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AN EVALUATION OF ALTERNATE PRODUCTION METHODS FOR PU-238 GENERAL PURPOSE HEAT SOURCE PELLETS

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Abstract – *For the past half century, the National Aeronautics and Space Administration (NASA) has used Radioisotope Power Systems (RPS) to power deep space satellites. Fabricating heat sources for RPSs, specifically General Purpose Heat Sources (GPHSs), has remained essentially unchanged since their development in the 1970s. Meanwhile, 30 years of technological advancements have been made in the applicable fields of chemistry, manufacturing and control systems. This paper evaluates alternative processes that could be used to produce Pu-238 fueled heat sources. Specifically, this paper discusses the production of the plutonium-oxide granules, which are the input stream to the ceramic pressing and sintering processes. Alternate chemical processes are compared to current methods to determine if alternate fabrication processes could reduce the hazards, especially the production of respirable fines, while producing an equivalent GPHS product.*

I. INTRODUCTION

Radioisotope Power Systems (RPSs) convert thermal energy to electricity. RPSs utilize thermal energy from energetic alpha particle produced during radiological decay. Plutonium-238 is an optimal isotope for this application decaying nearly completely by alpha decay while generating minimal secondary radiation from decay products or spontaneous fission. A pellet of plutonium oxide generating its own heat is shown in Figure 1.

To produce a pellet, Pu-238, which is stored in the form of plutonium oxide powder, is dissolved into an aqueous solution. This nitric acid solution of Pu-238 is the input stream to producing plutonium-oxide pellets for general purpose heat sources (GPHS).

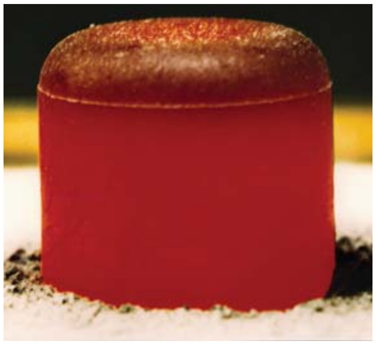


Fig. 1. Photo of plutonium-238 oxide pellet.

The same radioactivity, alpha decay, that produces the thermal energy is also hazardous to people. The primary hazard from alpha producing radioisotopes is inhalation of fine powders. In addition, the mobility of material increases as the particle size gets smaller. As the current process for GPHS production requires material be ground into fine powder, processes that eliminate the fine powder operations will reduce the inhalation risks and improve contamination controls. This paper evaluates alternate processes that could be used to improve the manufacturing process for Pu-238 fueled heat sources.

II. BACKGROUND

The current process will be reviewed and problems highlighted before discussing alternate processes.

II.A. Current process

The production of GPHS pellets ready for encapsulation may be separated into ten processing steps.[1,2,3,4] These steps are shown in Figure 2. The steps can be grouped into two subprocesses—granule production and pellet production as depicted in the figure. This paper focuses on the granule production portion of the process. The granule steps are described below.

Oxalate Precipitation

The input stream to the pellet production process is plutonium-nitrate in an aqueous solution. The first processing step is to adjust the valence of plutonium to the +III state and blend with oxalic acid to precipitate plutonium oxalate as shown in the general reaction equation:

$$2Pu(NO_3)_3 + 3H_2C_2O_4 + 9H_2O \rightarrow Pu_2(C_2O_4)_3(H_2O)_6 \bullet 3(H_2O) + 6HNO_3 \qquad (1)$$

The plutonium material precipitates in rosette- and lath-shaped structures. These structures are shown in Figure 3. The size of the precipitate varies from 0.7 μm to 55 μm. The material is collected on a metal filter at the bottom of the precipitator and transferred to a furnace for further processing.

