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A PILOT PLANT
FOR THE PREPARATION OF URANIUM TETRACHLORIDE
BY FLUIDIZATION

ABSTRACT

A pilot plant for the preparation of uranium tetrachloride by fluidization from uranium trioxide was designed, constructed and tested. Batches consisting of 100 grams of 50-200 (U.S. number) mesh oxide were converted in 50-minute reaction periods to tetrachloride of excellent texture, 98.8% chlorinated, 97.0% immediately available as product. The fluidizer contained no moveable parts and was mechanically easy to handle.

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SUMMARY

A pilot plant for the preparation of uranium tetrachloride by fluidization from uranium trioxide was designed, constructed, and tested. Batches consisting of 100 grams of 50 to 200 (U.S. number) mesh, bulk treatment oxide were converted in 50-minute reaction periods to tetrachloride of excellent texture, 96.8% chlorinated, 97.0% available immediately as product.

Chlorination was accomplished with carbon tetrachloride vapors, diluted with dry nitrogen during the initial stages of reaction. The temperature of the gas was 320°C; that of the solids was varied between 280° and 420°C during chlorination. About 250 cc of carbon tetrachloride was necessary for complete conversion of 100 grams of oxide.

Two types of equipment were tested and the system that proved superior was employed in obtaining the results listed above. It consisted of: a nickel reaction chamber conical in shape, 35 inches in height, 4 inches in diameter at the top, 1 inch at the base; a nickel loading unit fastened to the base of the cone, 1 inch in diameter, 12 inches high, tapering down to a 1/8 inch gas inlet pipe at its base; a pot to vaporize carbon tetrachloride; and condensers to trap excess vapors.

A series of experiments utilizing pure carbon tetrachloride vapors resulted in caking and partial fusion of the product. Dilution of the gas with dry nitrogen during the initial stages of reaction facilitated the proper dissipation of heat and yielded a product of excellent texture. About

40% (by volume) nitrogen dilution was employed during the first 8 minutes of reaction, 20% during the second, and pure carbon tetrachloride during the remaining $\frac{3}{4}$ minutes.

An initial temperature of 280°C was found high enough to start reaction yet sufficiently low to prevent the heat of chlorination from caking the solids. A final temperature of about 400°C was necessary to complete chlorination within a period of 50 minutes.

Various particle size ranges were tested and a maximum yield of available product, 97.0%, was obtained with 50-200 mesh (U.S. number) oxide. Most of the material that was not removed as product, adhered to the walls of the cone. The remainder was entrained in the gas stream and trapped in the condensers at the outlet of the system.

It was thought that an increase in the range of particle size employed, and the yield of available product could be effected by increasing the diameter ratio of the reaction chamber, and the size of the charge.

INTRODUCTION

Preliminary experimental work on the preparation of uranium tetrachloride by a fluidization technique has been described in Report C-5.350.3, Series A. A laboratory procedure had been developed wherein unactivated Malinkrodt uranium trioxide was converted into a good grade of tetrachloride in a period of 20 minutes, using carbon tetrachloride vapors at 240° to 280°C. On the basis of these results it was determined to carry out further work on a pilot plant scale of operations.

The principle involved in the "fluidization" technique is the suspension of a vertical bed of solid particles in a stream of gas passing upward through the bed, setting each particle into violent turbulent motion.

A large surface area is thereby exposed and the desired reaction greatly facilitated.

It was believed that a fluidization process would yield a product of good texture and quality with a minimum of equipment and mechanical difficulty.

APPARATUS

Fluidization System I, Figure I

The first fluidization system constructed and tested consisted of the following:

- A. A nickel, steam-jacket, pot for the vaporization of carbon tetrachloride.
- B. An orifice with valves on either side for the regulation of vapor flow.
- C. A tee before the orifice to permit nitrogen dilution of the vapors.
- D. Six feet of 1/2 inch stainless steel pipe wrapped with nichrome wire, and 6 feet of 1/8 inch pipe inside the furnace for the purpose of superheating the carbon tetrachloride vapors.
- E. A nickel cone, 4 inches in diameter at the top, 1 inch at the base, and 40 inches in height placed inside a furnace.
- F. A 1 inch valve at the base of the cone for unloading product.
- G. A tee at the top for loading charge.
- H. A condenser and liquid trap for excess carbon tetrachloride vapors.

