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Pilot-Scale Demonstration of the Modified Direct Denitration Process to Prepare Uranium Oxide for Fuel Fabrication Evaluation

F. G. Kitts

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Chemical Technology Division

PILOT-SCALE DEMONSTRATION OF THE MODIFIED DIRECT DENITRATION PROCESS TO PREPARE URANIUM OXIDE FOR FUEL FABRICATION EVALUATION

F. G. Kitts

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EXECUTIVE SUMMARY

The Uranium–Atomic Vapor Laser Isotope Separation (U-AVLIS) Program has the objective of developing a cost-competitive enrichment process that will ultimately replace the gaseous diffusion process used in the United States. Current nuclear fuel fabricators are set up to process only the UF_6 product from gaseous diffusion enrichment. Enriched uranium–iron alloy from the U-AVLIS separator system must be chemically converted into an oxide form acceptable to these fabricators to make fuel pellets that meet American Society for Testing and Materials (ASTM) and utility company specifications. A critical step in this conversion is the modified direct denitration (MDD) that has been selected and presented in the AVLIS Conceptual Design for converting purified uranyl nitrate to UO_3 to be shipped to fabricators for making UO_2 pellets for power reactor fuel. This report describes the MDD process, the equipment used, and the experimental work done to demonstrate the conversion of AVLIS product to ceramic-grade UO_3 suitable for making reactor-grade fuel pellets.

The MDD process starts with a purified uranyl nitrate solution and converts it to UO_3 powder with desired ceramic properties. A continuous operation in which an ammonium nitrate–uranyl nitrate solution is fed into a 4-in.-diam rotary calciner to discharge UO_3 powder has been demonstrated. The process starts with purified uranyl nitrate solution to which ammonium nitrate was added to yield an NH_4^+/U ratio of 2.6. This forms a double salt of uranyl nitrate–ammonium nitrate. The liquid feed (500 g U/L) was then metered into the rotating kiln at a rate of 20-30 mL/min. The kiln furnace temperature was maintained at 600°C, and the temperature of the kiln center tube varied from 480 to 530°C. Initial runs produced about 60 kg of free-flowing UO_3 powder from miscellaneous uranium oxides that contained 1.0-1.3 wt % nitrate and had a surface area of approximately 6 m^2/g. The surface area, particle size, and pellet fabrication behavior of the MDD powder are very similar to those of a good ammonium diuranate product. This characterized MDD product was shipped to Pacific Northwest Laboratory, where it was successfully converted to UO_2 nuclear fuel pellets with 94-96% of theoretical density using a variety of UO_3 powder reduction conditions.

Using refined operating conditions developed in the initial runs, 33 kg of UO_3 powder was prepared from purified AVLIS separator product from the Mars facility. This material meets the ASTM chemical specifications for ceramic-grade UO_2 (ASTM C753). The 33 kg of UO_3 powder has been blended, characterized, and packaged in 2-L containers to be made available to nuclear fuel fabricators for further development of reduction and fabrication processes for making UO_2 fuel pellets.

1. INTRODUCTION

The objective of the Uranium–Atomic Vapor Laser Isotope Separation (U-AVLIS) Program is to develop, demonstrate, and deploy the U-AVLIS technology to provide low-cost, reliable, and environmentally safe uranium enrichment services to utility customers. A conceptual design has been prepared for a production plant capable of producing enriched uranium at assays of up to 5% ^{235}U. The plant consists of the primary process systems—laser, separator, feed conversion, and product conversion—along with their respective control systems and the buildings that house them.

The product from the AVLIS separators is enriched uranium–iron alloy metal in the form of metal discs, called splats, that must be dissolved in nitric acid, purified by solvent extraction, and thermally converted to UO_3 powder that can be used to make fuel-grade UO_2 pellets for power reactors. The UO_3 prepared from purified uranyl nitrate must have specific physical properties in order to be converted to UO_2 that can make reactor-grade fuel pellets. The commonly used process for direct thermal denitration of uranyl nitrate produces UO_3 that has poor properties for this purpose. A modified direct denitration (MDD) process has been developed to produce a fine, high-surface-area UO_3 powder with properties suitable for fuel pellet fabrication.[1] The MDD process has been selected by the AVLIS program for conversion of uranyl nitrate to ceramic-grade UO_3.

The current effort is to document the MDD process as outlined for use by the AVLIS program and demonstrate the production of UO_3 in pilot-scale quantities. This material will be distributed to commercial fuel fabricators to develop procedures for reduction to UO_2 and fabrication into fuel pellets that meet specifications for reactor-grade fuel.

2. MODIFIED DIRECT DENITRATION PROCESS

The MDD process starts with purified uranyl nitrate [$UO_2(NO_3)_2$] solution to which ammonium nitrate (NH_4NO_3) is added to yield an NH_4^+/U ratio of 2 to 2.6. In the temperature range of 280 to 350°C, the resultant double salt, $(NH_4)_2UO_2(NO_3)_4$, decomposes from the solid state without melting to produce a relatively high-surface-area, free-flowing UO_3 powder with ceramic properties required for the fabrication of nuclear fuel pellets. The easily dispersed UO_3 agglomerates are mostly in the −6 mesh size range with a nitrate content of less than 2 wt %. The friable MDD product differs from oxide produced by direct thermal denitration of $UO_2(NO_3)_2$. Without NH_4NO_3 addition, the pure component melts prior to decomposition with the subsequent production of a low-surface-area UO_3 consisting of glassy shards. The MDD process has been demonstrated extensively at Oak Ridge National Laboratory (ORNL) in rotary kilns of both 3- and 4-in. diam.

2.1. CHEMISTRY

More $UO_2(NO_3)_2$ has been converted to UO_3 by direct thermal denitration than by all other conversion processes. The UO_3 produced by direct denitration is suitable for the preparation of other uranium compounds such as UF_4 or UF_6, but it has very poor properties for the fabrication of nuclear fuel pellets. When $UO_2(NO_3)_2$ solution is heated, brown fumes evolve from a syrupy, clear melt boiling in the range of 185 to 195°C. As denitration proceeds, the melt thickens to a paste forming a glassy cake, which then cracks into low-surface-area pieces. When NH_4NO_3 is added to the $UO_2(NO_3)_2$ solution as in the MDD process (NH_4^+/U mole ratio of 2), continued evaporation

produces a yellow slurry and then dry yellow crystals. Decomposition on heating to 350°C produces a fine, high-surface-area UO_3 powder with ceramic properties suitable for pellet fabrication.[1]

The formation of NH_4NO_3-$UO_2(NO_3)_2$ double salts has important effects on the thermal denitration process for the preparation of UO_3 and its physical properties. Thermogravimetric analysis has shown that thermal decomposition of $(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O$ proceeds in three distinct steps: (1) dehydration occurs at 50°C; (2) the anhydrous tetranitrate decomposes exothermically, without melting, at 170-270°C to form the trinitrate salt; and (3) the trinitrate decomposes endothermically, without melting, at 270-300°C to form amorphous UO_3. Subsequent heating to 500°C causes crystallization of the UO_3 (ref. 2).

