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PREPARATION OF YTTRIUM FLUORIDE IN FLUIDIZED BEDS

by

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I. ABSTRACT

The batch fluid-bed hydrofluorination of yttrium oxide to yttrium fluoride of low residual oxygen content was studied in a 3-inch Monel column. Bed temperature, hydrofluorination time, and hydrofluoric acid excess were studied, and the contamination due to equipment corrosion was determined. A sample of the fluoride was converted to metal and analyzed for impurities. A brief investigation of the reaction kinetics was also made on the thermobalance.

II. SUMMARY

Yttrium fluoride with approximately 0.10 per cent residual oxygen and 85 ppm nickel was prepared from Michigan Chemical Company yttrium oxide in nine hours at 600 C by batch, fluid-bed hydrofluorination in a three-inch diameter Monel column. Metal prepared from the fluoride was found to be equivalent in purity to current production material. Yttrium oxide, produced by Dow Chemical Company, was hydrofluorinated, to residual oxygen contents of 0.10 to 0.15 per cent in seven hours at 600 C and 700 C.

Extrapolation of the data from the fluid-bed tests indicates that 14-hour batch hydrofluorinations in a 12-inch diameter unit at 600 C should give equivalent conversion on oxide charges of one hundred pounds. Additional development work would be required to determine whether a continuous process is feasible.

III. INTRODUCTION

Yttrium is separated from the rare earths with which it is usually associated by the use of ethylenediaminetetraacetate (EDTA) solutions on cation exchange columns.⁽¹⁾ The eluate is treated with oxalic acid to precipitate yttrium oxalate which is then calcined to the oxide. Both Dow Chemical and Michigan Chemical Companies (MCC) have produced the pure oxide. The Dow oxide has been reported to be less reactive toward hydrofluorination in the preparation of yttrium fluoride.

The fluoride from which metal is made by reduction with calcium⁽²⁾ has been produced at Ames Laboratory by direct hydrofluorination in batch rotary reactors.⁽³⁾ An Inconel tube charged with fifty pounds of oxide is

inserted in an electrically heated furnace. Anhydrous hydrofluoric acid gas is passed over the oxide as the furnace temperature is raised to 700 to 750 C during a 5- 6-hour period and held at this temperature for an additional three hours. The tube and its contents are rotated intermittently during the last three hours. Other methods of preparing the fluoride, such as reaction of the oxide with ammonium bifluoride at a temperature of 125 C,⁽⁴⁾ and hydrofluorination of compounds other than the oxide,⁽⁵⁾ have been investigated with varied success.

The hydrofluorination of yttrium oxide is rapid and highly exothermic (162 kcal/mole of oxide*). Conversion levels above 99 per cent are desired because unconverted oxide enters the metal, and poor fabrication properties of the metal are primarily attributed to the presence of non-metallic inclusions including yttrium oxide.⁽⁶⁾

The use of the fluid-bed technique was considered for the hydrofluorination reaction because of the high heat-transfer coefficients available in fluidized beds and the good temperature control which minimizes local overheating and sintering. It was hoped that these characteristics would permit greater conversion in shorter residence time.

The purpose of this brief program was to determine the degree of conversion attainable in a fluid-bed system and to obtain a preliminary estimate of the time-temperature cycle required.

IV. TYPES OF OXIDES

Samples of the Dow and Michigan oxides were received as minus 325-mesh powders. These were compacted on a smooth-roll flaking machine made by the Komarek and Greaves Company of Chicago, Illinois, and then ground. A fraction between 40 and 200 mesh was separated as feed material. In addition a batch of unground oxide, about 85 per cent plus 40 mesh, was obtained from the Michigan Chemical Company. This material required no compacting, only a light grinding, to produce a fluidizable fraction suitable for use in the reaction column. Bulk densities and surface areas of the bed fractions were as shown in Table I.

TABLE I
Physical Characteristics of Yttrium Oxides
(40 to 200 mesh fraction)

Type of Oxide	Bulk Density g/cu cm	Surface Area, sq m/g
Dow Chemical, Ground ^a	2.0	11.0
Michigan Chemical, Ground ^a	1.9	10.1
Michigan Chemical, Unground	1.1	-

^aCompacted and granulated

*Calculated from data in Glassner, Alvin, "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500 K," ANL-5750, 1957.

The ground Michigan oxide and the Dow oxide are similar both in bulk density and surface area; the greater porosity of the unground Michigan oxide is apparent from its low bulk density.

