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TECHNOLOGY—FEED MATERIALS

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THE PREPARATION OF URANIUM TRIOXIDE

FROM URANYL NITRATE SOLUTION

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Written by: Harold Yeager

Work done by:

R. W. Bragdon, C. D. Harrington
J. A. Kyger, R. R. Midlan, J. R.
Ruhoff, H. E. Thayer, H. L. Wibbels,
J. H. Yeager

Contribution of:

Mallinckrodt Chemical Works
H. V. Farr, Technical Director

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THE PREPARATION OF URANIUM TRIOXIDE
FROM URANYL NITRATE SOLUTION

I. PURPOSE

To convert pure uranyl nitrate ($UO_2(NO_3)_2$) solutions into uranium trioxide.

II. DISCUSSION

In the proposed uranium dioxide plant at Mallinckrodt Chemical works, it became necessary to convert pure uranyl nitrate into uranium trioxide powder as an intermediate product in the preparation of uranium dioxide. It was later desired to produce a finished product of UO_3 which contained less than 1.5% combination of water and nitrate as impurities. An experimental program on a plant scale had to be undertaken to determine the correct conditions necessary to produce this pure UO_3 .


III. EXPERIMENTAL

A. Laboratory Experiments

Laboratory experiments for converting uranyl nitrate to uranium trioxide may be divided into two groups: (1) thermal decomposition of uranyl nitrate solution to uranium trioxide with evolution of oxides of nitrogen, and (2) precipitation of uranium salt with ammonia or hydrogen peroxide.

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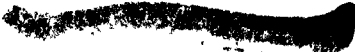
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A uranyl nitrate solution was heated in a stainless steel evaporating dish over a sand bath until a solid material was formed. The water solution of uranyl nitrate used had a boiling point of 130°C. Oxides of nitrogen started to evolve at 202°C. At a temperature of 230°C the material hardened to the point where stirring with a rod was impossible. The conversion to UO₃ had been accomplished and the only problems left by this process was plant equipment capable of powdering the hard cake formed in making UO₃.

Another method of thermal decomposition was tried in which uranyl nitrate hexahydrate crystals were slowly added to a heated stainless steel pan so that each addition immediately flashed to UO₃. This method had possibility for equipment giving continuous decomposition. However, time did not permit further investigations along this line.

Cold, strong ammonia water was added to a cold water solution of uranyl nitrate until the slurry was distinctly alkaline to litmus paper. An orange-yellow precipitate was formed which filtered slowly, though not impossibly for plant filtration. The cake obtained was dried at 120°-130°C and a lumpy cake was formed which could be easily powdered.



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Cold H_2O_2 solution was added to a strong solution of uranyl nitrate. A yellow precipitate was formed which was extremely difficult to filter.

B. Plant Experiments

The method for converting $UO_2(NO_3)_2$ to UO_3 by thermal decomposition was chosen and equipment was installed. The container used was a fifty-gallon, cylindrical, thirty-inch inside diameter by twenty inches, one-half inch thick, 347 stainless steel kettle. The kettle was heated by a gas-fired furnace. Stirring was accomplished by a large, single-blade stirrer powered by a geared 7-1/2 horsepower motor. Fumes from the decomposition products were vented to a nitric acid recovery unit. Figure 1 shows the complete apparatus used.

A uranyl nitrate solution which had been concentrated to a boiling point of $117^\circ C$ was added to the kettle and stirring and heating was begun. The contents of the kettle were found to undergo the following changes:

- (1) The uranyl nitrate was concentrated by further boiling.
- (2) Oxides of nitrogen were evolved.
- (3) An orange pasty material was formed.
- (4) A thick lumpy material was formed.
- (5) An orange powder was formed.
- (6) The evolution of oxides of nitrogen ceased.

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After the completion of the decomposition of uranyl nitrate to uranium trioxide, the kettle was found to contain about 75% powder which would sift through a thirty-mesh screen. The remaining 25% was very hard cake which had to be chipped off the walls of the kettle.

C. Preparation of Purified Uranium Trioxide

The uranium trioxide produced as an intermediate in the production of uranium dioxide usually contained a combination of water and nitrates which was greater than two per cent. It was desired to make a finished product of UO_3 which contained less than 1.5% combination of water and nitrate (measured by loss on ignition at $525^{\circ}C$). It was also desired that the U_3O_8 in the purified UO_3 be less than 0.1%. Hence, a testing program was undertaken in the production plant to determine the proper operating conditions for producing pure UO_3 .

The only control used in heating the kettles used in the plant was by measuring the stack temperature of the burned gases. Although the stack temperature gives a good indication of the quantity of heat supplied to the pot, the stack temperature does not give a good indication of the actual temperature of the material in the kettle. Because it was difficult to install a thermometer inside the kettle, a thermocouple was

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welded on the center of the bottom of the pot and the thermocouple was insulated to give an approximate temperature of the wall of the kettle. Temperature readings were taken for a normal cycle in the kettle and the data are shown in Figure 2.