Decomposition products from the MDD process have the same chemical makeup as those products from simple thermal denitration of a $UO_2(NO_3)_2$ solution, plus some N_2O and H_2O derived from NH_4NO_3 decomposition. The surface area, particle size, and pellet fabrication behavior of the MDD powder are very similar to the UO_3 product produced by the ammonium diuranate (ADU) precipitation conversion process. More power reactor fuels have been fabricated from the product of the ADU process than from all other $UO_2(NO_3)_2$ conversion processes.[3]

2.2 EQUIPMENT

The MDD process developed at ORNL uses well-demonstrated denitration equipment to prepare UO_3 powder with desired ceramic properties for UO_2 pellet fabrication. Since the MDD UO_3 is formed by the decomposition of solid crystals, the oxide properties depend on the crystallization conditions. A rotary kiln with liquid at the feed point and a distinct region of crystallization was selected for the double-salt decomposition reaction. The desired UO_3 powder properties may not be duplicated in a fluidized bed or agitated trough where the feed is sprayed onto UO_3 solids.

The heart of the MDD process and the work described herein is a rotary kiln purchased from the Harper Electric Furnace Corporation in Lancaster, New York. The kiln is equipped with an inclined 4-in.-ID, 60-in.-long stainless steel tube, which rotates within a heated chamber that is 18 in. long, 16½ in. wide, and 22 in. high (see Fig. 1). It is heated by eight cylindrical elements: each has a 2-in. diam, is spirally wound over a 19½-in. length, and has ~1-kW capacity. These are inserted vertically from the top in two rows, one on either side of the rotating tube. The ends of the 60-in.-long tube are sealed to stationary end fittings by rotating graphite rings supported by stainless steel bellows. A stationary 1-in.-OD center tube traverses the entire length of the kiln. The liquid feed is injected through a ¼-in. tube (located inside the center tube) into the rotating kiln within the heated zone. Several ⅜-in.-diam holes drilled in the stationary center tube allow steam and decomposition gases to pass out of the upper end of the kiln countercurrent to the feed. Inside the rotating tube within the heated zone, two 1-in.-diam stainless steel rods roll free to break up agglomerates as the solids form and promote heat transfer. These "breaker bars" are kept in place longitudinally by two washers concentric with and welded to the stationary center tube. A disc or dam located about midway in the heated zone divides the center tube into the wet upper end and the dry lower end adjacent to the granular solids. The center tube temperature is measured by a thermocouple resting on the bottom of the center tube about 2 in. into the heated zone from the dry end. By the time the oxide product is discharged from the lower end of the kiln countercurrent to an air purge, it has cooled enough to be collected in either 2- or 4-L polyethylene bottles.

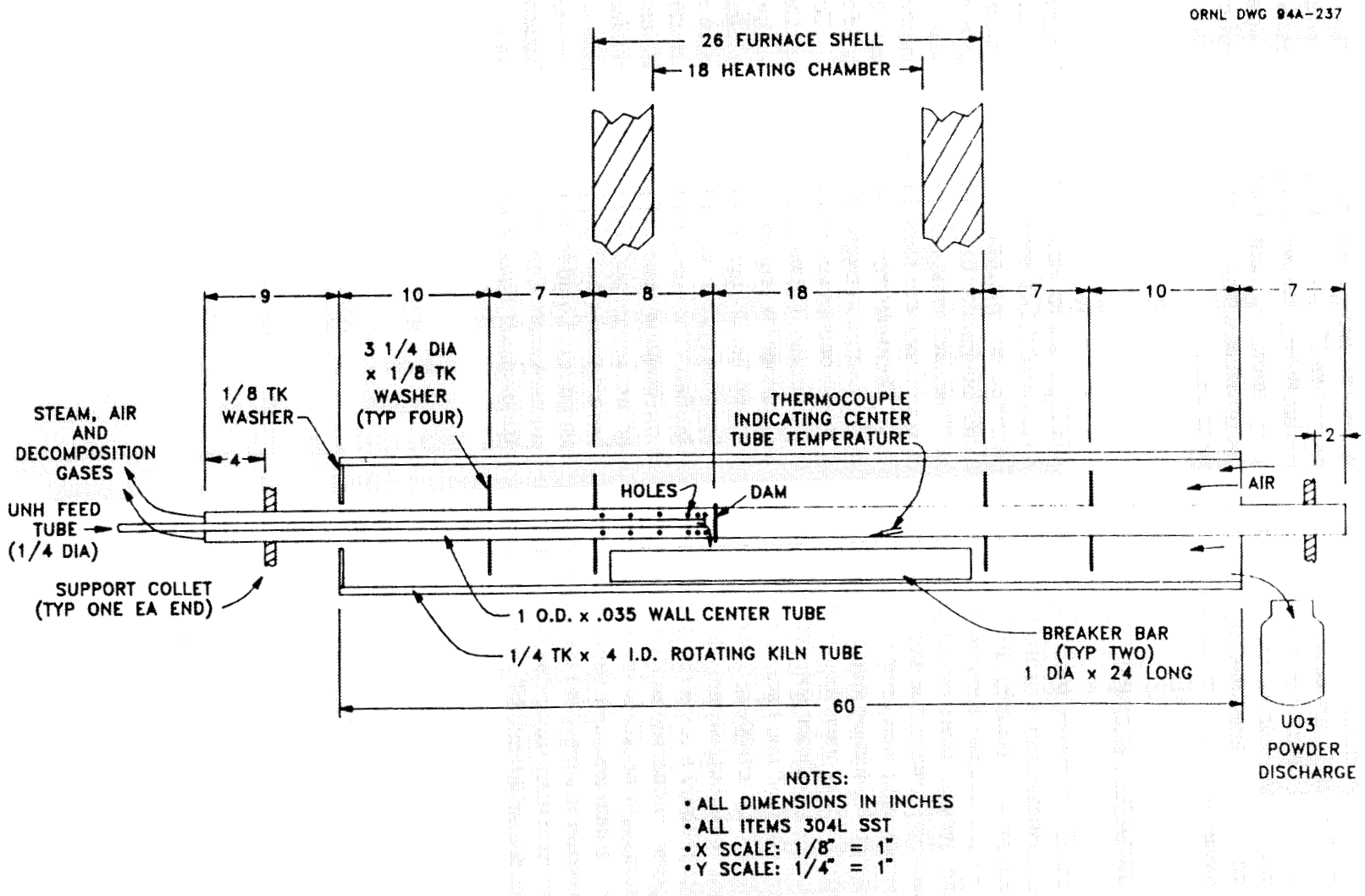

Fig. 1. Schematic showing spatial relationships in the rotary kiln.

The other two pieces of equipment vital to kiln operation are the furnace controller and the feed pump. At a set point of ~600°C, the control thermocouple in the heated compartment will be held at ±1°C by the furnace controller, regardless of small load variations, with no attention by the operators. A rotary-type peristaltic pump with small-bore polyvinyl tubing gave constant feed rates within 5% over several hours of continuous operation. For stable kiln operation established by a constant center tube temperature and constant product discharge rate, dependable furnace control and unvarying liquid feed rates are absolutely essential.