V. APPARATUS AND PROCEDURE

The tests were conducted in a three-inch diameter Monel column, 3½ feet high (Figure 1). The upper one-foot section was an expanded, six-

inch diameter disengaging section containing two nine by three-inch porous Monel bayonet filters (Grade G, 10-micron pore size, Micrometallic Co.) to retain entrained solids. The filters were kept clean by blowing back with a heated nitrogen stream. A porous Monel plate (Grade F, 20-micron pore size, Micrometallic Co.) was used as a fluidizing gas distributor. The reactor was heated electrically with four 1000-watt calrods wound on the unit; temperature control was maintained manually with Variacs. Thermocouples were installed in the gas inlet, at

two points in the bed zone, and in the filter zone. The weight of the bed was indicated by a manometer connected to pressure taps in the column.

Batch runs were made using two to four pounds of oxide as a charge. The bed was initially fluidized with nitrogen. Superficial gas velocities ranged from 0.5 to 0.7 ft/sec, about 50 per cent above the minimum fluidizing velocity for the bed. When a bed temperature of 150 C was reached, anhydrous hydrofluoric acid gas, metered through an orifice from a cylinder mounted on a scale, was combined with the nitrogen stream. The gases were preheated in a packed tube mounted in a furnace. As the temperature rose, the acid rate was adjusted to control the reaction and limit the bed temperature to the desired value. As the run proceeded, the nitrogen flow (except for line purges) was gradually reduced to zero (usually within 1½ hours of start-up). The off-gas containing excess hydrofluoric acid, water of reaction and nitrogen passed to a partial condenser, then to a caustic scrubber, and was finally exhausted to the stack.

Bed samples were taken through a purged side-entering tap during the run and from the discharged bed at the end of the run. The bed was discharged through a bottom draw-off; small amounts of powder remaining on the porous plate and on the filters were collected separately.

VI. RESULTS

The operating conditions and analytical results for all of the completed runs are summarized in Table VII. The effects of specific variables on the degree of conversion are discussed below. Runs were compared on the basis of residual oxygen content of the fluoride determined by spectrographic intensity ratio analyses⁽⁷⁾ at Ames Laboratory and by a KBrF_4 fluorination method⁽⁸⁾ at ORNL. In a number of cases there was disagreement between the methods which prevented drawing firm conclusions as to the effect of the process variable studied. The spectrographic method is not calibrated in terms of absolute oxygen content, but intensity ratios of 0.4 to 0.5 correspond to approximately 1000 ppm oxygen. Total fluorine was determined by a pyrohydrolysis method.

A. Thermobalance Reaction Rate Studies

A brief investigation of the yttrium oxide-anhydrous hydrofluoric acid reaction was made on a thermobalance. The equipment utilized a reaction tube furnace and a Sartorius analytical balance equipped with a recording head and amplifier and had a sensitivity of 0.1 milligram.

One-half to two-gram samples of oxide were reacted. Tests were made at 600 C on the Dow oxide and the unground Michigan Chemical oxide. The anhydrous hydrofluoric acid rate was about 13 g/hr. Preliminary tests showed an initial weight loss of about 2 per cent when heating the sample in nitrogen, probably due to the loss of carbon dioxide.⁽⁹⁾ This initial weight loss was followed by a small gradual weight gain before the introduction of the anhydrous hydrofluoric acid. This was apparently due to reaction with anhydrous hydrofluoric acid desorbed from the walls of the unit.

The data are plotted in Figure 2 as per cent weight gain, assuming 2 per cent adsorbed carbon dioxide in the sample. The initial phase of the reaction was extremely rapid. The Dow oxide reacted initially somewhat more slowly than the Michigan oxide, but the overall conversions after 20 minutes were comparable. The rates of both materials slowed significantly at about three-fourths completion. A difference between the Michigan and Dow oxide reaction rates is evident. The data are typical of results obtained in the fluid-bed tests, an initial rapid conversion (at times to 95 per cent) followed by a much slower rate of conversion.

B. Effect of Fluidized-Bed Temperature

Typical data to show the effects of bed temperature on the degree of hydrofluorination in fluid-bed runs are shown in Table II. In equivalent run periods (7 hours), greater conversion was achieved at 600 C than 500 C. Some additional improvement was obtained at 700 C (although on the Dow

oxide the KBrF_4 analyses indicate the reverse trend). The data indicate that the Michigan oxide converted to a slightly greater extent than the Dow oxide, reported to be somewhat less reactive, although the residual oxygen contents of both were in the range of 1000 to 1500 ppm. Two methods were used to reach the operating temperature - a gradual increase over a two or three-hour period or a rapid increase in about 45 minutes; little difference in results was noted.

