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**FORMATION OF UO_2 -CARBON MIXTURES
AND CARBIDE OR NITRIDE
FUEL MATERIAL IN A SPRAY REACTOR**

DECEMBER 1968

**AEC RESEARCH &
DEVELOPMENT REPORT**

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FORMATION OF UO_2 -CARBON MIXTURES
AND CARBIDE OR NITRIDE FUEL MATERIAL
IN A SPRAY REACTOR

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December 1968

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FORMATION OF UO_2 -CARBON MIXTURES AND CARBIDE OR NITRIDE FUEL MATERIAL IN A SPRAY REACTOR

E. A. Coppinger

INTRODUCTION

Carbides and nitrides of uranium and plutonium are being investigated as fuel materials for fast nuclear reactors.⁽¹⁻⁵⁾ Such materials are attractive because of their high thermal conductivity and density of fissile material. Many processes for the production of these fuel materials are being studied.⁽²⁻¹³⁾ Some processes produce carbides and nitrides by reacting the pure metals or hydrides with an appropriate reactant. However, such processes are inherently expensive because the metal must first be produced from the uranium and plutonium nitrate products from nuclear fuel reprocessing plants. In other processes now under intensive study, carbides are produced by the carbothermic reaction of uranium-plutonium oxide and carbon.^(8,10,12) Nitrides are produced in a similar fashion by the introduction of nitrogen to the system.^(12,13)

Cost reductions appear to be possible with carbothermic processes using oxide instead of more expensive metal as the starting material. However, most carbothermic processes still require several process steps to produce feed material for the actual carbothermic reaction. The procedure involves production of suitable oxides from nitrate solution, mechanical mixing of the oxides with carbon, pelletizing, crushing, and screening. To eliminate these steps and to provide a truly continuous process, the one-step production of nitrides or carbides directly from nitrate solutions in a spray calciner has been proposed.⁽¹⁴⁾ Sugar in the feed stream would provide the source of carbon. The process would also apply to the production of intimate mixtures of uranium oxide or uranium-plutonium oxide and carbon. Such mixtures of oxide and carbon could be used as the feed material for production of carbides or nitrides in a second batch or continuous reactor.

A scouting study was undertaken to determine the feasibility of the proposed process. This report describes the study and presents the experimental results.

SUMMARY

The production of an intimate mixture of UO_2 and carbon directly from a nitrate solution containing sugar was investigated in 15 exploratory runs in a spray calciner. This mixture of UO_2 and carbon is a key intermediate in the one-step production of carbides or nitrides in a modified spray reactor. The mixture is also a necessary intermediate in other equipment arrangements for production of nitrides and carbides by the carbothermic reaction. Results indicate that an intimate UO_2 -carbon mixture can be produced. The carbon content can be readily varied over a wide range bracketing the amount required for subsequent carbide or nitride production.

Two small samples of the UO_2 -carbon mixture with slightly different carbon content were tested for conversion to uranium nitride in a high-temperature furnace. The samples were held at 1600°C in flowing nitrogen until CO evolution ceased. The product was primarily uranium nitride. Analytical results from one sample indicate a final composition of 5.34 wt% nitrogen, 7800 ppm oxygen, and 350 ppm carbon. The carbon and oxygen contents were reasonably low for this initial attempt to convert powder from the spray calciner to nitride. Further improvement can be expected by adjustment of the initial carbon content.

A thermodynamic investigation was made to determine the feasibility of producing nitrides directly from nitrates in a spray calciner. A standard calciner design consisting of a heated tower with an atomizing nozzle at the top and a filter section at the bottom was assumed. While calculations indicate the process to be thermodynamically possible, minimum temperatures of 1800 to 2000°C are required even when methane is substituted for much of the sugar in order to reduce the partial pressure of CO in the equilibrium gas mixture. Thermodynamics indicate that the partial pressure of CO has a significant effect on the minimum temperature required for relatively complete conversion.

As a result of the thermodynamic investigation, a novel modification of a spray calciner has been conceived for operation at more reasonable temperatures. The reactor consists of two sections. The upper section is a standard radiant-heat spray calciner with metal walls and a filter chamber at the bottom. A radiant-heat, high-temperature section is attached below the filter chamber. Reaction gases are removed in the filter chamber and the solid particles fall into the high-temperature section. Nitrogen or argon is introduced at the bottom of the reactor. The gas flows up through the high-temperature section countercurrent to the falling solids and sweeps the CO produced by the carbothermic reaction out through the filters. Complete conversion can be obtained at lower temperatures because the partial pressure of CO is steadily reduced as the solids fall countercurrent to the flowing gas.

The favorable results of the experimental program have demonstrated the feasibility of the upper portion of the modified spray reactor. Further development work is required to determine the feasibility of the lower high-temperature section and a one-step process. Such work will require study of reaction kinetics and nitride or carbide production in the high-temperature section. A criticality and design study is also needed to determine the feasibility of producing uranium-plutonium nitrides or carbides in a spray reactor in a glove box.

TECHNICAL BACKGROUND

Production of carbides and nitrides of uranium and plutonium by the carbothermic reaction of oxides and carbon has been extensively investigated in recent years. Such emphasis was prompted by potential reduction in production costs. The carbothermic reactions are used in the spray calcination process discussed in this report. The proposed process, an investigation of the thermodynamics, and possible equipment alternatives are discussed in the following subsections.

PROCESS DESCRIPTION

The basic process involves the formation of carbides or nitrides of uranium and plutonium in a radiant-heat spray calciner by reaction of

the nitrates with an excess of sugar. For nitride production, the reaction is carried out in a nitrogen atmosphere. For carbide production, the reaction is carried out in an argon atmosphere. The use of methane in the atomizing gas is a potential modification. The methane reacts with the nitrate ion and water in the feed solution, thereby reducing sugar requirements.

An aqueous solution of uranyl nitrate or uranyl-plutonium nitrate, HNO_3 , and sugar is sprayed into the top of a radiant-heat spray calciner through an atomizing nozzle using either argon or nitrogen as the atomizing gas. Heat is supplied to the liquid and gas by the heated walls of the calciner. The small liquid drops quickly dehydrate and the nitrates, HNO_3 , and sugar react to produce solid particles containing UO_2 or $(\text{U}, \text{Pu})\text{O}_2$ and carbon. Earlier work on calcination of waste nitrate solutions containing sugar indicates that this reaction can be accomplished at temperatures in the range of 600 to 800 °C.⁽¹⁵⁾

Once this intimate mixture of oxide and carbon is available, carbides or nitrides can be produced by the appropriate carbothermic reaction. The general carbothermic reactions for production of uranium carbide or uranium-plutonium carbide are as follows:

The general carbothermic reactions for production of uranium nitride or uranium-plutonium nitride are as follows:

These reactions are generally carried out at temperatures of 1500 to 1700 °C in batch or fluidized-bed systems where the CO is swept out by flowing nitrogen.