Laboratory experiments had indicated that U_3O_8 was not formed at a temperature less than $525^{\circ}C^*$. An inspection of Figure 2 will show that the powder temperature only reached $850^{\circ}F$ ($454^{\circ}C$). Hence, it might be possible to remove the excess of water and nitrate by continued heating so that the powder temperature never exceeded $525^{\circ}C$. Hence, a number of runs were made in which extended heating was applied after powder had formed. The extended heating was controlled by the stack temperature. Runs were made to stack temperatures of $650^{\circ}F$, $600^{\circ}F$, and $400^{\circ}F$. Samples of the powder were tested at time intervals after powder was formed. The results obtained are tabulated below.

* Bragdon, R. W. and French, C.L., The Loss on Ignition Test for Chemical 264 Purified, Mallinckrodt Chemical Works. November 10, 1944, 40-188.

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Run No.	Stack Temp. °F	Elapsed Time after Powder Formed Hours	Loss on Ignition at 525°C %	HCl Insolubles ^(a) %
1	650	1.0	1.80	0.002
1	650	1.75	1.37	0.003
1	650	3.25	0.88	0.008
1	650	3.50	0.86	0.008
2	600	1.0	2.03	0.002
2	600	3.0	0.60	0.005
3	600	1.0	0.15	0.001
3	600	3.0	0.12	0.003
4	400	0	7.48	0.001
4	400	3	1.30	0.020
4	400	4	1.25	0.025
5	400	1	4.29	0.001
5	400	3	1.19	0.002

(a) The percent X_3O_8 was measured by the per cent of the powder insoluble in HCl.

On the basis of the results obtained above, it was believed that UO_3 of sufficient purity could be made by continued heating in the kettles at a stack temperature of 600°F for a period of two hours.

IV. SUMMARY

Uranyl nitrate can be converted into uranium trioxide by thermal decomposition. This can be accomplished in gas-fired 347 stainless steel kettles with proper agitation to break up the hard cake which forms.

By controlled subsequent heating, UO_3 can be obtained which contains only a trace of water, nitrate, and X_3O_8 . Continued heating of the powder may be sufficiently controlled by the stack temperature of the burning gases.

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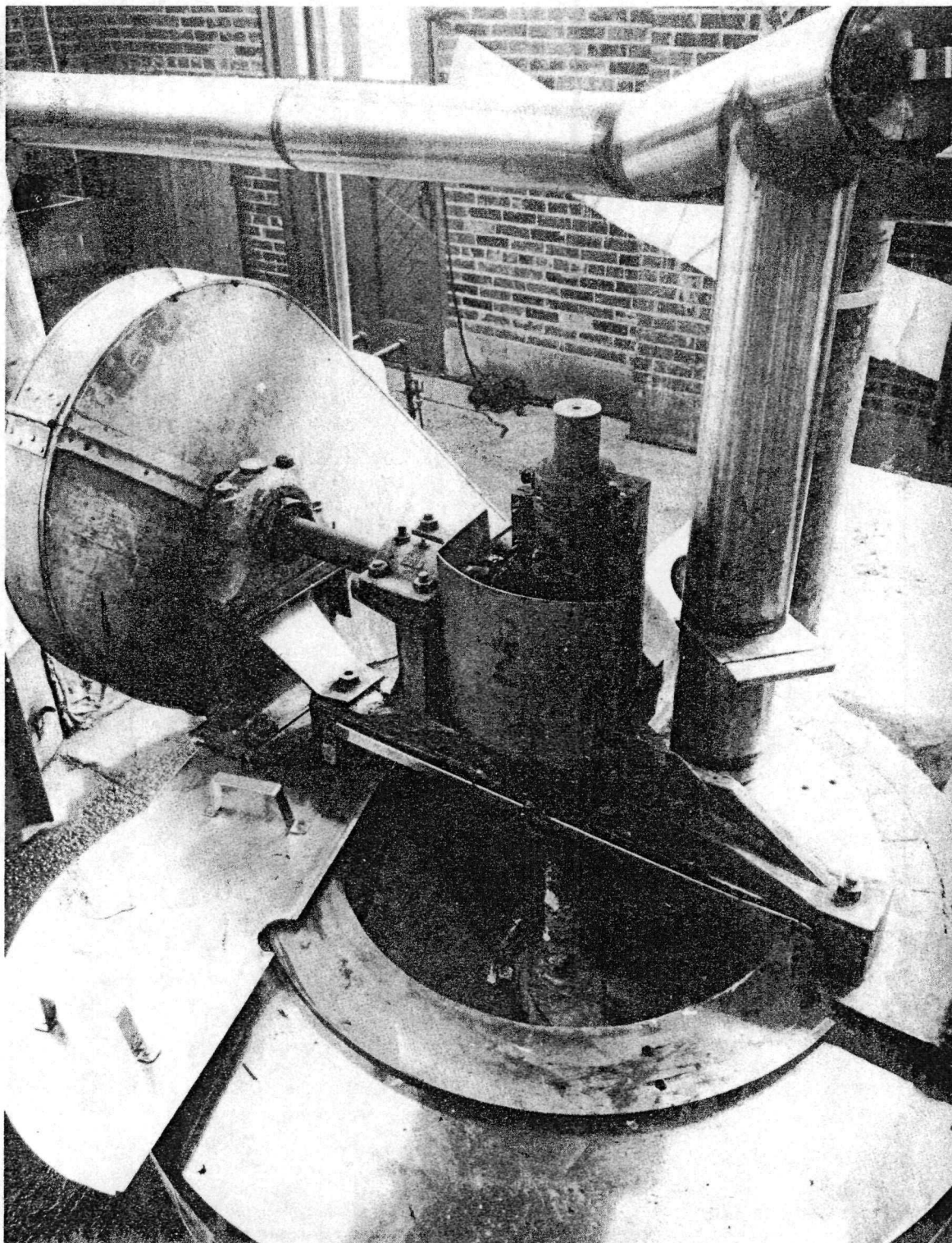