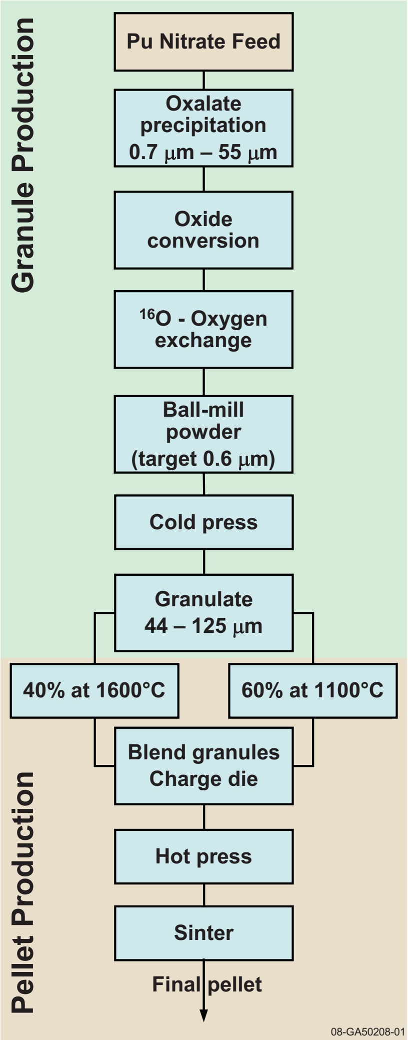


Fig. 2. Process flow of current GPHS pellet production.

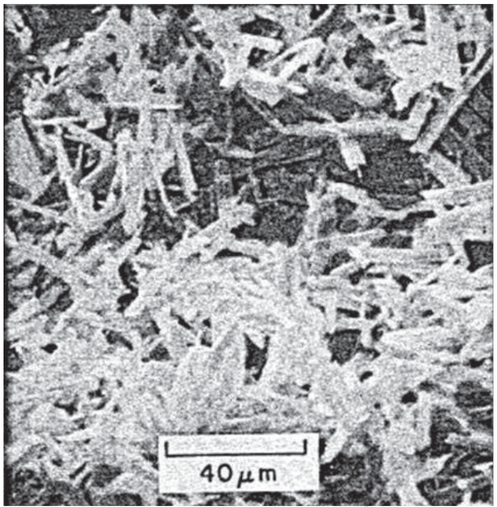


Figure 3. Oxalate precipitate structures.[5]

Oxide Conversion

The second processing step involves heating the oxalate precipitate driving off any remaining moisture. Nominal furnace temperature during calcining is 735°C.[6] This dries the precipitate and converts the plutonium oxalate to plutonium-oxide, PuO_2 by the following reaction:

$$Pu_2(C_2O_4)_3(H_2O)_6 \bullet 3(H_2O) + 2O_2 \xrightarrow{\Delta} 2PuO_2 + 6CO_2 + 9H_2O \quad (2)$$

Oxygen-16 Exchange

Next, the plutonium oxide feed powder is heated in an O-16 environment to replace the O-17 and O-18 isotopes present in the feed with O-16. The initial oxide is produced with natural oxygen and has a neutron emission rate in excess of 17,000 n/s-g ^{238}Pu.[2] The neutron emissions are primarily caused by (α,n) reactions from the presence of O-17 and O-18 isotopes in the normal oxygen used during the precipitation and calcining operations. The exchange is accomplished by heating the feed powder in a furnace in an atmosphere of flowing Ar saturated with $H_2{}^{16}O$.

Ball Milling

Ball milling the feed powder is required to produce the desired particle size and powder morphology. This is, to some extent, a normalizing step to eliminate differences in surface activities and powder packing from one lot of feed powder to the next. As described above, the powder consists of two types of particles and has a mass-median diameter of about 2.7 µm. Data during the Cassini program showed mass-median particle size of 20 µm. One type of particle is rosette-shaped; the other is lath-shaped. The lath-shaped particles have an extremely high surface activity, low packing density and cause the material to shrink excessively when sintered. The results of developmental studies show the reactivity of the feed will be adequate for bonding during hot pressing if the powder is milled to produce a mass-medium diameter of about 1 µm.[2]

Cold Press and Granulate (Slugging and Screening)

The slugging and screening operations are performed to convert the ball-milled powder to granules of the size desired for hot pressing. The plutonia powder is cold pressed to form a green pellet at 60% theoretical density. The pellets are then broken and screened to size and the <125 µm fraction is collected. The activities that involve handling the ball-milled material such as opening containers, weighing contents and loading dies, spread the most contamination within the gloveboxes.