2.3. PROCESS FLOWSHEET

The MDD equipment is shown schematically in Fig. 2. All except the furnace controller, designated SCR, is located in a walk-in hood with dimensions 12 ft wide × 8 ft high × 4 ft deep in Laboratory 113, Building 3019. Liquid feed is prepared by mixing H_2O, HNO_3, UO_3, and NH_4NO_3 in a 30-gal, stainless steel makeup drum and then pumped to the Pyrex feed tanks (6-in. diam by 3 ft high), where it can be metered to the kiln. The feed tank gauge glasses, ~⅜-in. ID, not only indicate the level in the tank but also are used to check the feed rate by pumping only from the gauge glass and measuring the rate of depletion. The other major system is the recirculating batch condensate collection system. At the beginning of a run, enough water to prime the recirculating pump (2 L) is measured into the stainless steel condensate reservoir (20 L). Condensate is continuously recirculated through a cooler, down through the packing (¼-in. ceramic Berl saddles) of the scrubber, and back to the reservoir. The scrubber is principally a solids de-entrainer since it was not sized to fully recover nitrate values. When liquid feed is initiated to the kiln, the off-gas stream containing steam, HNO_3 vapor, decomposition gases, and air passes upward through the scrubber, where most of the condensables are liquified. The noncondensable gases continue through an updraft condenser and a knockout pot into the building vessel off-gas system, which maintains a slight vacuum on all of the equipment. As the run progresses, the volume of condensate in the reservoir increases and periodically must be diverted to the building low-level liquid waste system. Rinse water is pumped to the kiln for a short time prior to liquid feed introduction to establish a near steady-state temperature profile within the evaporation zone of the rotating tube. Rinse water is also introduced at the end of a run to purge the small-diameter liquid feed injection tube.

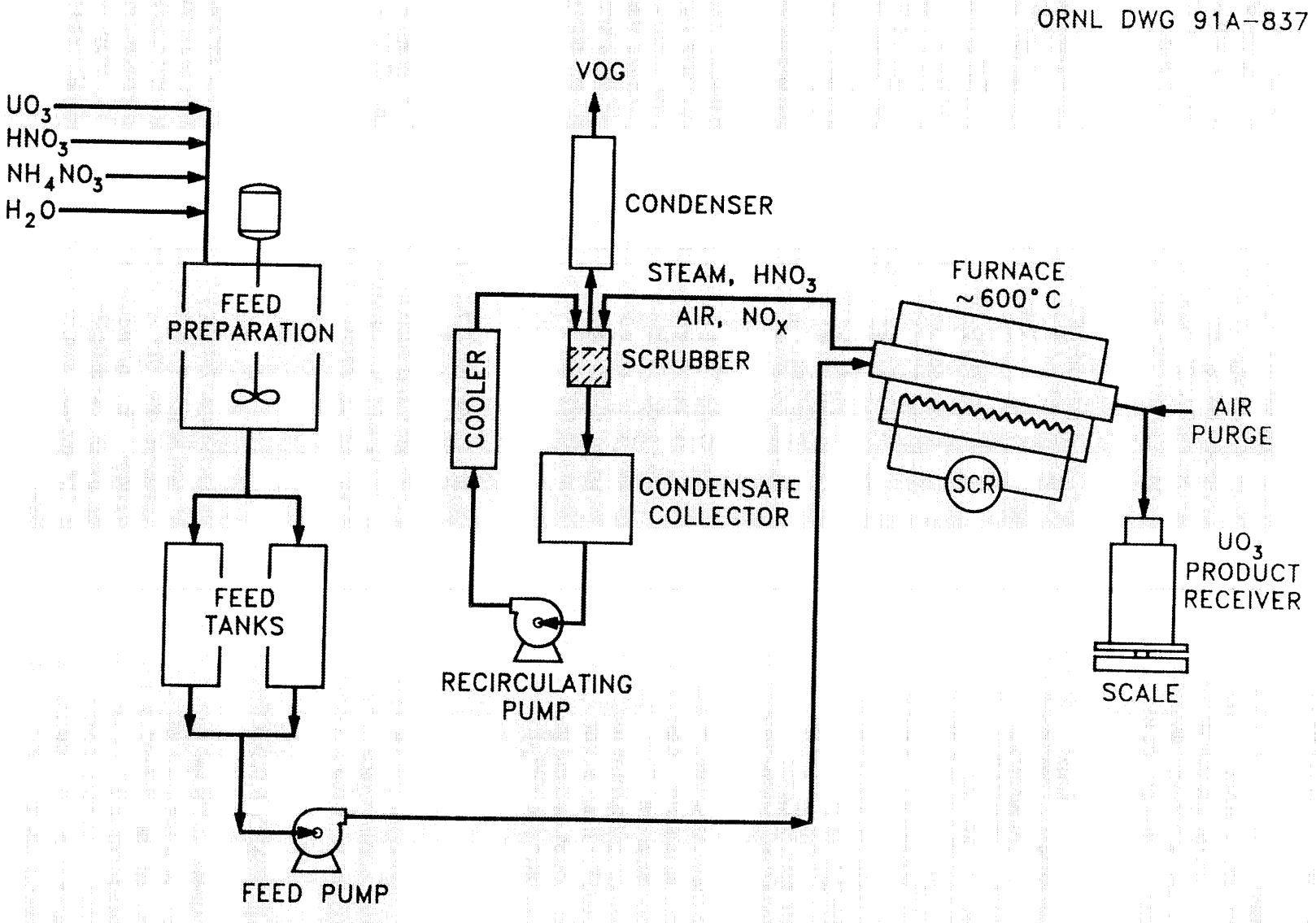

Fig. 2. Schematic of MDD process equipment.

2.4. OPERATING CONDITIONS

In earlier work (1989) with the 4-in.-ID rotary kiln located in Building 3019, 180 kg UO_3 was produced in a series of short runs under a fairly wide range of operating conditions as shown in Table 1. Although the material produced was free flowing and of good appearance, it contained 8.2% NO_3^-, which was not considered representative of MDD product and was not used for further evaluation. Portions of this material were dissolved to provide feed for runs described later.

Table 1. Rotary kiln conditions in producing 180 kg UO_3 powder

Characteristic	Range	Characteristic	Range
Feed composition		Air purge, scfm	~0.1
U, g/L	300-500	Furnace temp, °C	550 ± 5
H^+, *M*	0 ± 0.5	Center tube temp, °C	350 - 475
NH_4^+/U ratio	2.6	Rotation, rpm	8-10
Feed rate, mL/min	25-40	Inclination, °to horizontal	3

From these early runs it was concluded that to lower the NO_3^- concentration in the powder product we should raise the center tube temperature, increase the residence time, improve the heat transfer, and increase the air purge rate. We experienced good operation with the speed of rotation and degree of inclination used previously, so a lower feed rate was decided upon to reduce the heat required for evaporation, reduce the solids inventory in the system, and thus aid heat transfer to the solids. It was decided to maintain the liquid feed composition near 500 g U/L, the H^+ or acidity near neutral, and the NH_4^+/U ratio at 2.6.

3. PILOT-SCALE DEMONSTRATION

The purpose of the three extended runs described in this section was to produce ~60 kg of UO_3 powder that is typical of that produced in a rotary kiln of reasonable size using the MDD process. The feeds were made by dissolving the off-specification material made previously.

3.1 ROTARY KILN OPERATION

The operation of the kiln, in principle, is quite simple and straightforward: the furnace temperature is held at a constant value by the controller, the kiln at a fixed inclination is rotated at a constant speed, the liquid feed is metered in at a constant rate, the air purge is constant, and the slightly reduced pressure fluctuates within a narrow range. The variability of operation must result from our inability to control or even be aware of the buildup and depletion of solids on the tube wall and breaker bars. As the powder is collected, the product bottle is weighed periodically and a grab sample is taken of the last material produced.

