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UNIFORMLY REACTIVE URANIUM DIOXIDE FROM A SINGLE OXIDATION-REDUCTION CYCLE

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A B S T R A C T

By use of a modified thermobalance and reactor as the primary experimental tool for sample preparation and evaluation, a process has been developed by which parent uranium feed materials of widely variable reactivity and composition may be converted to a uniformly reactive uranium dioxide. Although numerous methods have been devised for improving the gas-solid reactivity of uranium dioxide toward hydrogen fluoride, none has overcome completely the initial variability of the available materials. Oxygen enrichment of uranium dioxide by incomplete reduction or partial reoxidation accompanied by intermediate cooling increased hydrofluorination reactivity by as much as 50 per cent. However, this intentional introduction of uranyl fluoride as an impurity in the uranium tetrafluoride product incurs a "fluorine penalty" in its final conversion to uranium hexafluoride. Furthermore, uranyl fluoride impurity levels of this order cannot be tolerated in uranium tetrafluoride intended for reduction to metal. Complete atmospheric reoxidation following the initial reduction of uranium feed materials to uranium dioxide produced urano-uranic oxide from which a stoichiometric uranium dioxide possessing uniform and much improved reaction characteristics could be made. Gains made available by the process are pointed out and problems remaining to be solved are formulated.

* Deceased.

UNIFORMLY REACTIVE URANIUM DIOXIDE FROM A SINGLE
OXIDATION-REDUCTION CYCLE

The effects of oxygen enrichment upon the reactivity of uranium dioxide toward gaseous hydrogen fluoride have been made the basis of an activation process which produces, independently of source and prior processing history, uranium dioxide of uniformly high reactivity.

Variability in the chemical and physical properties of those purified uranium materials which are available for the production of feed for the gaseous diffusion plants or for the production of uranium metal has increased enormously in the last decade. This change has occurred largely as a result of technological and engineering advances made in the fields of uranium ore processing and recovery of spent reactor fuel elements to produce purified uranium trioxide feed materials. Because of this variability, operations for converting these materials to uranium dioxide and thence to uranium tetrafluoride by gas-solid reactions have been more difficult to perform at optimum production levels.

Numerous investigators at Argonne National Laboratory (18,50), Battelle Memorial Institute (6,44,45,48), Hanford Atomic Products Operation (10,32,33), Harshaw Chemical Company (9), Los Alamos Scientific Laboratory (4), Mallinckrodt Chemical Works (22,24,42), National Lead Company of Ohio (7,11), New Brunswick Laboratory (16,38), and elsewhere (19,49), as well as those with Union Carbide Nuclear Company (2,12,34,47), have sought to establish a more exact definition of the chemical behavior of these feed materials in terms of their more easily measured properties. Gross correlations have been observed between oxide reactivity and such intrinsic factors as surface area (3,27), surface roughness (35,42), particle size and uniformity (29,41), crystal structure (6,41,44), and impurities (8,21,40). Even prior history appears to be an important factor perhaps through some indeterminate influence on one or more of these factors (1). Indeed, the nature of the observed variability is so complex and of such magnitude that no simple test scheme has been devised to predict accurately the conditions required for optimum processing of the various feed materials. Furthermore, there is no indication that the changes which might readily be made in process conditions with any existing type of production equipment would permit dependably uniform production rates to be maintained from all the types of feed materials which have been encountered. In a continuous process such as that used for the production of uranium tetrafluoride, the necessity of making major variations in the conditions employed from one material to another is obviously undesirable.

EXPERIMENTAL APPROACH AND DISCUSSION

Application of Thermobalance to the Problem

A modified thermobalance and gas-solid reactor (36) built to provide close control of both the temperature and the gaseous atmosphere, as well

as incorporating resistance to corrosive chemical attack, was the primary experimental tool for both material preparation and product evaluation. Figure 1 shows a flow diagram of the balance, the reactor, and the manifolds used in this investigation. The reactor and gas pre-heater are shown in greater detail in figure 2. Operating details are reported elsewhere (36).

First-order type plots (logarithm of unconverted solid vs. reaction time) of thermobalance data taken during the hydrogen reduction and subsequent hydrofluorination of three uranium feed materials with greatly different reactivities are shown in figures 3 and 4, respectively. The production difficulties which would result from processing these three materials in the same plant on successive days are fairly obvious. This was the nature of the problem; not only were the materials extremely variable in their chemical activity, but some of them showed little tendency to give an acceptable degree of conversion to uranium tetrafluoride. This meant greater quantities of elemental fluorine were required for the eventual conversion to uranium hexafluoride.