Particle Size Distribution

Typical mass particle size distributions of calcined PuO_2 are shown in Figure 4. The log normal statistics suggest no decrepitation on calcining or fracture on stirring. The size distributions of both plutonium oxalate and PuO_2 are usually bimodal, representing a distribution of individual lath particles and a distribution of agglomerates of laths.

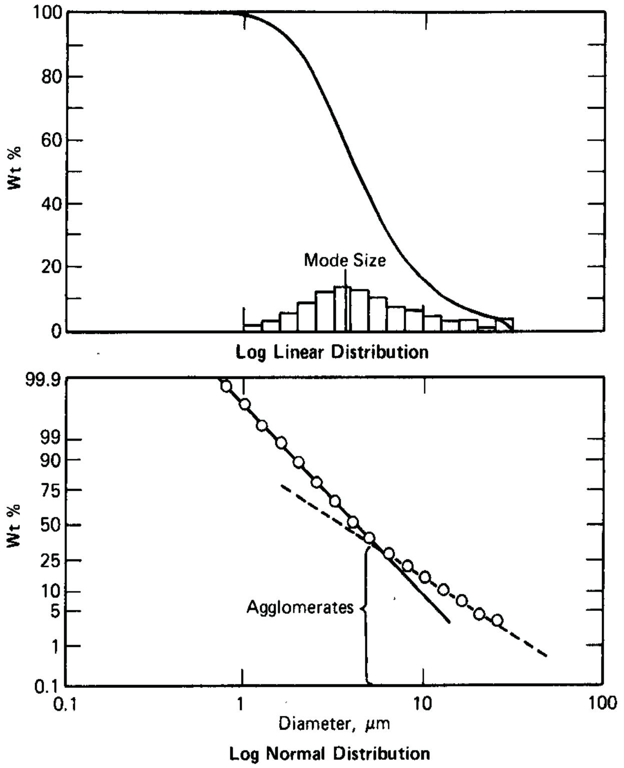


Fig. 4. Particle size distribution of PuO_2 from calcining.

II.B. Problems with current process

The current process requires milling Pu-238 material into a fine powder (less than 1 µm) as described above Experience has shown that powder particulates less than 10 µm maximize risk for personnel exposure by inhalation and dispersion to the environment. As shown in Figure 5, material in the 0.5-5 micron range is most susceptible to inhalation and subsequent lodging in the lung tissue.

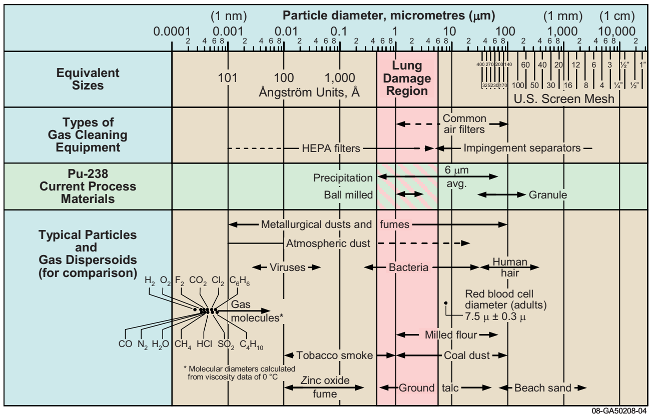


Fig. 5. Comparison of Pu-238 particle size to respirable materials.

In addition, this small particle size increases the mobility of the Pu-238 material by airflow and recoil energy produced during alpha decay. These factors increase contamination spread, make decontamination more difficult, and enhance the material's corrosive nature. Pu-238 reacts with process equipment, increasing breakdown and repair times. The fine powder is more difficult to confine, degrades and penetrates gloves and rubber seals, and increases the complexity of transferring material without spreading contamination.