In the MDD process equipment, an aqueous feed containing uranyl nitrate and NH_4NO_3 at NH_4^+/U ratios of ~2.6 is introduced into the heated portion of a 4-in.-ID stainless steel pipe rotating within a rectangular furnace maintained at ~600°C. The liquid is evaporated immediately, leaving a solid double-nitrate salt which decomposes to a fine powder without melting or going through a gummy, molten stage. Two 1-in.-diam stainless steel breaker bars rotate on the inside surface of the heated section of the kiln to assist with heat transfer and to prevent the buildup of a thick layer of solid at the point of evaporation. The product exits the lower end of the kiln, countercurrent to an air purge, as a free-flowing UO_3 powder.

3.2. PREPARATION OF URANIUM OXIDE PRODUCTS

Three extended runs (designated KN-16, -17, and -18) of ~17, 40, and 35 h of continuous operation were made in the 4-in.-ID rotary kiln. The three feed compositions were similar, and operating conditions (see Table 2) were in a narrower range than in the 180-kg campaign, which required numerous feed batches, startups, and shutdowns.

Table 2. Rotary kiln conditions in producing ~60 kg UO_3 powder

Characteristic	Range	Characteristic	Range
Feed composition		Air purge, scfm	0.39-0.52
U, g/L	492-501	Furnace temp, °C	600 ± 15
H^+, *M*	0.03-0.09	Center tube temp, °C	505 ± 25
NH_4^+/U ratio	2.6	Rotation, rpm	10
Feed rate, mL/min	28-21	Inclination, ° to horizontal	3

The data in Tables 3, 4, and 5 show that the product in the three runs was collected in 7, 11, and 11 bottles, respectively, with about 1-3 kg per bottle. The first bottle from run KN-16 was an exception in that product was removed early to isolate the startup material. Analyses later showed this was unnecessary. The first product data weights shown for each bottle indicate the amount of powder that had been collected when a grab sample was taken; the final weight for each bottle is the total net weight of powder collected. The liquid feed and air purge rates used during the filling of the product bottles are also tabulated. The compositions of the condensate batches indicated in Tables 3, 4, and 5 are discussed in Sect. 3.4, Effluent Treatment.

Table 3. Production of 12 kg UO_3 by the MDD process: Run KN-16

Product data			Process conditions		
Bottle no.	Σ Net wt (g)	LOI[a] (%)	Feed rate (mL/min)	Air purge (scfm)	Condensate batch no.
1	672	3.72	28	0.65	1
2	1300 2042	3.43 3.66	28	0.39 0.52	1
3	1116 1821	3.78 4.16	28	0.52	1
4	957 1985	4.67 4.26	28	0.52	1
5	994 1935	5.74 4.80	28 23	0.52	2
6	814 1868	6.43 6.46	23	0.52	2
7	765 1646	4.57 4.62	23	0.52	2

[a]LOI = loss on ignition.

Table 4. Production of 24 kg UO_3 by the MDD process: Run KN-17

Product data			Process conditions		
Bottle no.	Σ Net wt (g)	LOI[a] (%)	Feed rate (mL/min)	Air purge (scfm)	Condensate batch no.
1	717 1738	3.46 4.24	25	0.52	1
2	1030	3.50	25	0.52	1
3	~400 1190 2550 3255	2.53 2.61 4.13 2.36	22	0.52 0.39	1 2
4	890 1690 2470	5.45 3.58 3.73	22	0.39 0.48	2 2
5	1447 2281	4.10 4.35	22	0.52	2
6	1256 2710	4.47 4.46	23	0.52	2
7	1047 2460	6.11 4.54	22	0.52	2
8	798 2538	5.56 5.45	21	0.52	3
9	1292 2239	4.84 4.75	22	0.52 0.39	3
10	845 1820	5.13 5.75	22	0.39 0.52	3
11	1224	4.65	21	0.52	3

[a]LOI = loss on ignition.

Table 5. Production of 25 kg UO_3 by the MDD process: Run KN-18

Product data			Process conditions		
Bottle no.	Σ Net wt (g)	LOI[a] (%)	Feed rate (mL/min)	Air purge (scfm)	Condensate batch no.
1	1084 2303	3.17 4.28	21 25	0.50	1
2	1336 2225	4.55 4.26	25	0.31	1
3	1157 2031	4.98 5.51	25	0.42	1
4	2134 2727	3.46 5.21	21	0.49	1
5	1067 1726 2697	5.30 3.36 3.98	21	0.49	1 2
6	1719 2334 2815	3.71	24	0.48	2
7	1409 2187	4.60	24	0.48	2
8	1518 2297	4.05	22	0.49	2
9	1621 1819	4.61	23	0.49	2
10	1358 2285	4.39 4.42	22	0.49 0.48	3
11	1579	4.83	22	0.48	3

[a]LOI = loss on ignition.

The percentage weight loss on ignition (LOI) to 900°C determined on the grab samples (results obtained after the conclusion of each run) is also shown in Tables 3, 4, and 5. These LOI values seemed to indicate an increasing trend, which was reversed by decreasing the feed rate. The LOI includes H_2O and other volatiles, NO_3^-, and oxygen lost in the transition to U_3O_8. These values were encouraging since they averaged only slightly more than half the nitrate content of the product powder produced in earlier campaigns (180 kg in 1989).

3.2.1. Screening and Preparation of −25 Mesh Powder, Run KN-16

In the first of the three runs, KN-16, each of the seven product bottles was separated into three size fractions using 6 and 25 mesh screens. The weights and LOI values for all three fractions are shown in Table 6. Although LOIs for the kiln fine and midsize fractions were comparable, the coarse-fraction LOI was much higher. Since the coarse material totaled less than 0.5 kg, it was excluded from further consideration. Since a fine product was desired and the midsize LOI was low, a mild size reduction was performed on the midsize fraction to allow it to be included in the acceptable product arbitrarily chosen as −25 mesh. To accomplish this, three stainless steel rods ~1-in. diam and ~8 in. long were placed in a 4-L bottle (~6-in. diam) with the midsize fraction and rotated for about an hour on a ball mill rotator. After this treatment the batch was placed on the 25 mesh screen; the small amount that did not pass was segregated for recycle with the original coarse material. The two midsize weights tabulated for each bottle are the as-screened (−6 +25 mesh) weight and the slightly lower weight of the −25 mesh material after milling. The powder was resampled after milling: the LOI values checked closely, and the NO_3^- values ranged from 1.0 to 2.0 wt %. Since combining, blending, and packaging for run KN-16 had to be accomplished before the NO_3^- values were determined, bottle number 6 was excluded because of its relatively high LOI value. The entire blended batch was sampled, but full characterization results (see Sect. 3.3) had not been received from the analytical laboratory at the Oak Ridge Y-12 Plant at the time of shipment.