Improvements in Uranium Materials Processing

Various developments have been more or less successful in improving the over-all productivity of uranium feed intermediates. Hydration of some of the less reactive uranium trioxides, or more precisely, converting them to uranic acid, is recognized as a means of improving their reaction behaviors during reduction and subsequent hydrofluorination (13). The improvement so achieved is retained even after thermal dehydration (33). The cubic crystal structure which results from dehydration above 415°C. (28,37,46) may be partially responsible for the high reactivity of this brick red oxide.

Continuous calcination of uranyl nitrate hexahydrate (UNH) in stirred (15,31,39,43) or gas-fluidized beds (20,25) appeared to end the quest for a continuous method of uranium trioxide production. The denitration proceeded smoothly, and the product usually was obtained as uniform, hard pellets particularly well adapted to the use of fluidization techniques for subsequent processing. The principal disadvantage to the first uranium trioxide feeds produced by continuous calcination was that they were all quite unreactive, and complete conversion to uranium tetrafluoride by gas-solid reaction was virtually impossible. Incorporation of sulfate ion by the addition of sulfuric acid, sulfamic acid, sulfur, or ammonium sulfate to the uranyl nitrate hexahydrate prior to denitration (14,17,30) allowed more reactive uranium oxides to be produced; but, although sulfate activation is now a generally accepted practice, it fails to activate all oxides uniformly. Variation of calcining conditions sometimes produces a different crystalline form of uranium trioxide with different reaction characteristics. Thus far, however, the correlation of structure and other intrinsic properties with reactivity has not been sufficiently absolute nor the production control precise enough to provide an ideal solution to the problem.

THERMOBALANCE FLOW DIAGRAM

Figure 1

Figure 2

HYDROGEN REDUCTION OF THREE URANIUM FEED MATERIALS AT 560°C.

Figure 3

HYDROFLUORINATION OF URANIUM DIOXIDE FROM
THREE URANIUM FEED MATERIALS AT 550°C .

Figure 4

Activation by Partial Oxidation

An effort to improve the hydrofluorination reactivity by pulverizing the uranium dioxide made from the continuously calcined pellets resulted in a greater improvement than could be attributed to increased surface area. By thermobalance experiment the 30 to 50 per cent improvement in reactivity proved attributable to partial atmospheric reoxidation during the milling operation (35). These experiments further showed that the significant improvement was dependent upon certain conditions. Attainment of a 6 per cent oxygen enrichment* accompanied by an intermediate cooling cycle was necessary to effect an improvement in the hydrofluorination kinetics. Above 10 per cent oxygen enrichment the improvement was proportional to the degree of this enrichment. Neither the cooling cycle nor the oxygen enrichment produced an appreciable improvement if used alone. Study of the complex uranium oxide phase system (35,48) indicates that both conditions are necessary to initiate formation of a second phase. Assuming that this formation of a second phase is the causative factor in the improved reactivity, it is not surprising that oxygen enrichment achieved by incomplete reduction of the higher valent uranium oxides was as effective as partial reoxidation of the stoichiometric uranium dioxide. It should be noted, however, that if during partial oxidation the oxygen enrichment went further than is economically desirable, as is discussed below, the uranium dioxide obtained upon re-reduction is no more reactive than the original dioxide unless the excess oxygen had caused the formation of urano-uranic oxide (35).

Calculation of the "uranium tetrafluoride equivalent" (5) of these partially oxidized materials in terms of the "fluorine penalty" incurred shows that some optimum degree of oxygen enrichment exists for each oxide beyond which the process would be decreasingly practical for the economic production of gaseous diffusion plant feed. The "uranium tetrafluoride equivalent" is defined as the sum of the percentage of the uranium found as the tetrafluoride plus one-half of the percentage of the uranium found as uranyl fluoride. In view of the requirements for improved reactivity by oxygen enrichment, the maximum "uranium tetrafluoride equivalent" for uranium tetrafluoride produced using oxygen enrichment is about 97 per cent. Since appreciable quantities of uranyl fluoride are detrimental to the bomb reduction of uranium tetrafluoride to uranium metal**, activation of uranium dioxide by oxygen enrichment is not applicable if metal is to be the finished product.

