which the bed temperatures were too low for efficient conversion of UF_4 to UF_6 by reaction with oxygen when UF_4 containing 1.0% carbon, preheated to 700°C, was used. In a test of the removal of residual carbon from UF_4 produced in the reduction-hydrofluorination reactor, the carbon content was reduced from 0.3 to 0.012% by combustion with O_2 at 680°C, without appreciable oxidation of the UF_4; however, portions of the bed that were overheated were partially converted to UO_2F_2 and UF_6.

5.0 OTHER REPORTS ON MOVING-BED REACTORS

NYO-1178
Dec. 5, 1952

Evaluation of the Moving-bed Process for the Production of Green Salt, H. H. Bulkowski et al.

Presents a preliminary process design and cost estimate of a new processing technique for the preparation of green salt (UF_4) from orange oxide (UO_3). The technique involves the application of the moving-bed principle for the contacting of solids with gases, a method which has been widely used in petroleum cracking. This is the first of a series of detailed reports prepared as part of a long-range survey program to explore and develop the possibilities of improving feed material processes.

NYO-2039

Summary Report on the Long-range Program for the Period Ending February 15, 1953, C. J. Rodden (New Brunswick Laboratory)

Contains data on moving-bed process for preparation of UO_2 and UF_4; fluidized process for production of UO_2 and UF_4; production of uranium metal from uranium oxides; extractive distillation of HF from its aqueous solution; and recovery of HF from magnesium fluoride scrap.

NYO-2040

Summary Report on the Long-range Program for the Period February 16 - April 30, 1953, C. J. Rodden, Director, New Brunswick Laboratory

Contains data on moving-bed process for the preparation of UO_2 and UF_4; production of uranium from uranium oxide; and recovery of anhydrous HF from its aqueous solution.

NYO-2044

Quarterly Progress Report for the Period Ending September 30, 1953, pp. 6-19, "Moving-bed Green Salt Process," R. LeGassie, E. Roszkowski

Modifications of existing laboratory processes for the extrusion, dehydration, and denitration of hydrated UO_3 pellets are discussed. Moving-bed reduction and hydrofluorination runs are described.

NYO-2045

Ibid. for December 31, 1953, pp. 6-25, E. S. Roszkowski et al.

Moving-bed reduction and hydrofluorination tests were carried out in production of UO_2 and UF_4. Specification-grade UF_4 was produced by re-hydrofluorination.

CF-54-3-170

FMPC Visit, March 18 and 19, 1954, R. E. Blanco, W. K. Eister, J. E. Moore

Reviews early design of FMPC moving-bed reactors and recommendations by the authors of modifications to improve operability. Other subjects discussed included spray calcination for raffinates; recovery of uranium from bomb liner slag; and preparation of ThF_4.

CF-54-4-175 — New Brunswick Laboratory Visit, April 9, 1954, R. E. Blanco, N. A. Krohn, J. E. Moore

Reviewed the status of the NBL work on the moving-bed process for UO_3 and UF_4 production.

CF-55-2-150
Feb. 17, 1955 — FMPC Trip Report, J. E. Moore

Reviewed the practices and problems in operation of the FMPC moving-bed reactors and lists suggested improvements to the FMPC reactors and to the process in production of UF_4 from UO_3.

CF-55-5-98
May 16, 1955 — Trip Report, FMPC, W. K. Eister and J. E. Moore

Discusses starch-UO_3 pelleting and reduction-hydrofluorination.

NLCO-600 — Summary Technical Report for the Period October 1 - December 31, 1955, Sec. 9.2, "Hydrofluorination Runs 28 and 29," W. Burkhardt et al. (4 pages)

In a moving-bed reactor hydrofluorination run in which 2/3 of the HF was routed to manifolds in the upper section of the reactor, the lower section of the reactor was not adequately heated. In another hydrofluorination run, pellets containing 7% starch were used as feed, operational difficulties were encountered, and the product, which had a carbon deposit on the surface, had a maximum UF_4 content of 85%.

CF-56-2-8
Feb. 3, 1956 — Trip Report, FMPC, F. R. Bruce, W. K. Eister, and J. E. Moore

Discusses results of reduction-hydrofluorination in moving-bed reactors.

6.0 PRODUCTION OF UO_3

K-444
July 15, 1949 — Spray Decomposition of Uranyl Nitrate Solutions to Uranium Trioxide, A. L. Allen et al.

A method employing the thermal decomposition of atomized uranyl nitrate solutions has been developed for the preparation of a more reactive UO_3.

K-1086
Feb. 22, 1954 — Thermal Decomposition of Uranyl Nitrate Hexahydrate, W. S. Wendolkowski and S. S. Kirslis

The thermal decomposition of uranyl nitrate hexahydrate was studied at 41.8, 75.6, and 126.3°C.

CF-54-6-60
June 9, 1954

Denitration of Uranyl Nitrate Hydrate, J. E. Moore

Compares spray calcination and moving-bed calcination of uranyl nitrate. Gives detailed data on moving-bed denitration.