Table 6. Sieve analysis and LOI for MDD-produced UO_3 powder: Run KN-16

Product bottle no.	Acceptable product, −25 mesh				Midsize, −6 +25 mesh as produced[a]		Held for recycle		
	Fines, −25 mesh as produced		Milled midsize				Midsize +25 mesh	Coarse +6 mesh	
	Wt (g)	LOI[b] (%)	Wt (g)	LOI (%)	Wt (g)	LOI (%)	Wt (g)	Wt (g)	LOI (%)
1	413	3.75	222	4.13	237	4.01	15	22	13.85
2	1273	3.82	708	3.97	743	3.82	35	36	4.86
3	930	3.73	835	3.95	855	3.89	20	36	7.09
4	1146	4.51	781	4.72	815	4.63	34	24	10.4
5	856	5.14	910	5.77	939	5.44	29	140	23.97
6	800	5.82	840	6.94	880	7.93	40	130	13.16
7	908	4.60	617	4.82	645	4.59	28	93	9.23

[a]Quantities labeled "as produced" were obtained by sieving the material discharged from the kiln with no size reduction.
[b]Loss on ignition (LOI) determined up to 900°C.

3.2.2. Product-Finishing Glove Box, Runs KN-17 and -18

The preparation of -25 mesh product from the UO_3 powder produced in run KN-16 (described above) was carried out in a hood in Laboratory 108, Building 3019. Since larger amounts were planned for future runs, it was obvious that a safer, more efficient method of handling, screening, and weighing had to be devised. Two unused standard 3-ft glove boxes were available; therefore, a 6-ft-long glove box was made by cutting ~13-in.-diam irregular holes in the adjacent sides of the two 3-ft glove boxes and bolting them together through backup flanges inside each box with a rubber gasket between the outer walls. The 6-in. bag-out port remaining on one box was replaced with the 12-in. port removed from its other side. The result was a versatile 6-ft-long box divided into two compartments with a large pass-through port between them and a 12-in. bag-out port in either end. A 2-in.-diam penetration in the bottom of one compartment allows the -25 mesh fraction of each product bottle to be dumped into the 50-L "blender bottle" supported underneath the box. This plastic bottle is screwed into its sealing plastic lid that is flanged to the bottom of the box.

The powder produced in runs KN-17 and -18 was processed in the new glove box using a different method for size reduction. Since run KN-16 had shown that all the -6 mesh material had satisfactory NO_3^- content, no attempt was made to separate the as-produced -6 +25 mesh fraction and the -25 mesh fines. The +6 mesh oversize was separated and set aside for recycle as before. The weights of the product and recycle material are shown in Tables 7 and 8.

Table 7. Sieve analysis and composition of run KN-17 material

Bottle no.	-25 Mesh product data			Recycle material	
	Wt (g)	NO_3^- (%)	LOI[a] (%)	+6 Mesh wt (g)	+25 Mesh wt (g)
1	1624	0.36	3.85	55	56
2	941	0.48	3.50	45	30
3	3186	0.36	2.91	55	9
4	2349	0.57	4.25	43	65
5	2130	1.38	4.23	92	52
6	2551	2.31	4.47	134	15
7	2316	2.13	5.33	92	33
8	1998	2.86	5.51	370	146
9	1947	2.12	4.80	192	83
10	1678	1.86	5.44	84	48
11	1108	1.47	4.65	80	27

[a]LOI = loss on ignition.

Table 8. Sieve analysis and composition of run KN-18 material

Bottle no.	−25 Mesh product data			Recycle material	
	Wt (g)	NO_3^- (%)	LOI[a] (%)	+6 Mesh wt (g)	+25 Mesh wt (g)
1	2159	0.61	3.73	65	57
2	2088	1.26	4.41	49	75
3	1798	1.84	5.25	103	113
4	1844	1.54	4.34	387	474
5	2238	1.51	4.21	255	184
6	2331	1.56	3.71	169	294
7	1939	2.15	4.60	96	137
8	2075	1.51	4.05	113	89
9	1545	2.09	4.61	149	107
10	2004	1.82	4.41	66	195
11	1441	2.01	4.83	85	32

[a]LOI = loss on ignition.

Roughly half of the −6 mesh powder, which also passed through the 25 mesh screen, was not weighed separately but was retained in the pan. This oxide was allowed to mix with the remaining product which passed through the 25 mesh screen upon gentle pressure with a fiber-bristle brush. The weight of that material which did not pass easily with brushing is tabulated as +25 mesh recycle material. The −25 mesh product fraction was analyzed for NO_3^- before blending. Due to the satisfactorily low average NO_3^- contents (product specification arbitrarily set at 2 wt %) of both runs, no bottle of product had to be rejected from either run KN-17 or KN-18.

3.3. CHARACTERIZATION OF THE UO_3 POWDER PRODUCTS

The compositions and physical properties of the three batches of UO_3 made for sample pellet fabrication fell within a reasonably narrow range (see Table 9). The uranium values compare favorably with the 83.2 wt % theoretical value for UO_3 considering the rather high LOI results, which also include the almost 2 wt % loss on decomposition to U_3O_8. A discussion with analytical chemistry personnel at the Y-12 Plant[4] indicated that the LOI numbers were high by almost a factor of 2 due to water pickup during the analyses. The nitrates (1.0-1.3 wt %) are well below the arbitrary specification of 2.0 wt %. Some water was found by x-ray diffraction to be bound as $UO_3 \cdot 0.8H_2O$. The particle densities of 5.8-6.2 g/cm^3 are 80-85% of the theoretical value for UO_3. The surface areas of 6-9 m^2/g were well within the target range of 5-15 m^2/g. The greatest variation was in the

particle diameter, with one run producing a maximum of 88 μm and the others showing 15 and 30 μm. For the sieve analyses, all material passed a 6 mesh screen, as produced, and was size reduced by gentle brushing through the 25 mesh screen. Any further desired size reduction of the agglomerated particles could have been accomplished with a minimum expenditure of energy. The uranium isotopic analysis confirmed that the material is normal uranium.

Table 9. Characterization of UO_3 powder products

Characteristic	Run no.		
	KN-16	KN-17	KN-18
Uranium, wt %	80.5	79.7	80.5
Nitrate, wt %	1.3	1.2	1.0
Water, wt %	0.93	0.63	0.52
Wt loss on ignition to 1000°C, wt %	8.2	7.6	7.8
Density, g/cm^3	5.80	6.22	6.00
Surface area, m^2/g	8.925	6.145	6.494
Particle diameter distribution			
@ 100 wt %, μm	≤88.00	≤14.92	≤29.85
@ 90 wt %, μm	≤73.30	≤9.11	≤12.41
@ 50 wt %, μm	≤24.43	≤3.14	≤3.93
@ 10 wt %, μm	≤3.19	≤0.78	≤0.95
Sieve analysis (100% through 25 mesh)			
+ 60 mesh, wt %	35.0	57.6	42.3
−60 +140 mesh, wt %	23.3	20.1	25.7
−140 +230 mesh, wt %	12.7	11.6	13.0
−230 +400 mesh, wt %	8.3	9.8	11.9
−400 mesh, wt %	20.7	0.9	7.1
Uranium isotopic analysis			
^{234}U, wt %	0.005	0.005	0.005
^{235}U, wt %	0.708	0.710	0.708
^{238}U, wt %	99.286	99.286	99.286

The impurities found in the three blended product batches are shown in Table 10. The two highest, iron and carbon, were present at ~100 ppm each in the UO_3 dissolved to make the feed for these runs. The fact that the chromium and nickel are not correspondingly high indicates that the iron did not come from corrosion of the stainless steel process equipment. Aside from iron and carbon, only sodium, thorium, copper, and sulfur were found to be greater than 25 ppm in any run. All of the elements found above their detection limit by the method of inductively coupled plasma analysis for trace quantities are listed in Table 10. A more sensitive analytical method would have to be used if phosphorus or sulfur was considered significant at values less than 100 ppm.

