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LIST OF EFFECTIVE PAGES

<u>Page Number</u>	<u>Page Count</u>	<u>Revision</u>
Issue Summary	1	0
i through iv	4	0
1-1 through 1-2	2	0
2-1 through 2-15	15	0
3-1	1	0
4-1	1	0
5-1	1	0
Total	25	

CONTENTS

	<u>PAGE</u>
ABSTRACT	iv
1. INTRODUCTION	1-1
2. PROCESS DESCRIPTION	2-1
2.1 BROTH MANUFACTURE	2-1
2.2 SPHERE FORMATION	2-3
2.3 PRECIPITATION, EXTRACTION COLUMN.....	2-3
2.4 WATER WASH COLUMN	2-3
2.5 ISOPROPYL ALCOHOL (IPA) WASH COLUMN	2-6
2.6 KERNEL DRYING	2-6
2.7 ROTARY CALCINE FURNACE	2-6
2.8 SINTERING FURNACE	2-11
2.9 TABLING	2-13
2.10 KERNEL ACCEPTANCE CRITERIA.....	2-13
3. CRITICAL PARAMETERS CHANGES	3-1
4. CONCLUSIONS	4-1
5. REFERENCES	5-1

FIGURES

	<u>Page</u>
1. Processing Sequence Yielding UCO Kernels	1-2
2. UCO Drop Columns	2-4
3. Precipitation Column	2-5
4. IPA Wash Column	2-7
5. Dryer	2-8
6. Dryer Condenser and Chiller	2-9
7. Calciner	2-10
8. Sintering Furnace	2-12
9. Table	2-14

TABLES

1. Inspection and Acceptance Criteria for LEU Fissile UCO Kernels	2-15
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ABSTRACT

UCO kernel fabrication was previously demonstrated at 2 kg per batch. The limiting factors were the size of the sintering furnace and the UCO drop columns. The former UCO drop columns also showed considerable variability in the quality of gelled microspheres.

A larger-size sintering furnace and a set of drop columns with an improved design were installed in 1987. The new set of drop columns and sintering furnace, in conjunction with other modular-sized equipment, were designed to produce the reference batch size of 5.5 kg of UCO kernels containing 5 kg of heavy metal (HM).

The new equipment was utilized in the manufacture of several 2 kg batches of UCO kernels and ran well. In the process development reported here, the batch size was scaled-up to 5.5 kg. While the equipment is performing as expected, some of the process parameters still need to be optimized.

In the body of this document is a description of the process to make UCO kernels via Gel Supported Precipitation (GSP) technology and the critical parameters that were changed to scale-up the kernel batch size to 5.5 kg, while meeting product specifications.

1.0 INTRODUCTION

UCO kernel fabrication was previously demonstrated at 2 kg per batch. The limiting factors were the size of the drop columns and the sintering furnace.

A larger-size sintering furnace and drop columns were installed with a design capability of 5.5 kg of UCO kernels containing 5 kg of heavy metal (HM).

The larger-size equipment was first used to make 2 kg batches. This allowed an opportunity to test the new equipment. Then, the kernel batch size was increased from 2 kg to the reference batch size of 5.5 kg. At present, process parameters are being optimized at the reference batch size of 5.5 kg.

This document details the critical UCO fissile kernel process parameters for broth preparation, sphere formation, washing, drying, calcining, sintering and tabling. Fig. 1 shows the processing sequence to make UCO kernels from UO_3 .

Fig. 1 Processing Sequence Yielding UCO Kernels

2.0 PROCESS DESCRIPTION

The UCO kernels manufacturing process, developed at General Atomics under a Department of Energy contract, consists of the following steps:

1. Broth preparation
2. Sphere formation
3. Precipitation
4. Water washing
5. Isopropyl alcohol washing
6. Drying
7. Calcining
8. Sintering
9. Tabling

On the process line, each of these steps is distinct and requires a physical transfer of the product from the previous step.

2.1 BROTH MANUFACTURE

Broth is the feed material that reacts with ammonia to produce the gelled microspheres that are converted downstream into ceramic nuclear kernels. Broth is made of 3 components:

1. Uranyl Nitrate (UNH) solution
2. Polyvinyl Alcohol (PVA) dispersion
3. Tetrahydrofurfuryl Alcohol (THFA)

2.1.1 UNH Solution

The UNH solution is prepared by dissolving UO_3 powder in nitric acid. UO_3 dissolves in nitric by disproportionation of the oxide anion to yield water.

To accelerate the dissolution rate, UO_3 is dissolved under vigorous agitation. Since less acid is used than is

stoichiometrically required by Equation 1, the final solution is acid deficient. UNH is stored in geometrically safe containers to await further processing.

Note: The UNH solution has been prepared in small quantities using laboratory equipment. The reference process equipment for the full batch size is to be installed later in the program.