Bickford, Rankin and Smith[8,9] have shown that variations in the particle size and particle dimensions of the PuO_2 powder cause wide variation in the density and microstructure of the fuel forms. Such variation can be accommodated by ball milling PuO_2 powder to the same particle size. However, this can only be done by adjusting milling time for each different calcined powder size. A more desirable approach is to produce calcined feed with reproducible size characteristics. Work at Savannah River[10,11,12,13] and elsewhere[14-18]has shown that widely different particle morphologies and sizes can be obtained from oxalate precipitation, depending on several factors. These include the valence of the plutonium in solution, the mixing sequence of plutonium nitrate and oxalic acid solutions, and the variables affecting initial supersaturation (nucleation–rate) and final solubility (particle growth rate).

III. STRATEGY

III.A. Objectives of study

The objectives of the evaluation are:

Objective 1: *Minimize the potential for airborne radioactive contamination release during fabrication of GPHS pellets.* To meet this objective, the fabrication techniques were evaluated that produce feed powder with particle sizes greater than 10 µm, thus eliminating or at least minimizing the production of respirable fines during processing.

Objective 2: *Reduce personnel radiation exposure during fabrication of GPHS pellets.* Exposure comes from several manual operations required during fabrication, and fine powder that spreads throughout the fabrication equipment and glovebox system. Three basic approaches are proposed to meet this objective: eliminate fines production, simplify the process by eliminating steps where possible, and eliminate manual operations.

Objective 3: *Improve the structural integrity of the unclad pellets while satisfying impact test and operating performance requirements.* Using the current process, heat source pellets routinely contain cracks after fabrication. Occasionally the pellets break apart during handling before being clad for radiological containment. Alternate fabrication methods may improve the integrity of the finished pellet by reducing internal stresses while satisfying the necessary performance requirements.

The decision to evaluate only processes for making GPHS pellets is based on the current plans for RPS deployments. The GPHS was developed in the 1970s and all NASA missions in the past 30 years have used this design.

III.B. Process inputs

The material specification requirements for GPHS heat sources have not changed significantly since the 1970s. Salient material portions from the specification[19,20,21] are summarized in Table 1.

Selecting proper weight fractions of various granule sizes for mixing can lead to optimized packing (high green pellet density). Discrete distribution of coarse and fine particles can be mixed so that the fine particles occupy the interstices between the coarse particles. This approach is illustrated in Figure 6 for two sizes (coarse and fine) of spherical particles. As the particle diameter ratio increases, the packing density improves. The maximum packing fraction is achieved when the ratio between nearest sizes is greater than about seven and the finer particles are dispersed in interstices. Coarse spherical particles must be at least a factor of seven larger than the fine spheres to fit in the interstices. In practice, mixtures of coarse and fine nonspherical powders in the size range of the granules used in the GPHS pellets seldom reach above 70% dense.

TABLE I

Purity requirement for new GPHS pellets

Attribute	Requirement
Actinide impurity	- less than 1 weight percent total content - less than 0.5 weight percent individual actinide impurity
Anionic impurity	- phosphorous content shall not exceed 25 µg/g
Cationic impurity	- less than 2,550 µg/g - less than 1,500 µg/g combined silicon, magnesium, calcium and aluminum[a] - *individual limits also exist but are excluded from this summary*
Granule size	- less than 125 µm

a. The impurities can affect performance by volatizing, transporting to, and plugging vent openings. Also, impurities can interact with iridium and lead to cladding embrittlement and or failure.

Achieving near 70% density using this proposed bi-model particle size distribution appears a favorable improvement to the current process. The current process only achieves 20% theoretical density.