Conceivably, the process can be carried out in one step in a high-temperature, radiant-heat spray calciner consisting of an insulated tower

with nonmetallic heated walls and a filter section at the bottom. However, the reaction gases, including CO formed by both the carbothermic reaction and the reaction of sugar with nitrate ion and water, flow downward with the solid particles to the filter section. Thermodynamics indicate the partial pressure of CO in the tower to be an important factor in obtaining relatively complete conversion to carbides or nitrides.

THERMODYNAMICS INVESTIGATION

A brief thermodynamics investigation of the one-step formation of carbides or nitrides in a spray calciner was made by J. D. Christian, Chemistry Research Department. A standard spray calciner design with a feed nozzle at the top and a filter section at the bottom was assumed. A hypothetical system consisting of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (UNH), sugar, and methane was also assumed. Methane was assumed to be the source of carbon for reducing UNH to UO_2 and sugar was assumed to be the source of carbon for producing UN from UO_2 by the carbothermic reaction. This system was used for determining minimum temperatures for UN formation because the partial pressure of CO in the equilibrium reaction gases renders it more favorable than a system containing dilution water and using sugar as the only source of carbon.

The simplified reaction system, including reaction (3) from the preceding subsection, can be considered as follows:

The overall reaction can be written as follows:

For the thermodynamic analysis, the spray calciner was considered to be a closed system at one atmosphere. This system resembles a spray calciner operating at steady-state with just enough material being removed to compensate for the material being added. At a total pressure of one atmosphere and at the necessary temperature of greater than 1500 °K, reactions (5), (6), and (7) will be essentially complete. Therefore, consideration of only the equilibrium of reaction (3), using the partial pressures of gaseous products corresponding to completion of reaction (8), is required. The partial pressures of N₂, H₂ and CO are calculated to be 0.0056, 0.5876, and 0.4068 atmospheres, respectively.

At a total pressure of one atmosphere, the activities of the solids in reaction (3) can be taken as unity and the partial pressure of the gases can be substituted for their activities. The equilibrium constant for reaction (3) can then be calculated in terms of the equilibrium partial pressures of the gaseous reactants and products as follows:

$$K_3 = \frac{(P_{\text{CO}})^2}{(P_{\text{N}_2})^{1/2}} = \frac{(0.4068)^2}{(0.0056)^{1/2}} = 2.2$$

Thus, in order to obtain complete conversion to UN in the assumed system, the calciner must operate at a temperature at which the equilibrium constant for reaction (3) is equal to or greater than 2.2. This minimum temperature can be calculated from the following expression relating the equilibrium constant and standard free energy change:

$$\Delta G^\circ = -RT \ln K$$

where

ΔG° = standard free-energy change, cal/g-mole

R = gas constant, 1.99 cal/(°K)(g-mole)

T = temperature, °K

K = equilibrium constant for a reaction

The minimum temperature for the assumed system is calculated to be 1980 °C.

The temperature can be reduced slightly by increasing the ratio of methane to sugar in the system. For example, if only enough sugar is

added to provide the "free" carbon for reaction (3), the overall reaction can be considered as follows:

The minimum temperature for this system is calculated to be 1920 °C.

If excess carbon is present at these high temperatures, nitrogen addition may be required to suppress the formation of carbides by reaction of the nitride with carbon as in the following reaction:

Actually, adjustment of the partial pressure of nitrogen could provide a means of attaining desired values of x in the formation of carbonitrides with the formula, $\text{U}(\text{C}_x\text{N}_{1-x})$. Nitrogen addition will also allow operation at a lower temperature due to a decrease in the ratio $(P_{\text{CO}})^2/(P_{\text{N}_2})^{1/2}$. The lower temperature, in turn, reduces the partial pressure of nitrogen required to suppress reaction (10). From a simultaneous solution of the equilibrium equations, reaction (10) is suppressed and the minimum temperature is reduced to 1875 °C by adding enough nitrogen to the system described by reaction (9) so that the partial pressures of N_2 , H_2 , and CO are 0.028, 0.672, and 0.300 atm, respectively.

The standard free energies of formation used to calculate values of K_3 and K_{10} as a function of $1/T$ are given in Table 1 at several temperatures. (16, 17)

TABLE 1. Standard Free Energy of Formation

Temperature, °K	ΔG_f° , kcal/g-mole			
	<u>UO₂</u>	<u>UN</u>	<u>UC</u>	<u>CO</u>
1800	-184.92	-32.50	-18.10	-64.34
2000	-176.48	-28.20	-17.70	-68.35
2100	-172.29	-26.05	-17.50	-70.34
2200	-168.12	-23.90	-17.30	-72.33
2300	-163.97	-21.75	-17.10	-74.31
2400	-159.84	-19.60	-16.90	-76.28

The operating temperature must be higher than calculated if the $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is diluted with water and sugar is used as the only source of carbon. The higher temperature is required because the reaction of carbon with the oxygen in the additional water and sugar increases the partial pressure of CO in the equilibrium mixture of reaction gases.

EQUIPMENT ALTERNATIVES

While the preceding calculations show the single-step formation of nitrides to be thermodynamically possible in a radiant-heat spray calciner, very high temperatures are required in terms of practical operating equipment and materials of construction. At temperatures above about 1650 °C, most potential materials for heating elements, gaskets, insulation, and the heated wall begin to develop severe undesirable properties such as permeability, low strength, and oxidation. With temperatures of at least 1800 to 2000 °C required for the reaction, the heating elements and hot wall must operate at even higher temperatures in order to attain the desired gas and particle temperature.

A novel modification of a spray calciner has been conceived for carbide or nitride production by the described process at more reasonable temperatures in the range of 1400 to 1650 °C. This conceptual spray reactor is shown schematically in Figure 1. The reactor consists of two sections. The upper section is a standard radiant-heat spray calciner consisting of an insulated tower with heated metal walls and a filter chamber at the bottom. The reaction and atomizing gases are removed in the filter chamber by withdrawing the gases from the reactor through porous-metal filter elements. The filter chamber can be either an enlarged cylindrical section at the bottom of the heated tower or a sloping side chamber as shown in Figure 1. The lower section is a radiant-heat high-temperature reactor consisting of an insulated tower with nonmetallic heated walls. The lower section is connected to the filter chamber with a fluid-cooled joint.