2.1.2 Polyvinyl Alcohol (PVA) Dispersion

PVA is a linear polymer with the structure $-(CH_2-CHOH)-$. The role of the PVA in the Gel Supported Precipitate (GSP) process is to adjust the rheological properties of the broth so that spherical droplets can be formed. In addition, PVA is a source of carbon for the UCO kernels.

PVA is dispersed in water under vigorous agitation.

2.1.3 Tetrahydrofurfuryl Alcohol (THFA)

Tetrahydrofurfuryl alcohol slows the rate of rheological changes in the stored broth. THFA has the following chemical structure:

2.1.4 Broth Mixing

UNH, PVA and THFA are mixed at temperatures above 40°C and then transferred to the broth tank to await further processing.

Note: At present, broth is made in small laboratory sized equipment. The reference process equipment for the full batch size is to be installed later in the program.

2.2 SPHERE FORMATION

Liquid microspheres are formed by breaking up a stream of broth flowing from the broth tank to a small diameter needle located at the top of the ammonia column. To improve day-to-day product reproducibility, the broth temperature is controlled with a heat exchanger.

Surface tension causes the broth droplets to form spheres as they exit the needle and fall through air. Then they react with gaseous ammonia (NH_3) to partially gell the spheres.

The microspheres are gelled and washed in 3 counter-current columns. The 3 columns are shown in Fig. 2.

2.3 PRECIPITATION, EXTRACTION COLUMN

The partially gelled kernels are collected in a 15.2 cm (6 in.) column. The column (see Fig. 3) is a continuous five-stage counter-current flow system. Gelled kernels flow by gravity while aqueous ammonia moves counter flow.

When uranyl ions react with ammonia, ammonium uranate (AU) is formed. While there is some disagreement over the formula of the precipitate obtained when uranyl nitrate reacts with ammonia, a likely reaction is:

Gelling continues as the microspheres travel through the ammonia column while precipitation of ammonium uranate begins and extraction of ammonium nitrate commences.

Kernels continuously settle in a receiver located at the bottom of the column. Kernels are transferred in a batch mode to the water column.

2.4 WATER WASH COLUMN

In this column, excess ammonia, THFA and nitrates are extracted. Gelled polyuranates proceed to the isopropyl alcohol column.

Kernels are fed to the four-stage water wash column. Kernels flow by gravity while deionized water moves counter flow. Fresh

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Fig. 2 UCO Drop Columns

Fig. 3 Precipitation Columns

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water is introduced into the lowest stage. An average residence time of 60 minutes is provided in this column.

Kernels settle by gravity into a receiver located at the bottom of the column. The receiver, which starts full of deionized water, fills up with kernels. Then kernels are transferred in a batch mode to the isopropyl alcohol wash column.

2.5 ISOPROPYL ALCOHOL (IPA) WASH COLUMN

In this column, water, ammonia, THFA and nitrates are extracted. The column consists of four stages and a bottom accumulator. Each stage is individually recirculated. The column is shown in Fig. 4.

Kernels are fed at the top of the four-stage IPA wash column. Kernels flow by gravity and the IPA moves counter flow. IPA feed is introduced at the bottom of the column.

The average kernel residence time is approximately 45 minutes. The kernel residence time is controlled by the flow of recirculated IPA entering each stage.

Kernels settle by gravity into a receiver located at the bottom of the column. When the kernel drop is completed, kernels and alcohol are transferred to the dryer feed tank.

2.6 KERNEL DRYING

All of the free water, alcohol and a significant amount of water of gellation are removed in the dryer. The dryer is shown in Fig. 5 and is described in detail in Ref. 1.

Kernels, in alcohol, are transferred from the dryer feed tank into the rotary dryer. The tumbling wet microspheres are dried with hot nitrogen. The hot solvent-rich nitrogen that exits the dryer is cooled in a heat exchanger to condense water and alcohol. Then the dry nitrogen is reheated and recirculated back to the dryer.

Kernels are considered dry when alcohol stops flowing from the condenser (Fig. 6). A significant volume shrinkage of the kernels occurs during drying. The volume of dry kernels is about 44% of the volume of the wet microspheres.

2.7 ROTARY CALCINE FURNACE

The rotary calciner is shown in Fig. 7 and is described in detail in Ref. 2.

Fig. 4 IPA Wash Column

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Fig. 5 Dryer

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Fig. 6 Dryer Condenser and Chiller

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Fig. 7 Calciner

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Calcining is a heat treatment that is characterized by the mildly exothermic decomposition of PVA. This reaction occurs mainly between 280° to 300°C. The thermal decomposition of PVA occurs in two stages. The first stage is primarily dehydration accompanied by the formation of some volatile products. The second stage produces carbon and some volatile hydrocarbons.

Also, during calcining, free and chemically bound water and ammonia are driven off and the uranium oxygen compound undergoes reduction with the evolution of CO. The calcination of AU occurs in several stages prior to the final reduction to UO_2 . Between 20°C and 200°C dehydration occurs. Thermal decomposition of AU occurs between 200°C and 350°C with loss of water and some of the ammonia. Between 350°C and 450°C ammonia retained in the solid reduces UO_3 to U_3O_8 and U_4O_9 . The final reduction to UO_2 occurs at 500°C.