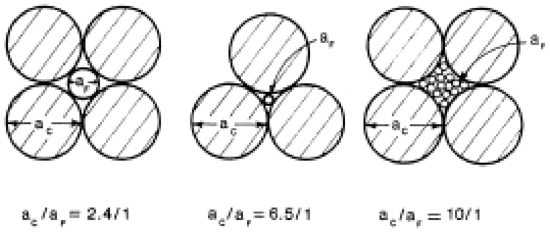


Fig. 6. Packing fine spheres in a planar interstice among coarse particles: ac = diameter of coarse particle, af = diameter of fine particle.[22]

IV. ALTERNATIVES DESCRIPTION

Eight alternate processes were evaluated for improving production of GPHS pellets. They are listed here and will be discussed below:

- Improved Oxalate Precipitation
- Ammonium Uranyl Plutonyl Carbonate Precipitation
- Hydroxide Precipitation
- Denitration
- Granat Flocculation
- Resin-bead Loading and Calcining
- Sol-gel Method
- Suspension/Temporary Binder Method

IV.A. Improved Oxalate Precipitation

In 1982, Savannah River Site (SRS) proposed a simplified approach to manufacturing GPHS pellets they had developed in the Plutonium Fuel Fabrication Facility. They proposed modifying the oxalate precipitation step to directly produce agglomerates of small PuO_2 crystals.[23] The crystals would be heat treated and loaded directly into the hot press die to produce the final GPHS pellets. Forming the large agglomerates directly allowed the fuel fabrication process to eliminate three steps, decrease personnel exposure, and reduce the risk of contamination release. SRS developed the process on a small scale and demonstrated its practicality first on a full scale using 20% Pu-240—80% Pu-239 oxide material and then using $^{238}PuO_2$ powder. Though the SRS tests were marginally successful, more development is needed to fine tune process parameters.

Figure 7 contains an improved oxalate precipitation process flowsheet, with some of the process parameter details. The plutonium nitrate feed is adjusted with 0.05M hydrazine and 0.075M ascorbic acid to adjust the Pu(IV) to Pu(III) just prior to precipitation. The plutonium is precipitated by the direct strike method by adding oxalic acid into the plutonium nitrate solution. Oxalic acid is added slowly for 10 minutes and then the solution is allowed to digest for 20 minutes with mixing. Adding oxalic acid slowly reduces the nucleation of plutonium-oxalate crystals. During the digestion period, the nuclei continue to grow 2-3 µm platelets forming rosette-shaped agglomerates. The agglomerates are filtered and washed. They contain sufficient structural integrity for handling. When converted to oxide, the strength of the agglomerates increases reducing the chance of producing powder from broken platelets.

In comparison, the current GPHS fuel fabrication precipitation produces fine particulate PuO_2 powders that have particles (4 to 6 µm), which are not agglomerated. Agglomerates are produced mechanically by ball milling to reduce particle sizes to <1 µm, cold-pressing into compacts, and granulating through sieves to form hot press feed agglomerates. Note in Figure 7 the lightly shaded boxes where the eliminated process steps took place.

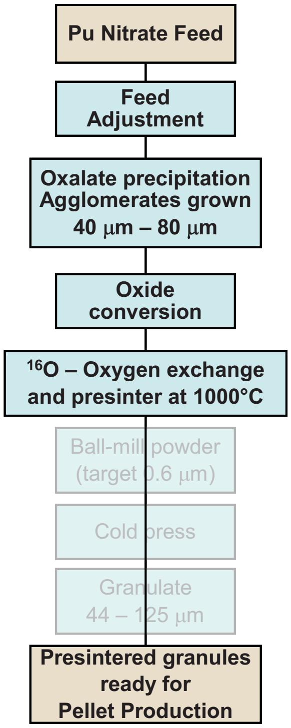


Fig. 7. Process flow for oxalate precipitation.

The improved process needs to produce large, 40 to 100 µm agglomerates strong enough to hold together during subsequent processing, and yet still contain an agglomeration of small crystals (particles 2 to 3 µm). This assures that during subsequent heat treatment and hot pressing there is sufficient activity to mildly densify and form final grain sizes ~10-20 µm. The granule agglomerates are shown in Figure 8.