* Oxygen enrichment is stated in terms of the amount of oxygen required to convert uranium dioxide to uranium trioxide; e.g., U_4O_9 has an oxygen enrichment of 25 per cent.

** Metal grade uranium tetrafluoride is normally defined as containing at least 96 per cent uranium tetrafluoride with no more than 2.0 per cent uranium dioxide or 2.5 per cent uranyl fluoride.

Reduction After Complete Reoxidation

In the conditions set forth above, it was implied that a second reduction following complete oxidation to urano-uranic oxide would result in a stoichiometric uranium dioxide of improved reactivity. This indeed is the case as was first reported by Cromer and Swinehart (9). Bard and his associates (3) at Los Alamos have reported progressive activation of uranium dioxide made from high-temperature sintered urano-uranic oxide by alternate oxidation and reduction treatments. This effect was confirmed in the present study and was found to hold over a wide range of conditions.

An optimized three-step activation process was sought which would involve only a single atmospheric oxidation between an initial and a final reduction step. In figures 5, 6, and 7 are shown the results of a systematic thermobalance investigation of the behavior of a randomly selected commercial uranium trioxide performed to establish temperature ranges for optimization of the three separate reactions involved in producing an activated, stoichiometric uranium dioxide. Since all the steps except the hydrofluorination step can be carried to completion in reasonable times with suitable adjustments in temperature, optimization of any given step is dependent upon knowing the effect of temperature changes in that step upon the hydrofluorination time. Thus, in this study the reaction temperature of each step was changed in turn while the temperatures of other steps were held constant. The step under investigation and the temperature conditions for the other steps are given in the legend of each of the figures. The optimum temperature for a given step is recognized as the minimum in the plot of temperature for that step versus comparative times for the fourth reaction, hydrofluorination to uranium tetrafluoride at 550°C. However, since other considerations such as more favorable kinetics for the step or more favorable temperature control during the step may influence optimization of the over-all process, temperatures slightly different from the minima in the figures may be chosen for the optimized process.

For the purpose of temperature optimization of the three activating steps, the exact degree of conversion to uranium tetrafluoride used in step 4 is not critical so long as the same conversion is used in evaluating a given step. Thus, for the figures 5, 6, and 7, the degree of conversion in step 4 selected for evaluating steps 1, 2, and 3, respectively, is different and, in each case, was selected to give convenient experimental conversion times. For example, in figure 6 the 80 per cent conversion to uranium tetrafluoride was selected because at a higher conversion percentage, such as 99 per cent, step 4 would have required hours rather than minutes in those cases where the oxidation had been performed at temperatures outside the optimum range.

In the study of the reactions, samples were normally heated or cooled in an inert gas to temperature and then the reaction was carried out at the designated temperature. In the legends of figures 5, 6, 7, and 8 this mode of operation is indicated by listing the gaseous reactant at

OPTIMIZATION OF INITIAL REDUCTION TEMPERATURE

Figure 5

OPTIMIZATION OF OXIDATION TEMPERATURE

Figure 6

OPTIMIZATION OF SECOND REDUCTION TEMPERATURE

Figure 7

OPTIMIZATION OF HYDROFLUORINATION TEMPERATURE

Figure 8

a designated temperature; e.g., "H₂ at 560°C." In some cases for the initial reduction, the sample was introduced into a cold reactor and the hydrogen flow started while the sample was heated to temperature. Because of the rapid heat-up the reduction is effectively accomplished at the indicated temperature, but to distinguish samples run in this manner the legend for this mode of operation is "H₂ to & at" the designated temperature.

Of the three activating steps, the step having the most sharply defined favorable temperature range is the oxidation represented in figure 6. This is evident from the steeply sloping sides of the broad minimum in the curve. Explanation of the apparent anomaly indicated by the broken circle at 300°C. was found in that this temperature is too low for oxidation to proceed much beyond the molecular composition of U₃O₇. The oxidation to U₃O₈ was then completed in the presence of residual air while the temperature was being raised in preparation for the second reduction. Thus, the major crystal rearrangement which occurs in the latter part of the oxidation took place in the temperature range associated with maximum activation. To make certain that the temperature would remain in the optimum range during the exothermic oxidation in step 2, a temperature of 350°C. which is near the low end of the broad minimum in figure 6 was selected for the optimized process.

