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TECHNOLOGY—FEED MATERIALS

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REACTION RATE OF THE FLUORINATION OF URANIUM DIOXIDE
AT A CONTINUOUSLY INCREASING TEMPERATURE

by

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SUMMARY

Using an apparatus described in a preceding paper, the reaction rate of the fluorination of Uranium Dioxide by Hydrofluoric acid was measured under the condition of a gradually increasing temperature. Uranium tetrafluoride made in this way does not show caking although final reaction temperatures ranged as high as 700°C. The rate of reaction was found to be greater than the rate measured under isothermal conditions at the highest temperature attained during the continuous increase as long as this final temperature is above 550°C.

EXPERIMENTAL

The apparatus described in a previous report was employed for these experiments. A 2,000 g sample of the same "standard" uranium dioxide used for the work reported in the above mentioned report was placed in the furnace, and the apparatus swept free of air with nitrogen. The furnace was then heated to about 200°C, and the HF flow substituted for the nitrogen. The temperature of the furnace was then continuously increased as the reaction proceeded until a desired maximum was reached. If the reaction was not complete at this point the furnace was maintained at the desired temperature until reaction reached completion. The progress of the fluorination was followed as described previously.

At the completion of the run, the sample was cooled in an atmosphere of HF to 200°C and in H₂ to below 100°C before it was withdrawn for observation.

The results of four runs differing in the rate at which the temperature was increased are tabulated below and plotted in figures 1 & 2. The temperature time curves are denoted by outline points and the fluorination curves by solid points.

Run 1 (200 - 655°C)

Time	Temperature	$\frac{\Delta W \times 100}{326}$
0 min.	200°C	0%
5	301	10.0
8	350	16.6
10	385	20.4
15	445	31.6
20	500	42.2
25	542	51.8
30	575	61.0
35	604	70.0
40	630	77.8

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45	650	83.7
50	653	87.0
55	653	90.0
60	655	92.9
65	655	95.1
75	655	97.7
85	655	99.2
100	655	99.2

Run 2 (190 - 535°C)

Time	Temperature	$\frac{\Delta W \times 100}{326}$
0 min.	190°C	0%
5	208	3.38
10	255	7.37
15	292	12.3
20	325	19.9
25	355	27.0
37	408	36.2
48	442	44.6
60	46.5	52.9
75	485	63.0
90	498	69.7
105	512	76.0
120	520	81.5
135	525	84.9
150	530	88.1
180	533	91.8
210	533	95.2
240	534	96.3
270	534	97.8
300	534	98.5
345	535	98.8

Run 3 (210 - 738°C)

Time	Temperature	$\frac{\Delta W \times 100}{326}$
0 min.	210°C	0
4	293	8.59
6	325	12.89
8	357	19.6
12	415	25.8
16	455	33.8
21	505	44.5
27	555	55.5
34	600	68.2

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40	630	77.7
46	655	84.8
51	672	90.7
55	683	93.6
60	695	96.8
65	707	97.1
70	715	97.1
76	725	97.7
90	738	97.7

Run 4 (250 - 650°C)

Time	Temperature	$\frac{\Delta W \times 100}{326}$
0 min	250°C	0%
4	265	6.45
8	312	12.6
12	350	20.6
17	395	27.9
24	445	37.2
36	510	54.9
45	547	64.8
59	585	77.2
70	605	86.4
80	622	92.8
85	626	95.6
91	632	96.9
102	640	97.9
110	645	98.4
120	650	98.4

Uranium tetrafluoride made by this technique was very easily broken into a granular powder in contrast to material made isothermally at temperatures above 500°C. The mechanism responsible for this caking phenomenon is unknown at present.

In the following table the time required for complete reaction as determined from curves in figures 1 & 2, the temperature of the furnace at complete reaction, and the time required to carry the reaction to completion under isothermal conditions at approximately the same maximum temperature are recorded.

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Run	Increasing Temperature		Constant Temperature
	Time for Complete Reaction	Temperature at Completion	Time for Complete Reaction
1	85 min.	650°C	100 min.
2	345	535	210
3	60	695	70
4	95	640	100

The reaction was completed in a shorter time when the temperature was increased during the fluorination in the three runs with the highest final temperature. It is believed that there is a correlation between this increased reaction rate and the absence of caking in the product. It is very plausible that the process of caking decreases the diffusion rates of the two gases (HF and H₂O) through the solid serving to decrease the reaction rate. When the reaction is carried out at constant temperature below 550°C, caking is less severe hence the reaction rate is not improved by a gradual temperature increase.

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Figure 1.

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Figure 2.

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