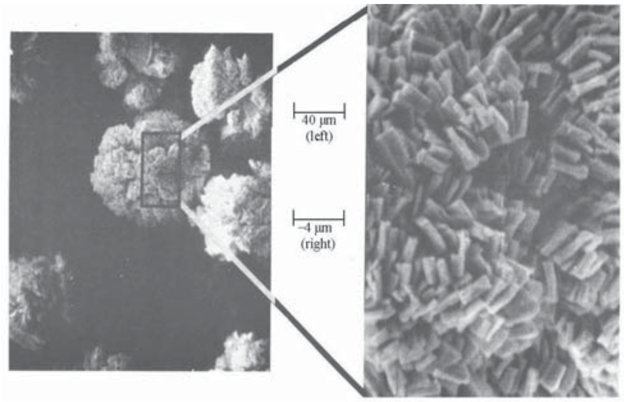


Fig. 8. Rosettes (agglomerates) produced by improved oxalate precipitation.[23]

IV.B. Ammonium Uranyl Plutonyl Carbonate Precipitation

Germany, Belgium and France investigated large-scale Pu-carbonate precipitation methods in the 1970s and early 1980s for spent nuclear fuel recycling.[24] The goal was to extract Pu from spent fuel and fabricate new mixed (uranium and plutonium) oxide fuel (MOX) fuel for Light-Water Reactor power production. Carbonate precipitation was particularly attractive for MOX production because the process allowed for coprecipitation of uranium and plutonium from nitrate feed streams. The most developed carbonate precipitation process is based upon the ammonium-uranyl-carbonate conversion process used for uranium fuel manufacturing. This process was modified for MOX production and is referred to as ammonium-uranyl-plutonyl-carbonate (AUPuC) co-conversion.[25]

The ammonium-plutonyl-carbonate precipitation (APuC) process is summarized in Figure 9. As with all precipitation methods, valance adjustment and control of the precipitating species must be performed for ligand reaction of the precipitation reactant. For APuC, the plutonium valance state in nitrate solution is typically in the +IV state. For ammonium carbonate precipitation, Pu^{4+} nitrate is first oxidized to the Pu^{6+} using concentrated nitric acid as the oxidant. Gaseous ammonia and carbon dioxide are bubbled into the hexavalent Pu-nitrate solution contained in a precipitation vessel. The following reaction produces the APuC.

$$PuO_2(NO_3)_2 + 6NH_3 + 3CO_2 \rightarrow (NH_4)_4PuO_2(CO_3)_3 + 2NH_4NO_3 \qquad (3)$$

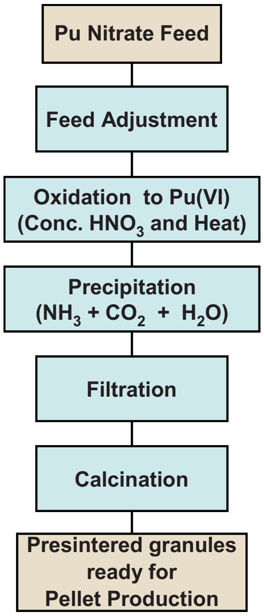


Fig. 9. Process flow for plutonium-nitrate conversion to oxide by APuC.

The $(NH_4)_4PuO_2(CO_3)_3$ precipitate is collected on a metal frit filter and washed with 15% $(NH_4)_2CO_3$ and alcohol. The triple carbonate decomposes to PuO_2 when dried in air at moderate temperatures.[26] The reaction is summarized by the following equation:

$$(NH_4)_4PuO_2(CO_3)_3 + O_2 \rightarrow PuO_2 + 4NH_3 + 2H_2O + 3CO_2 + {}^3/_2O_2 \qquad (4)$$

MOX production performed by the AUPuC method indicated that the oxide crystals were of moderate size with an average particle size of 50 µm, and 90% of particles were greater than 10 µm. The calcined oxide product had good sintering activity and produced dense free flowing powder. The Pu(VI) ammonium carbonate is not stable and decomposes in air to the monocarbonate.[26] This may be a potential issue in the high alpha and temperature environment associated with Pu-238 precipitation and oxide conversion. The sintered oxide product produced highly sintered, dense crystals with low porosity. Figure 10 shows a micrograph of the sintered oxide.