Table 10. Impurities in UO_3 powder products
(in micrograms per gram of uranium)

	Requirements[a]	KN-16	KN-17	KN-18
Aluminum	75	7	11	19
Barium	--	0.2	0.3	0.3
Cadmium	--	0.3	0.4	0.4
Calcium	(Ca + Mg) 150	17	15	22
Carbon	--	117	50	61
Chlorine	(Cl + F) 300	7	4	5
Chromium	150	8	10	19
Cobalt	75	<0.2	<0.2	0.2
Copper	200	23	30	30
Fluorine	(F + Cl) 300	7	0.4	<0.2
Iron[b]	200	116	140	185
Lead	200	8	2	2
Magnesium	(Mg + Ca) 150	8	9	14
Manganese	200	7	2	3
Nickel	150	5	7	14
Potassium	--	<15	<15	20
Silicon	150	7	4	7
Silver	--	<2	0.6	<0.6
Sodium	--	42	57	60
Strontium	--	0.03	0.04	0.04
Sulfur	--	74	<100	<100
Thorium	10	18	45	46
Tin	200	8	3	3
Titanium	200	3	1.5	2.4
Yttrium	--	0.13	0.16	0.16
Zinc	200	18	19	24
Zirconium	--	4	5	5

[a]From *U-AVLIS Production Plant Conceptual Design Report, Volume 14, Initial Deployment Option,* LP-91-142, Vol. 14, June 1992.
[b]Only critical element of concern in MDD process.

3.4. EFFLUENT TREATMENT

The gas stream exiting the upper end of the kiln countercurrent to the feed contains steam, nitric acid vapor, NO_x, N_2, and O_2. It first contacts a short section of wetted packing, which serves mainly as a solids separator to trap any fine UO_3 carried by the gas. It then passes through a condenser and finally through a knockout pot before entering the building off-gas system. The condensed liquid is collected in a tank from which it is recirculated by a centrifugal pump through a heat exchanger (cooler) and is sprayed over the packing in the de-entrainer mentioned previously. A minimum volume of ~2 L of water is required to charge the system initially, and the maximum capacity is ~20 L. For a material balance only final volumes and concentrations are required. These values are presented in Table 11.

During run KN-16, two batches of condensate were collected. The first batch contained the overheads collected during the filling of the first four product bottles (as indicated in Table 3) and a portion of the fifth. The second batch contained the overheads collected during the remainder of the run. Duplicate samples were analyzed, and the averaged values were used to calculate quantities shown in Table 11. Assuming that all the H^+ is nitric acid, the 36.8 mol of nitrate recovered is ~40 wt % of that contained in the uranyl nitrate feed. This low recovery is not surprising because the "scrubber" was not optimized to recover nitrate values and the decomposition products of NH_4NO_3 are reported[1] to be H_2O, N_2, O_2, and N_2O and not recoverable NO_x. In runs KN-17 and KN-18 (Tables 4 and 5), only single samples of each batch of condensate were analyzed, but the apparent recoveries remained ~40 wt %. The uranium values in the condensate can be recovered by concentrating it and using it in the formulation of feed for subsequent runs.

Table 11. Values recovered in the recirculating condensate

Run no.	Batch no.	Volume (L)	Uranium		Total acid	
			(g/L)	(g)	(*M*)	(mol)
KN-16	1	16.5	2.22	36.6	1.36	22.4
	2	12.5	0.62	7.8	1.15	14.4
KN-17	1	11.2	7.26	81.3	1.57	17.6
	2	18.0	3.94	70.9	1.64	29.5
	3	9.3	6.40	59.5	1.93	18.0
KN-18	1	16.5	4.40	72.6	2.3	38.0
	2	20.0	3.30	66.0	2.2	44.0

4. DEMONSTRATION WITH MARS SEPARATOR PRODUCTS

A batch of uranium-iron alloy that was processed through the AVLIS equipment (although not actually enriched) has been designated Mars separator product. A 50-kg quantity of this material was dissolved in nitric acid; the resulting uranyl nitrate solution was purified by solvent extraction, concentrated by evaporation, formulated into MDD feed, and calcined to UO_3 in the 4-in.-ID rotary

kiln in Building 3019. The dissolution, purification, and evaporation operations were completed by the ORNL Robotics and Process Systems Division (RPSD).[5,6]

4.1. DISSOLUTION AND PURIFICATION

Approximately 50 kg of uranium separator product from the Mars facility at the Lawrence Livermore National Laboratory was processed in the Integrated Process Demonstration Facility at ORNL to test metal dissolution and solution purification. The natural uranium–iron alloy splats were dissolved in 9.5 *M* nitric acid, and the resulting uranyl nitrate solution was purified by solvent extraction using 30 vol % tributyl phosphate in normal paraffin hydrocarbon as a solvent. A continuous rotary dissolver was used for dissolution, and advanced centrifugal contractors were used for solvent extraction.

The Mars facility utilized an integrated uranium separator system, and the material withdrawn from the separator pod is representative of U-AVLIS metal product in terms of metal shape, iron content, and the presence of other contaminants. Since this separator test involved no process laser light and was not an enrichment experiment, the product was isotopically the same as the natural uranium fed to the test.

The dissolver system uses a rotary dissolver with a nominal feed rate capability of 240 kg U/d. The dissolver drum consists of an auger enclosed in a cylinder. The vessel lies horizontally, forming eight stages between the turns of the helical walls of the auger. Metal is introduced at one end of the drum, and nitric acid flows countercurrent to the movement of metal, which is transferred from one stage to the next by rotating the drum one complete turn. The liquid product stream flows into digester tanks, and off-gas is routed to two condensers and then to an NO_x scrubber. The solvent extraction system includes 18 stages of 5.5-cm-diam centrifugal contractors and has a nominal throughput of 100 kg U/d. Six stages are used for extraction, four stages for scrubbing, and eight for stripping.

Metal feed rates to the dissolver were limited due to the facility's NO_x emission permit. Metal was fed at the rate of about 250 g every 4.5 min, and the time between stage transfers was set at 1.5 h. The uranium-iron alloy was dissolved readily in the nitric acid, leaving 0.5 wt % undissolved residue, a third of which was uranium. The uranium concentration in the dissolver product solution was about 150 g U/L, and only six elements exceeded the concentration limits established in the American Society for Testing and Materials (ASTM) specification for nuclear-grade uranyl nitrate solution, ASTM C788.

Following feed adjustment to 178 g U/L and 4.3 *M* HNO_3, the solution was fed to the solvent extraction system. Analytical results showed that iron and all other AVLIS-specific product contaminants were effectively removed by a single cycle of solvent extraction purification. The amount of uranium lost with the raffinate was on the order of 0.1 wt %.