FIGURE 1. Schematic Diagram of Modified Spray Reactor

The modified spray reactor is expected to operate by spraying an aqueous solution of uranyl nitrate or uranyl-plutonium nitrate, HNO_3 , and sugar into the top of the reactor as described earlier. Oxide-carbon particles are formed in the upper section and flow downward through the heated tower along with the atomizing and reaction gases to the disengaging and filter section where the gases are removed from the reactor. The heavier solid particles fall through the filter section while the fines are carried to the filter elements by the gases. The fine particles are collected on the filters and are intermittently blown off by programmed blow-back gas. The extremely small particles agglomerate on the filters and eventually form particles heavy enough to fall out of the filter chamber into the high-temperature section when the filters are blown back.

The powder flows downward by gravity through the high-temperature section which operates in the range of 1400 to 1650 °C. Either argon or nitrogen, for carbide or nitride formation, respectively, is introduced at the bottom of the reactor. The gas flows upward through the reactor countercurrent to the falling solids and sweeps the CO produced in the carbothermic reaction upward and out through the filters. Thus, the partial pressure of CO in the gas stream around the solids is steadily reduced as the solids fall countercurrent to the flowing gas. The reduced partial pressure of CO allows relatively complete conversion to carbide or nitride at lower temperatures. The product can be collected in one or more product receivers attached to the bottom of the high-temperature section. The product will have to be blanketed with argon as it cools in the receivers to keep uranium sesquinitride from forming.

On the basis of the work reported here and extensive studies on calcination of radioactive waste solutions, the reactor design described in the foregoing paragraphs is uniquely applicable to the powder from a spray calciner. The high-temperature section of the reactor requires high gas-solid reaction rates to reduce residence time. Earlier work has indicated that the addition of sugar to various waste solutions fed to a spray calciner result in a very reactive form of carbon.⁽¹⁵⁾ Also, microscopic examination of particles from waste calcination and the work reported here has

shown that the particles are very porous agglomerates of small fragments of larger shattered drops. This visual observation and a low bulk density indicate a large surface area for the powder and very short diffusion paths for reaction gases. These inherent physical properties are conducive to high gas-solid reaction rates.

Another potential equipment alternative would be the use of a standard radiant-heat spray calciner to produce an intimate mixture of UO_2 and carbon, and another continuous gas-solid contactor or batch vessel to convert the mixture to carbide or nitride. An example of this equipment arrangement is to use the UO_2 -carbon mixture from the spray calciner as the starting material in carbothermic processes now under development.

Obviously, an intimate mixture of oxide and carbon is a necessary intermediate in the production of carbides and nitrides by the carbothermic reaction. Such a mixture is necessary in the production of carbides or nitrides in one step in the modified spray reactor in Figure 1 and in other types of batch or continuous gas-solid contactors. In view of the importance of the oxide-carbon intermediate, the experimental program was oriented toward a scouting study of the production of a satisfactory mixture of UO_2 and carbon directly from nitrate solution in a spray calciner.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

An existing spray calciner was used for the experimental program. The equipment, feed materials, and operating procedure are described in the following subsections.

EQUIPMENT DESCRIPTION

The spray calcination equipment consists of a spray calciner and necessary auxiliaries to heat the unit, feed the reactants, handle the off-gas, receive the condensate, and collect the product. This equipment is shown schematically in Figure 2.

FIGURE 2. Schematic Diagram of Spray Calciner Equipment

The heated wall of the spray calciner is 10 ft long and is constructed in three sections. The 4 1/2 ft long top section and 2 ft long bottom section are 8 in. Schedule 10 stainless steel pipe. The 3 1/2 ft long, 8 3/8 in. ID center section is 16 gage Inconel[®] sheet.

Solid particles and gases are separated in a filter section attached to the bottom of the calciner. This section is constructed of 8 in. Schedule 10 stainless steel pipe. A vertical portion directly below the calciner wall is about 2 ft long. A 4 ft long side chamber slopes upward from the bottom of the vertical portion. This side chamber contains four sintered, stainless steel filter elements connected to a common manifold and off-gas line. Two of the filter elements have a mean pore size of 65 μ and are 2 in. in diameter by 12 in. long. The other two elements have a mean pore size of 35 μ and are 2 3/4 in. in diameter by 14 in. long. The filters can be individually cleaned by a pneumatic blow-back system. This system involves the use of a high pressure gas introduced downstream from the filter through a small diameter throat. An air-driven vibrator is attached to the outside wall of the sloping side chamber. This vibrator can be used to vibrate the calciner and filter section to minimize powder holdup on interior surfaces.

Heat is supplied to the spray calciner by ten 2000 W Calrod[®] heaters banded around the outside of the top section and, additionally, by an electric current passing at low voltage through the entire wall of the unit. The current comes from a welding transformer equipped to supply secondary voltage in 16 steps up to a maximum of 6.4 volts. The current used in this program has been about 2800 A at 5.6 volts. About 75% of the energy from the transformer is used in heating the Inconel center section. The Calrods generally operate at one-third to one-half of full power and are limited by the allowable sheath temperature. Heat is supplied to the filter section by two 2000 W Calrod heaters spirally wrapped around the outside wall.

[®] International Nickel Co.

[®] General Electric Company

Solids are collected in a receiver attached to the bottom of the filter section in a direct line with the heated tower. Solids either fall directly into the receiver or are blown downward from the filters by the filter blow-back system.

Feed solution metered through a rotameter enters the calciner through a pneumatic atomizing nozzle.* The nozzle is installed outside the calciner with the orifice protruding through a water-cooled insert at the center of the top cover plate. The nozzle is held down and sealed against an asbestos gasket by a toggle clamp. Atomizing fluid (compressed air or other gas) is metered through a rotameter. Nitrogen was used as the atomizing gas in this program.

Temperatures throughout the reactor and filter section are measured with thermocouples. The reactor temperature profile is measured by thermocouples pressing against the outside of the heated wall at different levels. The signal from a thermocouple 79 in. below the top flange is used to control power from the transformer. The signal from a thermocouple 42 in. below the top flange is used to control power to the Calrods on the top section. The signal from a thermocouple about 6 in. below the top of the vertical portion of the filter section controls power to the Calrods on the filter section. The internal temperature is measured at a point 47 in. below the top cover plate. Temperatures are continuously recorded and controlled by temperature controllers actuating on-off contactors.