Fluidization System II, Figure II

Based on the difficulties encountered in the first system, a second was designed, constructed and tested. It consisted of the following:

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- A. A nickel, steam jacketed pot for the vaporization of carbon tetrachloride.
- B. An orifice with valves on either side for the regulation of vapor flow.
- C. A tee before the orifice to permit nitrogen dilution of the vapors.
- D. A differential flow manometer, and a static pressure manometer to detect plugging of the vapor lines.
- E. Six feet of 1/2 inch stainless steel pipe wrapped with nichrome heating wire to superheat the carbon tetrachloride vapors.
- F. A 35-inch nickel cone, 4 inches in diameter at the top and 1 inch at the base.
- G. A detachable loading unit: 1 inch in diameter, 18 inches high, tapering down to a 1/8 inch U-tube; flanged at the top to attach to the cone; and supplied with a union at the end of the U-tube to connect to the vapor line-- all made of nickel and wrapped with nichrome wire.
- H. A glass head flanged to fit onto the top of the cone.
- I. Two glass condensers and a liquid trap to catch excess carbon tetrachloride.

PROCEDURE

Fluidisation System I, Figure I

The first fluidization system was operated as follows:

- A. Carbon tetrachloride was loaded into the vaporizer and low pressure steam admitted into the steam jacket.
- B. The furnace and nichrome heating jacket were turned on.
- C. A charge of uranium trioxide was loaded into the top of the reactor by means of a funnel.

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D. The valve past the orifice was opened wide while the valve between orifice and vaporizer was used to regulate flow. The differential flow manometer facilitated the reproduction of flow rates.

E. After the reaction period, the two flow valves were shut and the valve at the base of the cone opened to unload product.

Fluidization System II, Figure II

The second fluidization system was operated as follows:

A. Carbon tetrachloride was loaded into the vaporizer and low pressure steam admitted into the jacket.

B. The furnace and gas heating jacket were turned on.

C. Bulk treatment uranium trioxide, previously sieved for 20 minutes to the proper mesh by means of a Ro-Tap and then calcined for 3 to 4 hours, was used as starting material. The loading unit was charged with a weighed quantity of the oxide; attached to the bottom of the cone and to the vapor line; and then the nichrome heating jacket turned on.

D. The valve past the orifice was opened and a rotameter-measured flow of dry nitrogen admitted into the system at the tee before the orifice.

E. The valve immediately above the vaporizer was opened to a position that gave a specified reading on the differential orifice manometer.

F. Temperature readings were taken at the loading unit (see Figure II), at the gas line immediately before the loading unit, and in the furnace surrounding the cone.

G. Differential and downstream static pressures were taken at the orifice.

H. At the end of a run the two flow valves were shut, the heating

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jacket on the loading unit turned off, and the loading unit detached and overturned to obtain the product.

RESULTS

Fluidization System I, Figure I.

The original fluidization system was found to be mechanically unsatisfactory:

A. The valve at the base of the cone did not operate properly after several runs. Particles of oxide worked their way into the mechanism and prevented proper closing.

B. The construction of the unit was such as to expose several threaded sections inside the reaction zone. These threaded sections offered settling surfaces to the solid particles and thereby caused hold-up and incomplete reaction.

C. The gas inlet pipe extending down the length of the inside of the cone interfered with proper fluidization.

D. The rectangular shape of the section immediately above the unloading valve caused the presence of unreacted oxide, and occasionally unreacted lumps in the product.

Fluidization System II, Figure II

Design Experiments -- Preliminary experiments on the second fluidization system were made with a glass loading unit of the same design as the one pictured in Figure I. The results were excellent. Oxide particles were absent from the product, and operation was smooth and simple.

It was observed that most of the charge remained fluidized in the loading unit itself. The cone operated as a trap for fine particles and very little material was carried over into the glass condenser system.

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The Texture Problem -- A metal loading unit of the same design as the glass apparatus was constructed and tested. The first problem encountered was the caking of the solid material, the consequent improper fluidization and incomplete chlorination. The solution of this problem was accomplished by diluting the carbon tetrachloride vapors with dry nitrogen during the initial stages of reaction, combined with careful control of flow rates.

Temperatures measured at the loading unit thermocouple indicated that the reaction initiated at 250°C and became rapid at 280°C. Without nitrogen dilution, temperatures rose uncontrollably during the first few minutes of chlorination and resulted in caking of the product. With dilution of the vapor, however, it was found possible to control the initial temperature rise and produce a product of good texture, free of cakes or lumps (see Table I.)

The Problem of Complete Chlorination -- After determining a method for producing material of good texture, succeeding experiments were directed toward the production of good quality tetrachloride; i.e. completely chlorinated. Runs JM-111 through JM-117 yielded an average of 98.8% chlorinated material of excellent texture (see Table I).

The Problem of Available Product -- The next series of runs were made with the object of obtaining a maximum yield of available product. An average yield of 97.0% was obtained with 50 to 200 (U.S. number) mesh oxide (see Table II and III).