4.2. CONCENTRATION BY EVAPORATION

Prior to preparation by evaporation, the purified solution was stored in five batches, each batch having been processed individually (i.e., each having a distinct processing history). Table 12

characterizes the preconcentration product solutions. Prior to evaporation, all product batches had been analyzed for a number of contaminant elements by a combination of inductively coupled plasma/atomic emission spectroscopy (ICP/AES) and spark source/mass spectroscopy (SS/MS). The material being processed was, ultimately, to be converted into uranium oxide suitable for use as nuclear reactor fuel. Acceptance criteria for the intermediate uranyl nitrate solution are listed in ASTM specification C788 for nuclear reactor-grade uranyl nitrate.

Table 12. Purification product solution concentrations

Batch no.	Uranium (g/L)	HNO_3 (*M*)
1	64.0	0.14
2	65.6	0.08
3	46.8	0.77
4	32.5	0.23
5	52.6	0.08

The preconcentration contaminant analyses of duplicate samples indicated that product solution batch number 3 contained iron at a concentration exceeding the maximum level specified in ASTM C788 (see Table 13). The SS/MS samples are analyzed without prior removal of uranium, whereas the ICP/AES analyses were performed after first stripping uranium from the sample by ion exchange. SS/MS values for iron are therefore subject to uranium absorbance overlap. In addition, SS/MS analysis provides poorer resolution than can be obtained by ICP/AES. RPSD and AVLIS program personnel agreed that, due to the high iron content, the third batch of feed material would remain segregated from the balance of the solution throughout processing and would be concentrated only after all other material had been processed.

Table 13. Concentration of iron in purified solution batch number 3 (preconcentration)

Sample no.	ASTM C788 limit (μg/g U)	Iron concentration by SS/MS[a] (μg/g U)	Iron concentration by ICP/AES[b] (μg/g U)
DRUM3-1	200	5342	421
DRUM3-2	200	16026	431

[a]SS/MS = spark source/mass spectroscopy.

[b]ICP/AES = inductively coupled plasma/atomic emission spectroscopy.

Prior to commencing the concentration process, the AVLIS program personnel and participants from the ORNL Chemical Technology Division (CTD) expressed an interest in having RPSD neutralize the excess free acid present in product solutions prior to concentration. This approach reduces the potential for contaminating solutions with equipment corrosion products during the evaporation process. At the request of the AVLIS program, RPSD agreed to perform a cursory determination of the feasibility of neutralizing solutions prior to concentration. However, three simple scouting tests determined that neutralization prior to evaporation would require a potentially lengthy and costly development effort. It was decided that the dilute purified product would be concentrated without any chemical adjustment.

Concentration of purified AVLIS uranyl nitrate solution was performed in a small thermosiphon evaporator obtained from CTD. This evaporator had previously been used to concentrate solutions for MDD feed. Prior to concentration of uranyl nitrate solutions, the evaporator was tested twice—first with water to verify installation and then with dilute nitric acid to evaluate system corrosion on passivated wetted surfaces. Analytical chemistry results from the acid concentration test indicated insignificant addition of contaminants as a result of evaporation.

Purified solutions contained in feed batches 1, 2, and 5 (see Table 12) were concentrated and collected in a product drum designated AVCONC-1. Concentration products from feed batches 3 and 4 were collected in product drums designated AVCONC-3 and AVCONC-4 respectively. Concentrated product solution uranium and nitric acid concentrations are presented in Table 14. Operation of the evaporator system was uneventful. Target evaporator vapor temperatures were obtained by control of the feed solution flow rate. The target temperature during the first evaporation run was 108°C. Target temperatures in subsequent runs were in the 106 to 107°C range, as the first-run product concentration was nearly high enough to result in solidification upon cooling.

Table 14. Concentrated AVLIS product uranium and HNO_3 concentrations

Product batch designation	Uranium (g/L)	Nitric acid (*M*)
AVCONC-1	561	0.40
AVCONC-3	255	2.05
AVCONC-4	315	1.07

Contaminant concentrations for product drums AVCONC-1 and AVCONC-4 are listed in Table 15. Contaminant analysis of material in product drum AVCONC-3 was not performed, as this material was known not to comply with ASTM C788 prior to evaporation. As the results indicate, concentrate batches AVCONC-1 and AVCONC-4 were within ASTM limits with the exception of one silicon concentration result for AVCONC-4. Given a tendency toward false high silicon indications by both SS/MS and ICP/AES analysis methods, it is expected that this product batch does, in fact, comply with the purity specification.

Table 15. Contaminant concentrations in product batches AVCONC-1 and AVCONC-4

Element	ASTM C788 limit (μg/g U)	AVCONC-1 (μg/g U)	AVCONC-4 (μg/g U)
Al[a]	75	15	--
Ca + Mg	150	65	<22
Co	75	<2	<4
Cr	150	<4	<7
Cu	200	<2	<4
Fe	200	27	<7
Mn	200	9	<7
Mo	200	<9	<16
Ni	150	<2	<4
Pb	200	<9	<16
Si[b]	150	53.5-125	127-227
Sn	200	<4	<7
Ta	200	<4	NA
Ti	200	<9	<16
V[b]	200	3.6-5.3	<7
W	200	<18	<32
Zn	200	<4	<7

[a]Aluminum result obtained by inductively coupled plasma/ atomic emission spectroscopy. All other results were obtained by spark source/mass spectroscopy.
[b]Results from duplicate samples are presented due to wide disparity. All other results were essentially identical for the duplicate samples analyzed.

Also note that the contaminant levels reported above are less than those previously reported for unconcentrated purified solutions. Comparison of analyses before and after concentration indicated that any addition of corrosion product during the evaporation process was negligible. Results after concentration also indicate that the credibility of the preconcentration analyses is limited by poor

resolution in the relatively dilute solutions. Indications from unconcentrated solution of contaminant levels exceeding the ASTM C788 limits may be contradicted by concentrated product analyses, which provide greater resolution on a basis of grams per gram of uranium.

4.3. KILN FEED PREPARATION

To formulate kiln feed from concentrate batch AVCONC-1 (see Table 14), it was necessary only to dissolve enough NH_4NO_3 to achieve an NH_4^+/U ratio of 2.6. The concentrate was transferred to the feed makeup drum in the walk-in hood (see Fig. 2), where it was heated (the NH_4NO_3 dissolution is endothermic) and stirred while the weighed batch of NH_4NO_3 was gradually added. While the solution was warm, it was recirculated to the concentrate drum to dissolve the small amount of uranyl nitrate crystals that had formed upon exceeding the solubility limit. When all the solids had dissolved, the stable feed solution for run KN-19 had concentrations ~80% of those shown for AVONC-1; the reduction was due only to dilution by the NH_4NO_3. This was the feed for run KN-19.

Since concentrate batch AVCONC-4 was both low in uranium and high in acid, it was decided to dissolve the UO_3 rejects from KN-19 (also Mars material) as well as NH_4NO_3 in formulating feed for KN-20: this tended to move both concentrations in the desired directions. The solids dissolutions were accomplished entirely in the heated feed makeup drum since the solubility limit had not been exceeded in AVCONC-4. Coincidentally, the amount of UO_3 dissolved kept the uranium in the adjusted feed at the same level as in the concentrate and reduced the acid to less than half the original value.

4.4. ROTARY KILN OPERATION

The rotary kiln (4-in. ID) in Building 3019 was operated in two extended runs to produce ~36.5 kg of UO_3 powder from the feeds formulated from the concentrates described earlier. The −25 mesh product is to be distributed to fuel fabricators for evaluation as UO_3 powder typical of the AVLIS enrichment process. Two runs were made with feeds (described above) of different uranium concentrations, and after acceptably low nitrate and impurity levels were confirmed in both products, the two were blended into a homogeneous batch of 33 kg and sampled for characterization.