Filtered gases from the reactor pass through a downdraft condenser and a scrubber before discharging into the building vacuum system. The condenser, a 4 ft length of 4 in. ID glass pipe, contains a cooling coil consisting of 30 turns of 1/2 in. Hastelloy C[®] tubing packed with 1/2 in. porcelain Intalox[®] saddles. The off-gas from the reactor enters the top of the condenser. Soluble gases are scrubbed from the gas by the

* Spraying Systems Company, Set-up No. 12

[®] Union Carbide Corporation

[®] The U.S. Stoneware Company

condensate as they pass through the packing. Condensate leaves the bottom of the condenser and is collected in a condensate receiver. Non-condensable gases leave the bottom of the condenser through a dip leg and discharge into the bottom of a scrubber.

The scrubber is a 4 ft length of 4 in. ID glass pipe containing a 60-turn cooling coil of 3/8 in. stainless steel tubing packed with 1/4 in. stainless steel raschig rings. The noncondensable gases are scrubbed as they pass up through the packing. Scrubbing solution is discharged into the top of the scrubber by a centrifugal pump. The solution drains from the bottom of the scrubber into a receiver serving as a head tank for the recirculation pump. The scrubbed gas leaves the top of the scrubber and discharges into the building vacuum system. Both water and aqueous NaOH solutions were used in this program.

Vacuum and/or pressure within the calciner is indicated on a manometer and controlled by manually adjusting the gas flow to the building vacuum system.

The filter section, product receiver, vacuum seal pot, condensate receiver, and a de-entrainment pot for the vent system for the feed tank are enclosed in a lucite hood. The hood is under a negative pressure to prevent contamination of the laboratory with UO_2 powder. Glove ports are provided in the hood for manual operations, and a door is provided for sample removal.

OPERATING PROCEDURE

Operation of the spray calciner is quite simple. The building vacuum system is started and the vacuum in the calciner is adjusted to about 10 in. of water. The heating systems are turned on and the calciner is preheated to the desired operating temperature of about 700 °C in the top section, 800 °C in the center Inconel section, and greater than 100 °C in the filter section. The heating period takes about 2 hr. During the last 30 min of the heating period, the desired amount of sugar is dissolved in the feed solution. After the operating

temperatures have been established, the feed solution is put into the feed tank. If the scrubber is to be used, the recirculation pump for scrubber solution is also started. Feed is not prepared or transferred to the feed tank earlier because of a possible reaction between the sugar and nitrate ion in the feed solution.

The experimental run is started by introducing nitrogen and water into the calciner through the atomizing nozzle. Nitrogen is introduced at the desired flow rate while the water flow rate is equivalent to the water in the aqueous feed solution at the desired feed rate. Since the calciner vacuum is maintained manually, it must be watched carefully during this portion of the startup. Water is used during the initial startup phase to establish stable operating conditions prior to the introduction of feed solution. After all streams have been operating at the desired conditions for 5 min, the water flow is stopped and the feed is quickly started. Temperatures and flow rates are then kept constant for the run period.

The shutdown procedure involves switching from feed solution to water to flush out the feed line and atomizing nozzle. The water is shut off after 5 min and the nitrogen flow rate is reduced to $0.2 \text{ ft}^3/\text{min}$. The heating units and scrubber solution are shut off and the calciner vacuum is manually adjusted to about 2 in. of water to reduce the possibility of air in-leakage. The nitrogen flow is maintained for 2 to 4 hr to protect the product from air or water vapor during the cooling period.

After the calciner has cooled to room temperature, the product receiver is removed to inspect and sample the product. After removal of the product collected during the run, the receiver is reattached to the calciner. The filters are blown back and the calciner vibrator is operated to remove any product powder clinging to the filters or calciner walls. The product receiver is again removed to inspect and sample the product. The filters were not blown back during runs in this program because the blow-back system operates on compressed air. The oxygen in the air would react with the sugar or carbon in the system.

MATERIALS

The aqueous feed solution contained uranyl nitrate, HNO_3 , and sugar. The composition of the feed solution for each experimental run is shown in Table 2.

TABLE 2. Feed Composition

<u>Run No.</u>	<u>U, M</u>	<u>HNO_3, M</u>	<u>Sugar, g/liter</u>	<u>Sugar/Uranium Weight Ratio</u>
1	1.51	1.5	240	0.668
2	1.46	1.17	298	0.858
3	1.45	1.44	346	1.0
4	1.37	1.36	327	1.0
5	1.45	1.44	404	1.17
6	1.51	1.5	360	1.0
7	1.48	1.47	360	1.03
8	1.41	1.46	426	1.27
9	1.39	1.44	422	1.27
10	1.37	1.45	491	1.50
11	1.18	1.5	540	1.92
12	1.37	1.45	491	1.51
13	1.37	1.45	491	1.51
14	1.10	1.4	578	2.21
15	1.18	1.5	560	1.99

The feed solutions were very viscous and had the appearance of clear yellow syrup. Some of the sugar did not dissolve in Run 14. A few very small particles of sugar were still suspended in the viscous solution after 2 hr of agitation. The sugar completely dissolved in all other runs. Target compositions were initially 1.5M U and 1.5M HNO_3 . Actual compositions varied from the target compositions primarily because of the difficulty in predicting the exact volume increase from sugar dissolution, and because uranium solubility limits precluded the use of higher initial uranium concentrations to compensate for the larger volume increases. Nitric acid was included in the

feed solution to simulate a system containing plutonium. Nitric acid, required to keep insoluble plutonium polymer from forming, is needed only when plutonium is present.

The uranyl nitrate was obtained by dissolving reactor-grade uranium metal in HNO_3 . Technical-grade HNO_3 was used for the metal dissolution and feed make-up. Consumer-grade refined sugar was used. Water-pumped nitrogen with a nominal purity of 99.97% was used as the atomizing gas. An aqueous solution containing 16 wt% NaOH was used in the scrubber during Runs 1 and 2, and water was used in Runs 3 and 15. The scrubber was not used in any other run.