The initial reduction reaction allowed a greater freedom of choice as demonstrated in figure 5. However, while there is a minimum in the hydrofluorination time as a function of the initial reduction temperature, the time required for reduction increases rapidly as the temperature is lowered. Thus, in considering maximum over-all process efficiency, a temperature higher than the minimum in the curve of figure 5 was selected for the optimized process to avoid achieving moderate gains in hydrofluorination rates at the expense of unreasonably long initial reduction times. The same considerations are involved in selecting the optimum temperature for the second reduction reaction (figure 7), although the range of choice of temperature for optimization of the process is more limited. The relatively shallow curve for the hydrofluorination reaction represented by figure 8 indicates considerable process flexibility. In the present study a hydrofluorination temperature of 550°C. was selected primarily for purposes of comparison with the unactivated parent oxides, many of which had been evaluated originally at this temperature. Table I presents a summary of the optimized reaction conditions.

It should be pointed out that essentially zero bed depth such as that encountered in fluid bed reactions has been assumed in establishing these conditions.

TABLE I

OPTIMIZED CONDITIONS FOR PRODUCTION OF URANIUM DIOXIDE
BY THE COMPLETE REOXIDATION PROCESS

Uranium oxide + H ₂	$\xrightarrow{\text{at } 675^{\circ}\text{C.}}$	UO ₂ + H ₂ O	Step 1
UO ₂ + O ₂ (air)	$\xrightarrow{\text{at } 350^{\circ}\text{C.}}$	U ₃ O ₈	Step 2
U ₃ O ₈ + H ₂	$\xrightarrow{\text{at } 560^{\circ}\text{C.}}$	UO ₂ + H ₂ O	Step 3
UO ₂ + HF	$\xrightarrow{\text{at } 550^{\circ}\text{C.}}$	UF ₄ + H ₂ O	Step 4

CONCLUSIONS AND RECOMMENDATIONS

Obviously a highly reactive uranium dioxide feed material can be made which undergoes a complete and rapid conversion to uranium tetrafluoride with the possibility of very efficient utilization of hydrogen fluoride. Figure 9 and its accompanying overlay focus attention upon a less obvious but possibly more important gain--production of a uniformly reactive uranium dioxide from uranium feed materials which differ widely in initial reaction characteristics. Such uniform reactivity would eliminate the many problems associated with having to adjust reaction conditions with each type of uranium feed being processed.

As in many other processes, such marked advantages are not gained without some cost. First, two extra steps are involved in the preparation of material for hydrofluorination by this procedure. Second, for a continuous process of this nature to be practical, adequately safe gas seals would be needed between the oxidation and reduction reactors. Third, the uranium dioxide and uranium tetrafluoride produced by this process exhibit lower bulk densities than the corresponding materials produced in the conventional manner. Because of this, some modification in material handling may be necessary. Noting, however, that current processing methods require uranium feed materials to be milled to a powder, that the uranium trioxide pellets produced by continuous calcination are activated about as well as the milled powder, and that the pellet form is retained throughout the process, the described activation would allow elimination of the milling operation and provide for effective utilization of fluidized bed processing techniques. Finally, the equilibrium of step 4 (7,23,26) is established so rapidly when such highly reactive uranium dioxide is undergoing hydrofluorination, a reactor design which incorporates countercurrent gas-solid flows or a staging of fluidized beds will be essential for realization of maximum efficiency in the

SAMPLE PREPARATION

HYDROFLUORINATION OF VARIOUS URANIUM DIOXIDES AFTER PROPOSED ACTIVATION

Figure 9

HYDROFLUORINATION OF VARIOUS URANIUM DIOXIDES AFTER INITIAL REDUCTION AT 560°C.

HYDROFLUORINATION OF VARIOUS URANIUM DIOXIDES AFTER INITIAL REDUCTION AT 560°C.

HYDROFLUORINATION OF VARIOUS URANIUM DIOXIDES AFTER PROPOSED ACTIVATION

Figure 9

utilization of hydrogen fluoride.

All of these problems have solutions, and the operating advantages which are to be gained from having a process capable of handling all types of feed materials under the same operating conditions indicate that careful consideration should be given to the use of the reduction-oxidation-reduction approach whenever a high conversion to uranium tetrafluoride from a variety of uranium feed materials is undertaken.

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