CF-54-10-137
Oct. 27, 1954

Status of Moving-bed Denitration Studies, N. A. Krohn

Describes laboratory-scale pelleting and denitration of uranyl nitrate.

CF-55-1-92
Jan. 18, 1955

ORNL Expansion of Metal Recovery Facility

Discussion includes small denitration facility for uranyl nitrate.

CF-55-1-97
Jan. 18, 1955

FMPC Trip Report, F. E. Harrington

Reviews denitration of uranyl nitrate to UO_3 and nitric acid recovery.

CF-55-4-40
April 6, 1955

Laboratory Study of Denitration and Reduction in the Moving-bed Process, N. A. Krohn

Describes laboratory work on denitration of uranyl nitrate to UO_3 and reduction to UO_2 in moving-bed reactor studies.

7.0 PRODUCTION OF UF_4

MCW-1
April 1, 1946

The Preparation of Pure Uranyl Nitrate from Black Oxide, C. R. Conard

Early work at Mallinckrodt refinery.

MCW-118
July 15, 1948

Equilibrium Ratio of Hydrogen Fluoride and Water in the Fluorination of Uranium Dioxide at High Temperatures, C. W. Kuhlman, Jr.

ISC-97
Aug. 21, 1948

The Use of Ammonium Bifluoride in the Preparation of Fluorides from Oxides, J. R. Long

Thorium, zirconium, zinc, and lead were converted to anhydrous fluorides by reaction with $NH_4F \cdot HF$.

MCW-142
Oct. 12, 1948

Reduction of Uranium Trioxide to Uranium Dioxide with Hydrogen, C. W. Kuhlman, Jr.

MCW-144
Oct. 19, 1948

Fluorination of Uranium Trioxide; Rate and "Apparent Equilibrium" Studies, C. W. Kuhlman, Jr.

MCW-175
March 14, 1949

Reduction of Uranyl Fluoride with Hydrogen, C. W. Kuhlman, Jr.

K-404
June 1, 1949

Conversion of Uranyl Fluoride to Uranium Tetrafluoride with Gaseous Reactants, H. A. Bernhardt et al.

Various methods were studied for the conversion of UO_2F_2 to UF_4 with gaseous reactants. H_2, NH_3, CCl_4, and Freon-12 were used in combination with HF or alone for the conversion. H_2 reduction of UO_2F_2 followed by hydrofluorination gave best conversion with a minimum number of undesirable features.

MCW-215
Sept. 2, 1949

Reduction of Uranium Trioxide with Hydrogen-Nitrogen Mixtures, C. W. Kuhlman, Jr.

MCW-217
Sept. 8, 1949

Reduction of Uranium Trioxide with Anhydrous Ammonia, C. W. Kuhlman, Jr.

K-657
Sept. 14, 1950

Conversion of Uranium Trioxide to Uranium Tetrafluoride, S. Bernstein et al.

Comparative data have been obtained on separate and simultaneous reduction and hydrofluorination of calcined UO_3 (low surface area) and spray prepared UO_3 (high surface area). When the two-step process of separate reduction and hydrofluorination was employed, no significant difference in the reactivity of the oxides was observed. However, when the simultaneous reduction and hydrofluorination method was employed, the high surface area oxide was more readily converted to UF_4.

K-680
Nov. 10, 1950

Electrochemical Preparation of Uranium Tetrafluoride, A. L. Allen et al.

First of two reports on electrochemical preparation of UF_4 from UO_3 (or UO_2F_2).

K-1009
May 7, 1953

A Laboratory Test for Evaluation of Uranium Trioxide as Feed Material, J. S. Fox

A laboratory comparative conversion test for UO_3 to UF_4 has been developed. The precision is 5%. The successful applications to feed plant problems and in development of hydration process technology for improved feed material are described.

K-1043
Oct. 10, 1953

Hydration of Uranium Trioxide for Improving Feed Materials Processing, J. S. Fox

The reactivity of UO_3 toward H_2 reduction and subsequent hydrofluorination to UF_4 has been increased by hydration. Two large-scale hydration processes were developed.

CF-54-7-57
July 12, 1954

Differential Equations for $UO_3 \cdot H_2O$ - UF_4 Converter and Analog Computer, S. H. Jury

Reviews data required to construct an analog computer to simulate a moving-bed reactor for converting $UO_3 \cdot H_2O$ to UF_4 with NH_3 and HF in one step.

CF-54-12-12
Dec. 2, 1954

Differential Equations for $UO_3 \cdot H_2O$ - UF_4 Converter and Analog Computer, S. H. Jury

Supplements CF-54-7-57.

ANL-5363
Dec. 30, 1954

Fluidized-bed Process for the Production of Uranium Tetrafluoride (Green Salt) from Uranyl Nitrate (Interim Report), A. A. Jonke et al.