Track Tests -- Track tests were made utilizing material from Runs 202, 203, 205, 212 and 216. The charge behaved properly and was reported as "good" by XB.

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TABLE I

All runs were made with 100 gram charges of Bulk Treatment uranium trioxide, 20 to 60 (U.S. number) mesh. The average quantity of carbon tetrachloride employed for each run was 250 cc, vaporized in an average of 50 minutes. Gauge pressure for all runs was 3 cms of mercury.

Run No. (Jm)	Gas Temp. (°C)	Solids Temp. (°C) (loading unit thermocouple)	Nitrogen Flow Time (min.) % by vol.	Total Reaction Time (min.)	Texture of Product	Percent Insolubles in product	Mol Ratio $\Sigma \text{Cl} / \Sigma \text{U}$	Percent Chlorination	
111	332	283 to 397	40 20 0	7 8 34	45	excellent	--	4.00	100.0
112	325	290 to 420	40 20 0	6 6 30	42	excellent	0.52	3.94	98.5
113	321	320 to 420	40 20 0	8 6 35	49	excellent	--	3.92	98.0
114	311	280 to 425	40 20 0	4 6 41	51	excellent	1.57	3.97	99.3
115	318	280 to 413	25 20 0	10 9 45	64	excellent	0.80	3.94	98.5
116	318	280 to 412	25 20 0	6 9 47	62	excellent	0.54	3.53	98.3
117	318	295 to 440	40 0	4 33	37	excellent	0.65	3.95	98.8

Note: Percent chlorination was calculated as the mol ratio $\Sigma \text{Cl} / \Sigma \text{U}$, divided by 4.

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TABLE II

The charge employed in all runs was 100 grams of 50 to 200 mesh (U.S. number) Bulk Treatment uranium trioxide. The texture of the product was in all cases excellent, and water solubility tests indicated the quality of the product to be excellent in all runs.

<u>Run No.</u> <u>(JM)</u>	<u>Wt. of</u> <u>Available Product</u> <u>(grams)</u>	<u>Percent</u> <u>Available Product</u>
201	128.8	100.4
202	126.5	98.6
203	123.0	95.9
204	121.0	94.2
205	124.0	96.6
206	126.2	98.4
207	122.5	95.5
208	127.2	99.1
234	120.0	93.5
235	126.0	98.2
236	123.0	95.9
237	125.0	97.4
<u>Average</u>		<u>97.0</u>

Note: Yield calculations were made on the basis of an average analysis (four samples) of 79.9% uranium in the Bulk Treatment charge material, and an average of 62.3% uranium in the product of Runs JM 111 through JM 117 listed in Table I.

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TABLE III

The charge employed in all runs was 100 grams of Bulk Treatment oxide. The texture of the product was in all cases excellent, and water solubility tests indicated the quality of the product to be excellent in all runs. Yield calculations were made on the same bases as those in Table II.

<u>Number of Runs</u>	<u>Mesh (U.S. Number)</u>	<u>Average Yield of available product (percent)</u>
8	20 to 50	90.6
17	50 to 100	95.6
6	50 to 140	95.9
12	50 to 200	97.0
4	<50	91.7

TABLE IV

The following are the results of a screen analysis conducted by D. C. Schumacher on Bulk Treatment uranium trioxide, July 10, 1945.

<u>Screen Size (mesh)</u>	<u>Particle Size (inches)</u>	<u>Percent (by wt)</u>
on 28	0.0232	17.2
48	0.0116	30.4
60	0.0098	8.6
80	0.0070	10.2
100	0.0059	6.2
200	0.0029	12.6
through 200	0.0029	14.4

⋮

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DISCUSSION OF RESULTS

Fluidization System I, Figure I

Moveable Parts -- Fine fluidized particles penetrated the intermost portions of the valve that was employed in the first attempt at pilot plant operation. It was concluded that valves, or moveable parts of any kind were to be avoided in the design of fluidization equipment.

Irregular Surfaces -- Threaded sections exposed internally in the conical reactor were found to form excellent settling surfaces for oxide particles. Material caked and settled on all irregular surfaces causing poor fluidization and a lack of uniformity in the product. For efficient operation it was considered that smooth internal surfaces were necessary.

Internal Downward Gas Feed -- The downward gas feed did not always fluidize material between the inlet and base of the cone, causing some oxide to remain caked and unreacted. Then also the long internal gas inlet pipe added further surface for adhesion. The system was, therefore, found unsatisfactory. It is, however, conceivable that it can be employed successfully with improved design and accurate construction.

Rectangular Sections -- The section of reactor immediately above the unloading valve was almost rectangular in shape, the closed valve being horizontal and the walls of the cone almost vertical. Unreacted oxide was invariably found in the corners of this section. It was, therefore, determined to avoid rectangular sections wherever possible.