In the first run (KN-19), the feed contained 456 g U/L and 0.3 *M* H^+. The furnace temperature was controlled at 600 to 610°C, and the center tube temperature was measured at 505 to 540°C. In both runs the NH_4^+/U ratio was 2.6, the kiln rotation was 10 rpm, the inclination was 3°, and the air purge was ~0.4 ft^3/min. The "kiln run" product of KN-19 was collected in nine bottles with net weights as shown in Table 16. Each of the nine batches of product was screened separately through 6 and 25 mesh screens. The weights of +6 mesh shown were separated and set aside for recycle. Initially a total of over 4 kg of the −6 +25 mesh fraction was segregated for recycle, but this rate of rejection would not have allowed product commitments to be met. Therefore, this material, no longer segregated by product bottle, was placed back on the 25 mesh screen and subjected to further "grinding" with a fiber-bristle brush; the −25 mesh material so produced is included as bottles number 10 and 11 in Table 16. The total of +25 mesh material finally rejected was only 411 g. The nitrate contents of samples from the nine original bottles ranged from 0.14 to 0.80 wt %, and the reworked material was slightly above their average at 0.54 and 0.57 wt % nitrate.

Table 16. Weights and nitrate contents of UO_3 powder

Bottle no.	"Kiln run" UO_3 wt (g)	−25 Mesh product		Rejects	
		NO_3^- (%)	Wt (g)	+6 Mesh wt (g)	+25 Mesh wt (g)
19-1	4,212	0.14	3,377	73	
19-2	3,330	0.61	2,539	82	
19-3	3,156	0.39	2,009	122	
19-4	3,371	0.66	2,285	334	
19-5	2,616	0.34	2,042	~150	
19-6	2,571	0.53	2,180	234	
19-7	2,768	0.37	2,291	154	
19-8	2,541	0.80	2,212	217	
19-9	2,869	0.72	2,685	91	
19-10		0.54	2,022		
19-11		0.57	1,830		
TOTAL	27,434		25,472	~1,450	411
20-1	2,420	0.35	2,121	276	14
20-2	2,427	0.29	2,095	314	10
20-3	2,195	0.59	2,060	126	4
20-4	1,904	0.86	1,710	179	6
TOTAL	8,946		7,986	895	34

In the second run (KN-20), the feed contained 316 g U/L and 0.4 *M* H^+. The furnace temperature was controlled at 600 to 606°C, and the center tube temperature was measured at 515 to 530°C. The product was collected in four bottles and screened as before except essentially all of the −6 mesh material was brushed through the 25 mesh screen initially; the weights of rejects for each bottle are recorded in Table 16. Nitrate contents of the −25 mesh products were in the same range as before.

4.5. PRODUCT BLENDING

The 15 bottles of product were poured into a 50-L plastic bottle and blended by rolling and upending. The blended material (designated KN-19/20) was then dispensed into eighteen 2-L plastic bottles with net weights (after sampling) as shown in Table 17. To characterize the product and to confirm the homogeneity of the blend, 50-g samples were taken from the 1st, 9th, and 16th bottles filled; a composite sample containing 10 g from the 2nd, 5th, 8th, 11th, and 14th bottles completed the set of four. An archive sample consisting of 20 g each from the same bottles as the composite laboratory sample was also collected.

Table 17. Weights of blended product ready for shipment

Bottle no.	Net wt (g)	Bottle no.	Net wt (g)	Bottle no.	Net wt (g)
19/20-1	2058[a]	19/20-7	1896	19/20-13	1851
2	2023[b]	8	1941	14	1872[b]
3	1941	9	1888[a]	15	1844
4	2027	10	1939	16	1852[a]
5	1868[b]	11	1923[b]	17	1887
6	1885	12	1886	18	712

[a]Fifty-gram samples removed.
[b]Thirty grams in samples removed.

4.6. CHARACTERIZATION OF MARS PRODUCT

Analytical results for the four samples taken from the KN-19/20 blend are presented in Table 18 and do not vary greatly from those of runs KN-16, 17, and 18 (see Table 9). The uranium is about 1 wt % higher, while the NO_3^- and H_2O are somewhat lower. The density is quite similar, and the surface area of ~8 m^2/g is within the range of 6-9 m^2/g. The impurities reported are those which could be attributed to corrosion in the kiln; they are lower than those in runs KN-16, 17, and 18 due to the purification step prior to concentration. Silicon was run because of the prior uncertainty. All others were $\leq$20 ppm or under the limit of detection. The particle size distribution of the Mars material UO_3 product was very close to that of KN-18.

Table 18. Analytical results for KN-19/20 blended product

	Sample no.			
	1	2	3	4
Uranium, wt %	81.35	81.39	81.34	81.40[a]
Nitrate, wt %	0.64	.60	0.61	0.70
Water, wt %	0.36	--	0.40	0.34
Density, g/cm^3				
Auto pycnometer	6.13	6.12	6.08	6.11
Scott volumeter	0.595	0.607	0.598	0.606
Surface area, m^2/g	8.09	7.98	8.17	7.99
Particle diam distribution				
@100 wt %, μm	≤29.85	≤42.21	≤29.85	≤29.85
@ 90 wt %, μm	≤16.67	≤22.63	≤17.10	≤12.88
@ 50 wt %, μm	≤6.19	≤9.67	≤6.36	≤4.73
@ 10 wt %, μm	≤1.27	≤2.66	≤1.55	≤1.14
Impurities, ppm				
Carbon	63	59	55	63
Iron	30	30	30	30
Chromium	<2	<2	<2	<2
Nickel	6	<1	6	6
Silicon	20	25	30	25
Others[b]	≤20	≤15	≤20	≤20

[a]Normal uranium confirmed: ^{238}U = 99.3%. X-ray diffraction found as major constituents UO_3 and an unidentified amorphous phase. No intermediate or minor constituents.

[b]Under detectable limit or as shown.

5. CONCLUSIONS

The following observations may be made concerning the MDD process.

1. The chemistry of the MDD process is well understood and well documented.

2. The 4-in.-ID rotary kiln is a durable piece of equipment capable of extended periods of continuous operation while maintaining process conditions within a narrow range.

3. In this equipment $UO_2(NO_3)_2$-NH_4NO_3 solutions can be calcined to free-flowing powder, mostly −6 mesh, with a nitrate content less than 2 wt % at temperatures of 480-530°C.

4. The powder screens freely and can be size reduced with small expenditure of energy.

5. The near-neutral solutions have not shown objectionable increases in contaminants from stainless steel processing equipment in either evaporation or denitration.

6. The Mars material exhibited the same processing characteristics, appearance, and physical properties as ordinary UO_3.

7. MDD-derived UO_3 powders can be reduced to sinterable UO_2 powder using reduction techniques that allow control of the final powder characteristics.[7]

8. The resulting UO_2 powders can be processed/sintered using standard powder preparation and pellet fabrication techniques to yield pellets with greater than 96% of theoretical density.[7]

9. Pellet microstructures appear similar to those of power reactor fuel, and because of the high final pellet densities, it is expected that they would remain stable during in-reactor operations.[7]

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