Figure 1--Decomposition Kettle.

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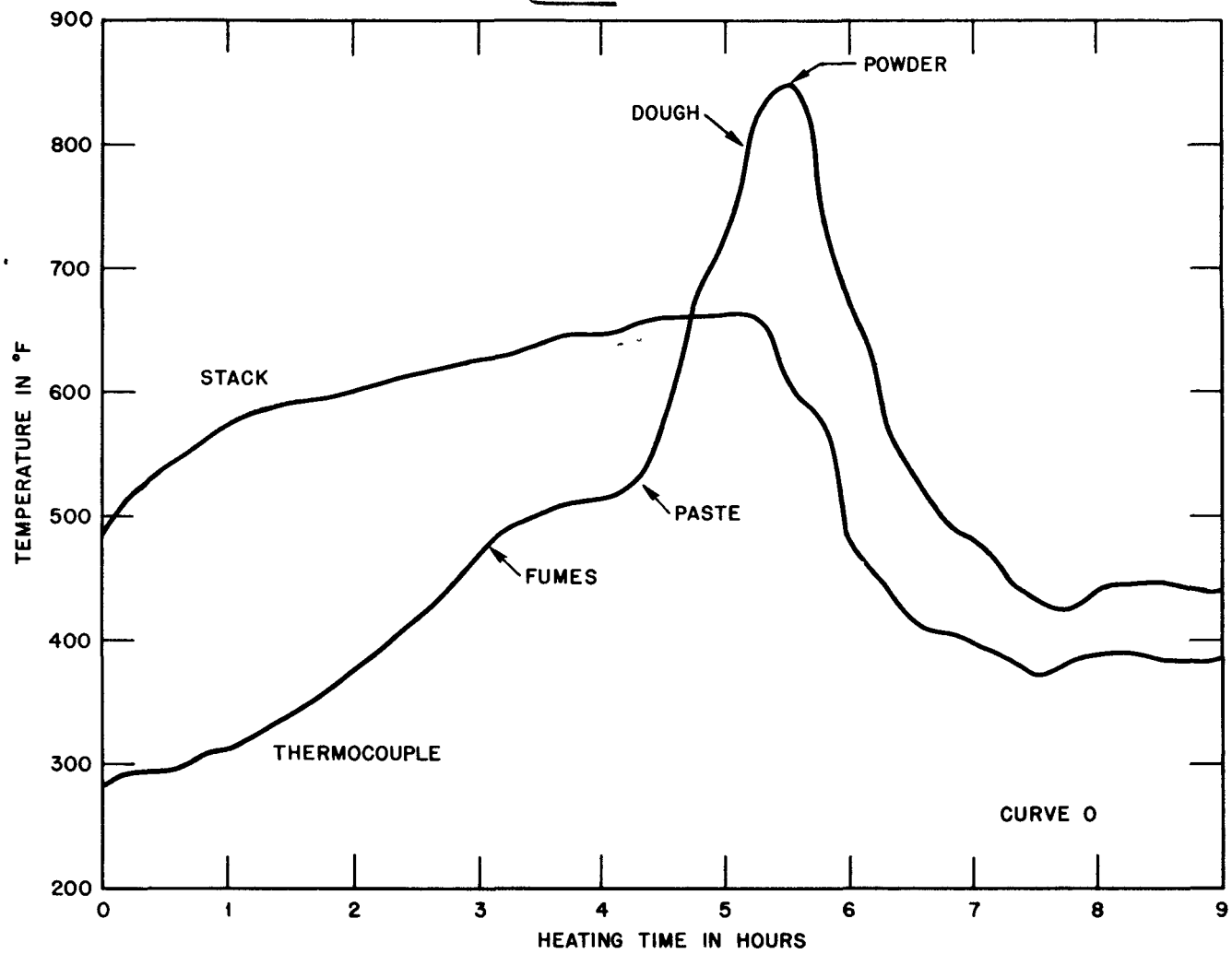


Figure 2