Fluidization System II, Figure II

Design Experiments -- The second fluidization system, employing a loading unit in place of a valve, proved satisfactory. The U-bend in the inlet gas line prevented solids from backing into the vapor system. The

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gradual taper of the gas line leading up to the 1-inch section of the loading unit eliminated corners and avoided the accumulation of oxide particles.

It was observed that most of the charge remained fluidized in the loading unit, the cone acting primarily as a trap for the finer particles. Therefore, the temperature most indicative of the progress of reaction was the one taken at the loading unit thermocouple, while the temperature of the cone remained relatively unimportant.

The Texture Problem -- From observations on the original glass experimental apparatus (see Report C-5.350.3, Series A), it was concluded that caking was caused by localized accumulation of heat. The formation of the tetrachloride from UO_3 and CCl_4 is an exothermic reaction and when it proceeds rapidly without proper dissipation of the heat of formation, caking and occasionally even fusion occurs. The dilution of the vapor stream with dry nitrogen reduced the caking tendency in two ways. It decreased the rate of reaction by reducing the concentration of carbon tetrachloride, and facilitated the removal of excess heat by addition of a volume of inert gas.

Reaction was found to proceed very rapidly during the first seven or eight minutes--a peak temperature often being reached four minutes after the start of chlorination. The greatest danger of caking or fusion occurs during this period since the largest part of the chlorination and heat liberation take place. Thereafter caking occurs infrequently and solid temperatures can be raised to as high as $440^{\circ}C$ with little danger. The procedure that was developed, however, provided for two stages of dilution lasting about 16 minutes (see table I, Results) to insure the production of good tetrachloride.

Actual operation of the system reveals that caking difficulties

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are immediately discernable on the static pressure manometer. During normal operation the static pressure remains fairly constant. As soon as a cake develops, however, the pressure changes radically. It either drops due to channeling of the gases or rises sharply because of the formation of a plug. Upon observing such a condition the reaction can be stopped without further waste of time.

The Problem of Complete Chlorination -- The production of analytically good tetrachloride was primarily a problem in achieving the last few percent of chlorination. Over 80% of the chlorination was accomplished in the first 10 minutes of reaction, and not all of the remaining 40 minutes was absolutely necessary but was considered advisable in the development of a safe standard procedure.

The Problem of Available Product -- The available product calculations (Tables II and III) were based on an average of 4 analyses of charge material showing 79.9 percent uranium in the oxide, and an average of 62.3 percent uranium in the product of Runs 111 through 117 (in Table I). The yield figures are, therefore, not perfectly accurate since product analyses were not made on the runs that were actually used to calculate yields. The inaccuracy, however, is on the conservative side. Runs 111 through 117 produced material that was, on the average, 98.8 percent chlorinated. If the products of the yield runs were not of similar quality, the uranium content would be greater than 62.3 percent, and the yields, therefore, larger than those listed.

The procedures of operation were similar throughout. Any variation in the quality of product could only have been caused by variation in the particle size of the charge material. The product, however, was

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constantly checked by water solubility tests, in which the operators achieved a high degree of proficiency.

Table III indicates that there exists a range of particle size which produces a maximum of available product. 20 to 50 mesh (U.S. number) and 50 mesh material, the two extremes in particle size range, both gave much lower yields than the intermediate ranges.

It is believed that the larger particles in violent agitation and subject to constant abrasion, break down into fine material which is entrained in the gas stream. Smaller particles, on the other hand, require a lower velocity for fluidization and the fines that they produce are not as easily entrained. The smallest range (> 200 mesh), however, may contain a quantity of material which has practically no settling velocity and cannot avoid entrainment.

Larger size particles not employed in reaction were easily ground to proper size. It was also found possible to make use of the fines. They agglomerated upon moistening and were, thereafter, also ground to proper size.

The operating range can undoubtedly be increased in both directions (from 50 to 200) by the installation of a greater diameter ratio in the reaction cone. More efficient trapping of the fines in such a unit would increase the yield of available product.

REVIEW AND RECOMMENDATIONS

The fluidization technique of tetrachloride production yielded 98.8% chlorinated material in a period of 50 minutes, 97.0% available immediately as product. The equipment contained no moveable parts and was mechanically easily handled.

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The range of particle size employed in the charge was 50 to 200 mesh (U.S. number). It is believed that this range can be increased by the construction of a cone with larger than a 4 to 1 diameter ratio.

It is furthermore believed advisable that experiments be made to determine the overall losses from the system, and efforts be made to further increase yields of available product.

HAP/ah

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FLUIDIZATION SYSTEM I

FIG. I H.A.P. 2-12-46

END