EXPERIMENTAL PROGRAM AND RESULTS

The primary objective of the experimental program was to determine whether the necessary intimate mixture of UO_2 and carbon could be produced from an aqueous solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, HNO_3 , and sugar in a spray calciner. Prior to experimental operation of the spray calciner, the possibility of a reaction between HNO_3 and sugar in the feed solution was studied to provide information on any necessary safety precautions. After adequate information was obtained, the spray calciner was operated under a variety of conditions. Analytical and special tests were performed on the product powders to determine their physical and chemical characteristics. The program and experimental results are described in sequence.

SUGAR- HNO_3 REACTION TESTS

The fact that sugar and HNO_3 will react vigorously in a heated aqueous solution is well known and has been studied extensively.^(18, 19) Several brief tests were made to determine the reaction initiation temperature in typical feed solutions. The tests consisted of slowly heating feed solutions of different compositions at a rate of about $0.5^\circ\text{C}/\text{min}$ and visually observing the start of the reaction. For solutions containing 1.3 to 1.7M U, 1.5M HNO_3 , and 0.67 g of sugar per gram of uranium, the reaction started at about 54°C when the solutions were heated

immediately after sugar dissolution. Small bubbles of reaction gas could be seen rising through the solution when the reaction started. Heating was stopped immediately after the reaction started in each test. The reaction continued to accelerate, however, and the solution temperature continued to increase for about 5 min before subsiding. The reaction became more vigorous at higher uranium and sugar concentrations. The temperature of a test solution containing 1.7M U, 1.5M HNO_3 , and 0.77M sugar increased rapidly to 99 °C after the reaction started and the solution turned to a sticky solid that foamed out of the beaker.

The reaction was observed during these heating tests to start without heating after an induction period. When solutions identical to those used in the heating tests were held at 24 °C without heating, the reaction started 37 hr after sugar dissolution. In another solution containing 1.3M U, 0.98M HNO_3 , and 1.9M sugar, bubbles of reaction were observed after the solution was held at 24 °C for 16 hr. These findings illustrate the need for careful storage procedures when sugar has been mixed with the feed solution. The findings also show the desirability of injecting the sugar solution into the feed solution just prior to the atomizing nozzle.

EXPERIMENTAL SPRAY CALCINER RUNS

The experimental runs were made in the spray calciner to explore the effect of several important operating variables on the production of UO_2 -carbon mixtures. These variables include the weight ratio of sugar to uranium, the gas/liquid weight ratio at the atomizing nozzle, the feed rate, and the temperature profile in the calciner tower. Operating conditions for each run are shown in Table 3. The temperatures in the calciner tower are shown in Table 4.

In general, the runs were smooth and easily controlled. About one liter of feed solution was used in each run. Filter-blow-back was not used during any run and, as a result, a steady increase of the vacuum downstream from the filters was required as the runs progressed. Because oxides of nitrogen were never visible in the off-gas from any of the runs, scrubber operation with a caustic scrubbing solution was discontinued after Run 2. Qualitative analytical tests showed

TABLE 3. Calciner Operating Conditions

Run No.	Operating Time, min	Flow Rates		Gas/Liquid Weight Ratio	Vibrator
		Feed, ml/min	N ₂ , scfm		
1	22	50.0	0.61	0.27	Off
2	25	44.0	0.58	0.30	Off
3	29	35.9	0.55	0.34	Off
4	27	40.7	0.53	0.29	Off
5	42	24.8	0.46	0.40	Off
6	29	34.5	0.54	0.34	Off
7	30	34.0	1.66	1.06	Off
8	50	20.2	1.10	1.18	Off
9	38	26.8	1.18	0.97	On
10	56	19.7	1.16	1.28	On
11	53	18.8	1.19	1.40	On
12	32	34.4	1.59	1.00	On
13	46	21.7	1.08	1.08	On
14	15	21.7	1.40	1.45	On
15	53	18.9	1.73	2.02	On

TABLE 4. Calciner Temperatures

Run No.	Temperatures, °C									
	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)	(I)	(J)
1	670	650	670	700	785	800	810	600	365	135
2	650	650	655	695	778	800	806	550	375	130
3	665	670	678	700	778	800	808	565	425	130
4	660	670	680	700	778	803	814	585	425	135
5	670	696	710	712	785	805	815	580	445	150
6	664	685	690	700	780	800	818	585	425	125
7	605	625	620	655	775	800	820	590	440	140
8	630	682	675	695	770	810	830	600	445	165
9	638	660	660	695	780	810	828	595	430	140
10	650	680	680	710	780	810	820	595	430	135
11	635	660	660	700	786	810	825	600	435	145
12	632	645	650	710	775	810	835	615	465	160
13	556	595	570	605	685	700	745	520	335	126
14	610	648	648	710	783	800	832	585	425	150
15	655	675	680	720	782	803	830	600	460	180

(A) Internal temperature 47 in. below top cover plate.

(B) Heated wall (top section) 9 in. below top cover plate.

(C) Heated wall (top section) 27 in. below top cover plate.

(D) Heated wall (top section) 42 in. below top cover plate.

(E) Heated wall (Inconel section) 67 in. below top cover plate.

(F) Heated wall (Inconel section) 79 in. below top cover plate.

(G) Heated wall (Inconel section) 91 in. below top cover plate.

(H) Heated wall (lower section) 115 in. below top cover plate.

(I) Wall temperature (filter section) 126 in. below top cover plate.

(J) Wall temperature (sloping side chamber) at center of filter elements.

the removal of CO_2 from the off-gas by the scrubbing solution. Water was used in the scrubber in Runs 3 and 15. The strong odor of ammonia exhibited by the scrubber water samples after these runs indicates that all or a portion of the nitrate in the feed solution reacts with sugar to form ammonia. The scrubber was not used for any other run.

Two separate batches of $\text{UO}_2\text{-C}$ powder were removed from the calciner after each run. The first batch was the product powder collected in the product receiver during the actual run. This powder ranged from about 31 to 86 vol% of the total powder produced during a run. The second batch was the powder clinging to the filters and interior surfaces of the calciner at the end of a run. This powder was collected by filter-blow-back and calciner vibration after removal of the product collected in the receiver during a run. The powder clinging to the filters (filter-blow-back powder) was, in every run, a uniform finely divided material with the appearance of black talcum powder. Typical product powder was slightly coarser than the filter-blow-back powder. However, microscopic examination showed the coarser powder to be only fragile porous agglomerates of the smaller fragments. Analytical samples of both batches of powder were taken after most runs.