FIGURE 2
THERMOBALANCE TESTS ON THE HYDROFLUORINATION OF YTTRIUM OXIDE

TABLE II

Effect of Bed Temperature on Degree of Conversion
(Hydrofluorination Time - 7 Hours)

Temp (C)	Michigan Oxide		Dow Oxide	
	Intensity Ratio ^a	O ₂ by KBrF_4 Fluorination, (%)	Intensity Ratio ^a	O ₂ by KBrF_4 Fluorination, (%)
500	-	0.62	-	-
600	0.52 to 0.54	0.10 to 0.27	0.72	0.12
700	0.40	0.12	0.49	0.16

^aRatio of oxygen and argon line intensities when sample is arced in known pressure of argon gas; 0.4 to 0.5 corresponds to about 0.1 per cent O₂.

C. Effect of Hydrofluorination Time

Data showing the effect of hydrofluorination time on degree of conversion are summarized in Table III. Results of seven and nine hours of continuous hydrofluorination at 600 C were essentially the same as results of 10- and 11-hour runs made in two passes, the intensity ratios ranging from 0.38 to 0.44 and KBrF_4 oxygen analyses being near 0.10 per cent. Similarly at 500 C, a 12-hour continuous hydrofluorination was equivalent to or perhaps slightly better than two 7-hour exposures (Runs 17 and 20, Table VII). Conversion to oxygen contents below 0.10 per cent, therefore, proceeds at an exceedingly slow rate.

TABLE III

Effect of Hydrofluorination Time on Degree of Conversion
(Temperature - 600 C)

(Bed Material - Michigan Chemical Co. Oxides
Hydrofluoric Acid Excess - $\sim$ 900 per cent)

Hydrofluorination Time, (hrs)	Intensity Ratio	O_2 by KBrF_4 Fluorination, (%)
7	0.40	0.12
9	0.38 to 0.42	0.06 to 0.11
10 ^a	0.43	0.10
11 ^a	0.44	-

^aMade in two passes.

D. Effect of Hydrofluoric Acid Excess

The analytical data shown in Table IV are not in good agreement with respect to the two methods of oxygen determination, but the indications are that a 10-fold stoichiometric excess of hydrofluoric acid at 600 C gives consistent conversion with intensity ratios near 0.4 and KBrF_4 oxygen analyses of about 1000 ppm. The Dow material showed residual oxygen content near 1500 ppm for similar excesses. A 500 per cent excess gave poorer conversion, both at 500 and 600 C. The time variable was not isolated in the runs shown in Table V, but comparison of runs made for similar durations (for example Runs 2 and 24, Table VII) also indicates that better conversion is obtained with larger reagent excesses.

TABLE IV

Effect of HF Excess on Degree of Conversion
(Bed Material - Michigan Chemical Co. Oxides)

Approximate HF Excess, (%)	Temp (C)	Intensity Ratio	O ₂ by KBrF ₄ Fluorination, (%)
590	500	-	0.62
1560	500	0.54 to 0.63	0.10 to 0.14
500	600	0.54	0.27
1000	600	0.38 to 0.49	0.06 to 0.11

TABLE V

Nickel Content of Fluoride Products
(Bed Material - Michigan Chemical Co.
oxide except where noted)

Temp (C)	Run	Length of Run (hr)	Nickel Content ^a (ppm)
500	12	7	50
	20	12	46
600	23	9	78
	24	9	87
700	3	7	192
	8	7	188

^aColorimetric analysis.

E. Other Variables

Other variations in operating procedure included the use of a nitrogen diluent in the fluidizing gas stream during an entire run (Runs 9 and 11) and the mixing of converted material with fresh oxide (50-50 mixture, Run 14). These procedures were intended to reduce the initial rapid reaction and decrease sintering, but no improved conversion was noted.

F. Corrosion Contamination

The extent of contamination of the yttrium fluoride product due to equipment corrosion during hydrofluorination is shown in Table V as determined by the nickel content of the run products. Starting oxides contained less than 10 ppm of nickel. The data show a slight increase in nickel pick-up between 500 and 600 C and a larger increase between 600 and 700 C. To meet the desired qualities of low metallic impurities and low oxygen content, operation at 600 C appears satisfactory.