The rotary calcining furnace employs a programmable heater controller to provide a slow heat-up to 300°C, followed by a soak of 30 - 60 minutes at that temperature. Then the furnace is ramped to 650° - 700°C and again held for a thermal soak at that temperature for 30 - 60 minutes. All ramps are linear. The heating cycle is followed by forced air cooling of the retort. The total cycle to unloading is approximately 24 hours.

2.8 SINTERING FURNACE

The final heat treatment of the UCO kernels is performed in a rotary sintering furnace shown in Figure 8.

The desired final kernel composition is a physical mixture of UO_2 and UC_2 , where UC_2 is less than 20 mol % and the balance is UO_2 . To arrive at that chemical composition and also obtain the desired final density of >10.5 g/cc a sintering temperature of at least 1800°C has to be reached.

The rotary sintering furnace employs a programmable heater controller for a slow heat-up to 1600°C, followed by a soak of at least 30 minutes. Then, the furnace ramps to 1800°C. At 1800°C there is a soak of at least 30 minutes, followed by a cooldown to room temperature.

The total cycle time is approximately 24 hours.

Fig. 8 Sintering Furnace

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2.9 TABLING

A vibrating table separates round from nonround kernels (see Fig. 9).

The table is slightly inclined in the Y-axis and vibrates in the X-axis. Therefore, round kernels exit through a trough located at the lower edge of the table, while nonround kernels exit at the inclined end of the table.

A split sample is obtained from the round kernel cut and is sent to the QC laboratory while the kernel product is placed in a transport container and sent to storage.

2.10 KERNEL ACCEPTANCE CRITERIA

Table 1 shows key UCO kernel properties, the analytical methods that are used to measure those properties and the acceptance criteria for low-enriched uranium (LEU) fissile UCO kernels.

Fig. 9 Table

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TABLE 1

INSPECTION AND ACCEPTANCE CRITERIA FOR LEU FISSILE UCO KERNELS

Composite Acceptance Criteria

Property	Inspection Method	Confidence Level (%)	Mean	Critical Region	Allowable Fraction In Critical Region
Total uranium, wt %	Gravimetric, DNAA ^(a) , X-ray, spectrography	75	≥87.0	(b)	(b)
Uranium isotopic composition, wt %	Mass spectrography	75	19.8-20.0	(b)	(b)
Impurities, (Fe, Cr, Ni), ppm-wt	Emission spectrography, atomic absorption, or spectrophotometry	75	≤100 ^(c)	(b)	(b)
Carbon, wt %	Gravimetric	(b)	(b)	(b)	(b)
Oxygen, wt %	Gas chromatography	(b)	(b)	(b)	(b)
Carbon/uranium (atomic ratio)	--	75	≤0.4	(b)	(b)
Oxygen/uranium (atomic ratio)	--	75	1.6-1.8	(b)	(b)
Density, g/cc	Mercury pycnometer	75	≥10.5	(b)	(b)
Diameter, um	Radiography, particle size, analyzer ^(d)	95	≤360	≥400	≤0.01

(a) Delayed neutron activation analysis

(b) Not specified

(c) Each impurity

(d) Sample size ≥200 kernels

3.0 CRITICAL PARAMETER CHANGES

Following are the critical parameter changes that were made to obtain a density of ≥ 10.5 g/cc in UCO kernels made at the reference batch size of 5 kg HM.

1. The broth volume was increased from 12 to 38 liters.
2. The diameter of the drop columns was increased from 4 to 6 inches.
3. An improved column design made the kernel residence time more uniform throughout the drop, and also more uniform from drop to drop. This is true for the precipitation column, the wash column and the IPA column.
4. Drying time was increased from approximately 4 hours to 13 hours.
5. The flow rate of inert gases and air in the calciner was held constant while the weight of kernels was increased by 175%.
6. Inert gas flowing to the sintering box was reduced from 250 SCF/h to 155 SCF/h.
7. Inert gas flowing to the sintering tube was held constant while the amount of kernels was increased by 175%. Therefore, the concentration of CO in the furnace during the ramp to 1600°C was increased by 175%.
8. The new sintering furnace is 6 inches in diameter, while the laboratory size furnace that was previously used was 4 inches in diameter.

4.0 CONCLUSIONS

1. The new set of drop columns and sintering furnace are operational and working within design parameters.
2. UCO kernels were made in the reference batch size of 5 kg HM at the desired density of ≥ 10.5 g/cc. The U/C/O ratio was also well within the specified range.

5.0 REFERENCES

1. Winkler, E., "Rotary Dryer," GA Specification No. 906321/A, August 2, 1983.
2. Winkler, E., "Rotary Calcine Furnace," GA Specification No. 906606/A, June 30, 1983.