Feed flow rates and sugar concentrations were varied in the first six runs, while the flow rate of the atomizing gas was held essentially constant. During Runs 1 and 2, a uniform finely divided black powder was collected in the product receiver. The increased sugar concentration and feed viscosity in Runs 3 through 6 apparently resulted in poor feed atomization, and the powder was a heterogeneous mixture of finely divided black powder and larger friable brown lumps. The lumps varied in size from roughly $1/32$ to $1/4$ in. in diameter. The lumps were apparently caused by incomplete sugar reaction in large droplets of poorly dispersed feed solution. This poor atomization was not surprising considering the viscous feed solution and the gas/liquid weight ratio of 0.27 to 0.40 initially used. Subsequent inspection of data⁽²⁰⁾ on pneumatic nozzle characteristics indicated the gas/liquid weight ratio for good nozzle performance should have been one or greater.

Gas/liquid weight ratios were increased after Run 6. Runs 7 through 15 were made at gas/liquid weight ratios in the range of 0.96 to 2.02, and a lump-free powder was produced in each run. Higher ratios were not investigated because the physical appearance of the powder indicated no need and because the filter-blow-back system would have required modification to allow filter-blow-back with nitrogen during calciner operation.

Once a satisfactory lump-free powder was obtained in Run 7, the sugar/uranium weight ratio was increased in Runs 8, 10, 11, 14 and 15 to determine the effect of increased sugar concentration upon the carbon content of the powder. The feed solution for Run 14 contained the highest sugar concentration used in the program. This sugar concentration was used to demonstrate the production of an oxide-carbon mixture with a carbon content greater than the stoichiometric amount required for subsequent production of uranium carbide. As mentioned earlier, a few small particles of undissolved sugar were suspended in the viscous feed solution when the run was started. The atomizing nozzle plugged 15 min after startup and the run was stopped prematurely. Presumably, the nozzle was plugged by the particles of undissolved sugar. The sugar concentration was reduced slightly in Run 15 and no further difficulties were encountered with the nozzle.

The calciner was continuously vibrated during Run 9 to determine whether a higher and more uniform carbon content could be achieved by reducing the residence time of powder clinging to the heated wall. The feed solution and calciner vibrator were started and stopped simultaneously. All other operating conditions were essentially the same as Run 8. Because carbon content of the powder was greater from Run 9 than from Run 8, the vibrator was used in all subsequent runs.

The effects of reactor residence time and calciner temperature were investigated in Runs 12 and 13, respectively. Run 12 was essentially identical to Run 10 except for a higher feed rate which reduced the residence time in the calciner for reaction gases and solid product. Run 13 was essentially identical to Run 10 except for a temperature reduction of about 100 °C along the heated wall of the calciner.

EXPERIMENTAL RESULTS

Results of carbon and uranium analyses are shown in Table 5. Uranium content, calculated as UO_2 , is also shown. Analyses are not shown for Run 7 because preliminary ignition tests in air at 900 °C indicated a low carbon content of less than 3 wt%. In most runs, the product powder was sampled in two or more locations to obtain data on product uniformity. Only one sample was taken in Runs 8 and 9 because, based on Run 7, the carbon content in the product powder was suspected to be too low for subsequent carbide or nitride production. The "top" samples were taken after careful removal of the top 1/2 in. of powder. "Middle" samples were taken from about the vertical center of the column of powder after careful removal of the upper half. "Bottom" samples were taken from the bottom inch of powder.

TABLE 5. Analytical Results

Run No.	Sample Location (a)	Composition, wt%		
		U	C	UO_2 (b)
1	Top	74.5	0.5	84.5
	Bottom	84.6	0.3	96.0
2	Top	77.5	2.6	87.9
	Bottom	69.8	2.1	79.2
	Blow-back	84.2	1.2	95.5
3	Top	78.9	5.6	89.5
	Bottom	78.0	7.3	88.5
4	Top	80.2	3.4	91.0
	Middle	75.0	7.6	85.1
	Bottom	72.1	-	81.8
5	Top	72.8	12.2	82.6
	Bottom	72.0	14.7	81.7
6	Top	79.5	6.1	90.2
	Bottom	74.9	11.6	85.0
	Lumps	66.9	12.2	75.9
	Fines	82.5	2.9	93.6
8	Middle	-	3.6	-
	Blow-back	-	3.6	-

TABLE 5. Analytical Results (contd)

Run No.	Sample Location (a)	Composition, wt%		
		U	C	UO ₂ (b)
9	Middle	-	5.4	-
	Blow-back	-	2.5	-
10	Top	-	8.7	-
	Bottom	73.0	9.3	82.8
	Mixed (c)		11.2	
	Mixed (c)		9.4	
	Blow-back	78.6	4.9	89.2
11	Top	68.7	13.6	77.9
	Bottom	-	11.6	-
	Mixed (c)		14.7	
	Mixed (c)		15.2	
	Blow-back	72.6	6.8	82.4
12	Top	73.0	11.5	82.8
	Bottom		10.6	
	Blow-back		5.9	
13	Top	73.7	10.3	83.6
	Bottom		9.9	
	Blow-back	71.1	11.2	80.6
14	Middle		8.1	
	Blow-back		9.8	
15	Top	70.5	13.5	80.0
	Bottom		14.9	
	Blow-back	74.1	10.0	84.1

(a) Top denotes 1/2 in. below top surface; middle denotes approximate vertical center of powder; bottom denotes bottom 1/2 in. of powder; blow-back denotes powder blown off filters; mixed denotes sample after vigorous mixing of product collected during a run.

(b) Uranium content calculated as UO₂.

(c) Duplicate samples.

The powder from Run 6, containing a heterogeneous mixture of finely divided black powder and brown lumps, was screened to separate the fines and lumps. The screen was 18 mesh with a 0.03 in. opening. Samples of both the lumps and fines were analyzed. The much higher carbon content of the lumps tends to verify that the lumps were caused by incomplete sugar reaction as a result of poor atomization of the viscous feed solution.

The filter-blow-back powder was sampled in Run 2 and Runs 7 through 15. As shown in Table 5, the carbon content was always lower in this material than in the product powder except for Run 13. The lower carbon content can possibly be explained by the longer residence time in the calciner for filter-blow-back powder. Some of the powder was probably clinging to the filters or hot wall for most of the run. Additional carbon burn-out was caused by the additional contact time with high-temperature steam and by the higher temperature of powder clinging to the heated wall. The filter-blow-back powder could also contain less unreacted or partially reacted sugar as a result of the increased residence time. The reason for the higher carbon content of the filter-blow-back powder from Run 13 is not known.