G. Reduction of the Fluoride to Metal and Metal Analysis

Yttrium metal is obtained by reduction of the fluoride at 1000 C with magnesium, calcium, and calcium chloride; a low melting yttrium-17 per cent magnesium alloy and a molten slag of calcium fluoride-calcium chloride of lower density are formed. The alloy is "de-magged" by vacuum distillation and arc-melted at a reduced pressure of 55 mm, producing a small ingot.

The fluoride prepared by batch hydrofluorination of Michigan Chemical Company oxide at 600 C for nine hours (combined products of Runs 23 and 24) was reduced to metal at Ames Laboratory. The analysis of the ingot is shown in Table VI.

TABLE VI

Analysis of Yttrium Metal Produced from
Fluoride Products of Runs 23 and 24

Calcium	250 ppm	Calcium	190 ppm
Nitrogen	175	Magnesium	32
Fluoride	750	Silicon	135
Oxygen	2250	Nickel	270

These analyses and visual observation (by Ames Personnel) of the slag separation and of the alloy indicate that the metal is equivalent to Ames' production material. For optimum application, the yttrium metal must have a minimum of metallic impurities and low oxygen content.

The nickel content of the metal ingot is twice that calculated from the nickel content of the fluoride assuming all the nickel remains in the metal; however, the oxygen content of the fluoride, approximately 1000 ppm, and the metal are in good agreement, as approximately 1000 to 1500 ppm oxygen are introduced in the reduction process.⁽¹⁰⁾ Further reduction of the oxygen content of the fluoride is desirable and might be accomplished by increased contact time.

TABLE VII

Summary of Run Conditions and Analytical Results on Fluid-bed Preparation of Yttrium Fluoride

Run	Type of Oxide	Oxide Charge (lb)	Temp (C)	Total Run Time (hr)	HF Excess Over Stoichiometric Requirements (%)	Total Fluoride ^a (w/o)	Oxygen/Argon Intensity Ratio	O ₂ by KBrF ₄ Fluorination (w/o)
2	MCC Ground	1.3	600	10	790	39.0	0.43	0.10
3	MCC Ground	2.0	700	7	840	39.0	0.40	0.12
5	Dow	2.0	600	7	870	38.4	0.72	0.12
7	MCC Ground	1.5	700	7	1270	38.8	0.49	0.08
8	Dow	2.0	700	7	640	38.0	0.49	0.16
9 ^b	MCC Ground	2.0	700	7	220	37.0	-	-
11	Run 9 Product	-	700	7	690 ^c	37.6	1.02	0.25
12	MCC Ground	2.0	500	7	590	37.8	-	0.62
13	MCC Unground	2.0	600	7	900	39.2	0.52	0.097
14	1.0 lb Dow Oxide plus 1.0 lb Run 8 product	-	700	7	-	38.2	-	0.10
15	MCC Unground	4.0	600	7	500	38.6	0.54	0.27 ^d
16	Run 15 Product	-	600	4	890 ^c	39.0	0.44	-
17	Run 12 Product	-	500	7	1560 ^c	-	0.63	0.14
20	MCC Unground	2.0	500	12	1550	38.5	0.54	0.12
23	MCC Unground	3.0	600	9	900	39.0	0.38	0.11
24	MCC Unground	3.0	600	9	1060	39.0	0.42	0.055
23+24	Combined Products Converted to Metal	-	-	-	-	39.1	0.38	0.12

^aTheoretical fluoride - 39.06 w/o.^bFluidization gas 1/3 anhydrous hydrofluoric acid, 2/3 nitrogen throughout run.^cCumulative.^dRechecked - same result.

VII. CONCLUSION

Good conversion of yttrium oxide to the fluoride at 600 C and 700 C was demonstrated in the three-inch diameter fluid-bed column. Operation at 600 C results in significantly less nickel contamination. The limited duration of the program did not permit optimization of variables such as bed height, hydrofluoric acid excess and fluidizing gas velocity. Consideration of a fluid-bed spray calcination step in the yttrium process is suggested for conversion of the ion-exchange column eluant directly to the oxide, to be followed by hydrofluorination to the fluoride.

Based on the conditions used in the preparation of the fluoride batches which were converted to metal, a 12-inch diameter column operating batch-wise in 14-hour runs at 600 C should give equivalent conversion on oxide charges of 100 pounds. A fluidizing gas velocity of 0.9 ft/sec would be required to obtain ten-fold excesses of hydrofluoric acid and to maintain good fluidization. Additional development work should be performed to investigate advantages of a multistage continuous unit in reducing hydrofluoric acid excess and producing purer fluoride.

VIII. ACKNOWLEDGEMENT

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Operation of the equipment was performed by M. Jones and R. Finley.

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