This interim report describes a proposed new processing technique for the production of UF_4 from uranyl nitrate solution. This technique involves the application of the fluidized-bed principle for the contacting of gases with powdered solids. In addition, this report describes a new application of fluidization developed at this laboratory and applied to the denitration of uranyl nitrate to produce UO_3.

Denitration rates of 100 lb/(hr)(sq ft) were demonstrated.

Bench-scale equipment for reduction and hydrofluorination has been constructed. One reduction run was completed.

CF-55-11-130
Nov. 29, 1955

The Ion Exchange-Excer Process for the Production of Metal-grade UF_4 from Crude Uranium Sources, I. R. Higgins

This report discusses two separate developments which tie together as a unit to produce metal-grade UF_4 without solvent extraction purification. The first development is the Higgins continuous countercurrent ion exchange contactor for treating all leach pulps and delivering a crude concentrated product, partially purified. The second development is an ion exchange conversion of crude uranium salt solutions to UO_2F_2 with subsequent electrolytic reaction to UF_4. The emphasis in this report is centered on the production of high-purity metal at the uranium ore mill site.

K-1251 — Oak Ridge Gaseous Diffusion Plant Quarterly Report, Oct. 1 - Dec. 31, 1955, pp. G-33 - G-38, "Feed Manufacture"

Discusses UO_3 reactivity tests; evaluation of Hanford continuous-calciner oxides; fluidization studies; vibrating tray studies; fluorine recovery.

ORNL-1696
March 19, 1956 — Development of Excer Process: I, I. R. Higgins and J. T. Roberts

A flowsheet, based on laboratory studies, for the Excer process for producing UF_4 from dilute uranyl nitrate solution is given. The uranium is sorbed on hydrogen-form cation-exchange resin and desorbed with aqueous HF. The resulting UO_2F_2 in dilute solution is electrolytically reduced, and the ppt, $UF_4 \cdot 3/4\ H_2O$, is dried and dehydrated.

ORNL-1979
March 27, 1956 — Ibid. II, J. A. Marinsky

Later developments in the Excer process, particularly with the ion-exchange membrane electrolytic cell.

CF-56-2-161
Feb. 29, 1956 — Removal of Carbon from UF_4 Pellets by Oxidation, L. M. Ferris

This report is concerned with the laboratory-scale removal of carbon from UF_4 pellets by combustion with oxygen. All attempts were about 75% effective at 600°C in removing 0.1 to 5.0 wt. % residual carbon from UF_4 pellets, which had been prepared from UO_3 by starch reduction and hydrofluorination in a single moving-bed reactor.

8.0 PRODUCTION OF UF_6

K-567
March 15, 1950 — The Reaction of Uranium Tetrafluoride with Dry Oxygen, S. S. Kirslis et al.

The reaction $2UF_4 + \text{dry } O_2 \longrightarrow UO_2F_2 + UF_6$ has been studied. A temperature of 740°C is required to initiate the reaction, which is rapid at 830°C. A 60% yield of UF_6 was obtained.

In the appendix the removal of carbon from UF_4 is discussed. At 550°C removal is slow, but at 650°C, the carbon content was reduced to 0.02%. There was little or no increase in hexavalent uranium.

K-819
Sept. 30, 1951

The Direct Fluorination of Belgian Congo Ore, R. H. Harrison

A study was made to determine the feasibility of the removal of uranium from Belgian Congo ore by successive treatment of the ore with HF and F_2. The UF_6 produced by this method was of sufficient purity to be fed directly to the gaseous diffusion cascade.

AERE-C/R-863
Feb. 13, 1952

A Study of the Reaction between UF_4 and O_2, C. J. Mandleberg, D. Davies

The reaction between UF_4 and O_2 was studied in detail. Reaction conditions, yields, and the nature of the residues formed are discussed.

ANL-5504
Jan. 1, 1956

Status Report on Development of Fluoride Volatilization Methods for Processing GE and ANPD Type Fuels, R. K. Steunenberg et al.

Describes a brief study of treatment with BrF_3 and related procedures for recovery of uranium as UF_6 from fuel elements.

9.0 CORROSION

BMI-255
Oct. 31, 1951

Progress Report on Corrosion Studies Connected with the Refining of Uranium, F. W. Fink et al.

The behavior of ten stainless steel alloys in cracked NH_3 at high temperature and the corrosion of metals and alloys in 50-70% HF are discussed. Work was started on the behavior of stainless steel in nitric acid.

BMI-268
June 15, 1953

Corrosion-Resistant Materials for Hydrofluoric Acid, H. A. Pray et al.

The behavior of metals and plastics in 38 and 48% aqueous hydrofluoric acid solutions at 50°F, 140°F, and the boiling point; of 50, 65, and 70% HF at 140°F; and of anhydrous hydrogen fluoride at 50°F was investigated.

CF-54-9-177
Sept. 27, 1950

Metallographic Examination of Thermocouple Wells from a Moving-bed Reactor, R. J. Gray

Inconel exposed to H_2O, HF, NH_3, and UF_4 at 120-790°C was almost unaffected.