Some variation in carbon content disclosed by comparing analyses of samples from different locations in the product receiver can be partially explained by analytical error. However, some of the variation can undoubtedly be attributed to the same factors causing the much wider variations between the product powder and the powder collected after filter-blow-back. The product powder is probably a mixture of powder that has fallen almost straight through the calciner and powder that has been clinging to the heated wall or filters for varied lengths of time. Nonequilibrium conditions can also cause nonuniform powder. The shortness of these runs permitted only a part of the powder to be collected during the steady-state portions. The rest was probably collected during initial adjustment of operating conditions and during shutdown. At this stage of development, the variation in carbon content

is not considered seriously excessive. Some variation must also exist in mechanically mixed UO_2 and graphite. Once the powder from the spray calciner is mixed, the porosity, small particle size, and large surface area should allow some variation in carbon content without seriously affecting the nitride or carbide conversion step.

The variation in carbon content can be reduced in several ways. More vigorous vibration can be used to reduce the length of time the powder clings to the hot interior surfaces. Frequent filter-blow-back with argon or nitrogen can be used to minimize contact time between high temperature steam and small solid particles clinging to the filters. Further optimization of the weight ratio of atomizing gas to liquid feed will reduce variations in drop size and any resulting differences in dehydration and reaction rates. Longer runs would provide more powder at steady-state conditions. Two product receivers on a valved manifold would allow elimination of powder formed at nonequilibrium conditions during startup and shutdown.

As expected, an increase in the sugar concentration, with other conditions held reasonably constant, will result in increased carbon content of the powder. This conclusion is best illustrated by Runs 1, 2, 4, 3, and 5 in sequence, and by Runs 7, 8, 10, 11, and 15 in sequence.

The effect of the gas/liquid weight ratio on carbon content can be seen by comparing Runs 6 and 7. When other conditions are held essentially constant, a higher gas/liquid weight ratio results in a lower carbon content in the powder. The probable explanation for this result is that the higher gas/liquid weight ratio contributes to better atomization and smaller drops. The smaller drops heat, dehydrate, and react quicker.

Analytical results show that both continuous vibration of the calciner and a lower temperature affect carbon content of the powder. Results from Runs 8 and 9, showing an increase in carbon content when the calciner is vibrated, are probably explained by a reduction in the residence time for particles clinging to the hot wall. Results from Run 12

and Run 10 show an increase in carbon content of the powder when the calciner temperature (as in Run 12) is reduced about 100 °C. This increase in carbon content is attributed to either less reaction between carbon and steam at the lower temperature, or to the presence of a small amount of unreacted or partially reacted sugar.

Following an analyses showing carbon content of the powders from Runs 10 and 11 to be greater than the stoichiometric amount required for nitride production, the product powder from each run was individually mixed thoroughly. Two duplicate samples, designated "mixed" in Table 5, were then taken of the mixed powder from each run. Similar samples were taken from the mixed powder for the thermogravimetric tests and nitride conversion tests discussed later. The average carbon content of the powder used in the thermogravimetric and conversion tests is considered as the average of the two duplicate samples.

X-ray diffraction analyses of samples from Runs 10 and 11 show the uranium present to be predominantly UO_2 . The diffraction patterns also indicate a very small crystallite structure.

The particle size and bulk density of the product powder was briefly examined. The bulk densities of the powders collected during Run 11 and Run 15 were 0.25 g/cm³ and 0.34 g/cm³, respectively. The bulk density of filter-blow-back powder from Run 15 was 0.40 g/cm³. Microscopic examination of the powder collected during Run 11 showed many small fragments less than 16 μ in diameter and many jagged agglomerates roughly 16 to 200 μ in diameter.

SUGAR UTILIZATION

The exact reaction between sugar, HNO_3 , and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is difficult to specify because competing reactions with different gaseous products can occur. Since oxides of nitrogen were not visible in the off-gas, reactions producing NO_2 can be eliminated. Since both NH_3 and CO_2 were found in the off-gas, a possible reaction between at least a portion of the sugar and HNO_3 is as follows:

At least a portion of the sugar could be reacting with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to produce an intimate mixture of UO_2 and the stoichiometric amount of carbon for subsequent UN production as follows:

A portion of the sugar could also be reacting with HNO_3 to produce N_2 , CO_2 , and H_2O as follows:

Similarly, if N_2 and CO_2 are formed, a possible overall reaction between a portion of the $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and sugar to produce an intimate mixture of UO_2 and the stoichiometric amount of carbon for subsequent UN production is as follows:

Inspection of the preceding equations shows that sugar utilization will be reduced if reactions (11) and (12) predominate. Also, calculations indicate that more sugar is required than is shown by reaction (11) and (12). For example, using the uranium and HNO_3 concentration in the feed solution for Run 9, the stoichiometric sugar requirement for reaction (11) and (12) is calculated to be 340 g/liter. Actually, a sugar concentration of 422 g/liter was used in Run 9 and the carbon contents of the product and filter-blow-back powder were only 5.4 and 2.5 wt%, respectively, as compared to 8.16 wt% predicted by reaction (12).

The poorer sugar utilization is due to reaction of sugar or carbon with steam and air in-leakage. The amount of sugar or carbon reacting with steam is, in turn, dependent on a number of process variables including the amount of steam in the system, the temperature profile in the reactor, the weight ratio of atomizing gas to liquid feed, and the holdup time. The sugar requirements must be determined experimentally for specific conditions and reactor design.

Sugar requirements could also be reduced by using H_2 and CH_4 in the atomizing gas in concentrations below the explosive limit.

THERMOGRAVIMETRIC TESTS

Thermogravimetric tests were run on samples of powder from three spray calciner runs to provide information on any weight loss prior to reaching the nitriding temperature. Samples of product powder from Runs 10 and 11 and filter-blow-back powder from Run 15 were tested. The tests, directed by F. P. Roberts, Applied Chemistry Section, were performed because material balances based on uranium and carbon analyses consistently indicated the presence of a small amount of some material other than UO_2 and carbon in the powder. The tests were performed on a Cahn Model RG Electrobalance whose function was to provide a continuous signal proportional to the weight of the sample. The signal was then recorded as a function of temperature.

The results verify the presence of some material other than UO_2 and carbon in the samples. Each sample had a weight loss of over 11% during heating in an argon atmosphere to 990 °C at a rate of 4 °C/min. Results of the tests are shown in Table 6.

TABLE 6. Results of Thermogravimetric Tests

<u>Temperature, °C</u>	<u>Sample Weight Loss, %</u>		
	<u>Run 10</u>	<u>Run 11</u>	<u>Run 15</u>
100	0.2	0.2	0
150	1.0	0.9	0.1
200	1.4	1.4	0.3
250	1.5	1.6	0.6
300	2.0	2.0	0.8
350	2.9	3.0	1.8
400	4.5	4.6	3.5
450	5.6	6.1	4.9
500	6.1	6.8	5.6
550	6.5	7.4	5.8
600	6.9	7.9	6.0
700	7.6	8.9	7.2
800	8.6	10.1	8.4
850	9.8	10.9	9.5
900	10.6	11.8	10.7
950	11.1	12.7	11.6
990	11.6	13.7	11.8

The pattern of weight loss as a function of temperature is very similar for each sample. The weight loss between 100 and 150 °C is considered to be adsorbed water. The most rapid weight loss, occurring between 300 and 450 °C, indicates the presence of some material which begins rapidly decomposing at about 300 °C. Partially decomposed sugar is the most likely material on the basis of studies of sugar decomposition.⁽¹⁰⁾ Uranium compounds containing both oxygen and carbon are also possibilities.

The samples from Runs 11 and 15 were held at 990 °C and continued to lose weight. The sample from Run 11, held at 990 °C for 2 hr, showed an additional weight loss of 3.75%. The sample was still losing weight when the test was stopped. The sample from Run 15, held at 990 °C for 1.5 hr, showed an additional weight loss of 2.3%. The sample was no longer losing weight when the test was stopped.

The problem of apparent carbon burn-out before attaining the nitriding temperature can be handled by increasing the initial carbon content to compensate for carbon burn-out. The feasibility of this technique is shown in a subsequent discussion of nitride conversion tests. The problem can be reduced or possibly eliminated by simple modification of the operating conditions and/or the calciner. Reduced feed rates increase residence time and allow attainment of higher particle temperature and more complete reaction. Higher ratios of atomizing gas to liquid reduce particle size and result in higher particle temperatures for a greater portion of the time in the reactor. Higher temperatures in the filter section and the bottom two feet of the calciner allow higher particle temperatures for a longer period of time. The product receiver can also be heated to allow reaction for a longer time.

NITRIDE CONVERSION TESTS

Small samples of the powder from Runs 10 and 11 were tested for conversion to uranium nitride. These tests were directed by E. T. Weber of the Ceramics Department. The experimental equipment consisted essentially of a graphite resistance furnace, temperature monitoring and

control instruments, oxygen and water analyzers for the reaction gas, and a carbon monoxide monitor for the exhaust gas. Approximately 1.5 g of $\text{UO}_2\text{-C}$ powder from Runs 10 and 11 were loaded into individual 1 1/2 in. diameter, tungsten-lined molybdenum crucibles. The crucibles were placed in the furnace and the system was purged with ultra-pure helium for over 16 hours. A helium flow rate of 0.5 liter/min was then established and the samples were heated to 450 °C in 75 minutes. The furnace was then switched to automatic control for a programmed rise to 1600 °C at a rate of 600 °C/hour. At 1250 °C, nitrogen gas at a flow rate of 2 liter/min was substituted for helium. The CO monitor indicated an immediate reaction as nitrogen was introduced, and the reaction was complete in 45 minutes. Indication by the CO monitor of an abrupt CO reduction at the end of the reaction suggests rapid diffusion of CO out of the reacting solid particles. After the reaction was complete, the temperature and nitrogen flow were held for another 90 minutes. The furnace was then programmed to cool and ultra-pure helium was substituted for nitrogen at 1350 °C. The sample from Run 10 shrunk to about one-fourth of its original volume during the conversion test, while the sample from Run 11 shrunk very little. The reason for the different amount of shrinkage is unknown.

Analytical results after the conversion tests are shown in Table 7.

TABLE 7. Sample Composition After Conversion to Uranium Nitride

<u>Sample</u>	<u>N₂, wt%</u>	<u>Oxygen, ppm</u>	<u>Carbon, ppm</u>
Run 10	5.34*	7,800*	350
Run 11	5.37	13,000	35,000

* Average of duplicate samples.

The sample from Run 10 looks reasonably good as a nitride when considering this was the first attempt to produce UN using a $\text{UO}_2\text{-C}$ mixture from the spray calciner. The stoichiometric amount of nitrogen in UN is 5.55 wt%. Both the oxygen and carbon content are reasonably low in the sample from Run 10. The residual oxygen and carbon content

could possibly be reduced by further adjustment of the initial carbon content. Residual carbon can also be removed by treatment with hydrogen at about 1000 to 1200 °C to form CH_4 . The sample from Run 11 contains too much residual oxygen and carbon. The high residual carbon content can be explained by the very high initial carbon content of the UO_2 -C mixture. The reason for the high residual oxygen content is not known. The average initial carbon content was 15 wt% in the sample from Run 11, as compared to the stoichiometric requirement of 8.16 wt% for UN production by the carbothermic reaction. The sample from Run 11 was used in the conversion tests because, as indicated by the weight loss during the thermogravimetric tests discussed earlier, a portion of the carbon apparently burns out before the nitriding temperature is reached. Since the exact amount was not known, samples from Runs 10 and 11 were used in the conversion tests to obtain data at two different initial carbon concentrations.

ADDITIONAL DEVELOPMENT REQUIREMENTS

The preceding sections have discussed the favorable results of this scouting study. Much study and development are still required to establish process feasibility and define satisfactory equipment for mixed uranium-plutonium nitride or carbide production. Several important items defined during the scouting study are listed as follows:

- A criticality and design study is needed very early in any future development program to determine the feasibility of installing a spray calciner of adequate size in a glove box.
- Further work is needed to provide a more uniform carbon content. In this regard, frequent filter-blow-back, vigorous calciner vibration, increased residence time, and higher gas/liquid weight ratios should be investigated.
- Conversion of the UO_2 -carbon mixture to carbide or nitride in the radiant-heat high-temperature section of the modified spray reactor should be studied. Initial kinetic studies could be done by producing UO_2 -carbon mixtures in a spray calciner and then feeding the mixtures into a small high-temperature reactor through a solids feeder.

- The use of H_2 and CH_4 in the atomizing gas in concentrations below the explosive limit should be investigated as a means of reducing sugar requirements.

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