Fig. 10. $(U,Pu)O_2$ crystals produced by AUPuC fabrication

Process control is extremely precise owing to gaseous reagent flow control and mixing. Moderate-sized precipitate and oxide particles are produced, but so is a fraction of fine powder. The precipitate product was easily handled and filtered well, but is only moderately stable and decomposes in air with time. Proprietary technology exists for the MOX Pu(VI) ammonium carbonate process and is a proven method for MOX production.

IV.C. Hydroxide Precipitation

Mound Laboratory fabricated the multi-hundred watt, spherical heat source through the mid to late 1970s using $^{238}PuO_2$ granule material produced by hydroxide precipitation. Thus, of the precipitation methods, only the plutonium hydroxide (Mound) and plutonium oxalate (Savannah River Laboratory [SRL] and LANL) precipitation methods have been used to generate plutonium oxide heat sources used in flight applications. Mound Laboratory chose the hydroxide precipitation process because it was essentially dust free and produced granules that could be directly heat treated and hot pressed. SRL proposed to produce $^{238}PuO_2$ by hydroxide precipitation,[27] but chose the oxalate method instead.

Plutonium (III) and (IV) readily form precipitates of $Pu(OH)_3$ and $Pu(OH)_4$, respectively, in the presence of hydroxide ion. Plutonium hydroxide precipitate formation is very effective because of the extremely low solubility of Pu(IV) hydroxide precipitate product[28]:

$$[Pu^{4+}][OH^-]^4 = 7 \times 10^{-56} \qquad (5)$$

The hydroxide precipitation process is generally nonselective with the formation of other cationic hydroxide precipitate species in addition to Pu hydroxide; therefore, the plutonium feed solution must be of high purity. The process can be performed either by direct strike (hydroxide added to Pu nitrate solution) or reverse strike (Pu nitrate solution added to hydroxide) to form the hydroxide precipitate. The Mound Laboratory process[29] to convert Pu-nitrate solution to the oxide is shown in Figure 11.

The Mound process involved feeding Pu(IV)-nitrate solution to a precipitator containing 4M ammonium hydroxide (reverse strike method). The $Pu(OH)_4$ precipitation was collected as a "cake," then filtered and washed with an ammonium hydroxide solution and water. The Pu hydroxide cake was vacuum dried, then dried in air to convert the product to a plutonium oxide cake. The $^{238}PuO_2$ cake is then crushed to produce shards of desired particle size, but with essentially no fine powder. A similar hydroxide precipitate process uses magnesium hydroxide to react with Pu nitrate solution[30]; however, for Pu-238 heat source applications, precipitation with ammonium hydroxide is preferred to minimize introduction of cationic impurities. Once the oxide had been sized, the powder was sintered at 1200°C and oxygen isotope exchanged with $^{16}O_2$ to reduce neutron emission. This powder was then hot pressed into approximately 1.5-in. spherical heat source units.

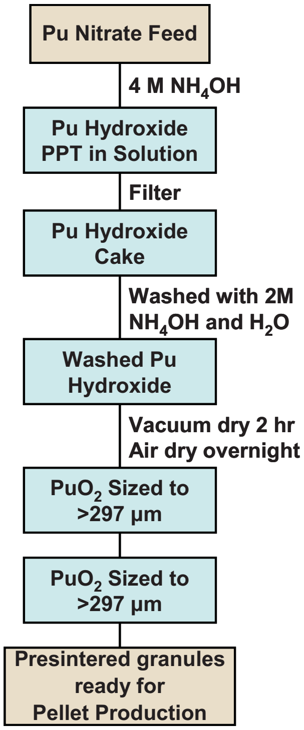


Fig. 11. Process flow for Pu-238 hydroxide precipitation.

Crushing of the $^{238}PuO_2$ cake product produced shard-shaped granules similar to those illustrated in Figure 12. For most heat source applications, the granules were sized to range between 53 to 250 µm in diameter after final sintering and with no fine powder.[31] After sintering, the granules were found to have open porosity with a density of approximately 10.2 g/cc or 89% theoretical density. The bulk powder density was generally determined to be 6.7 g/cc. Other thermodynamic, mechanical, electrical, chemical, and physical properties of this oxide material can be found in Reference 32.

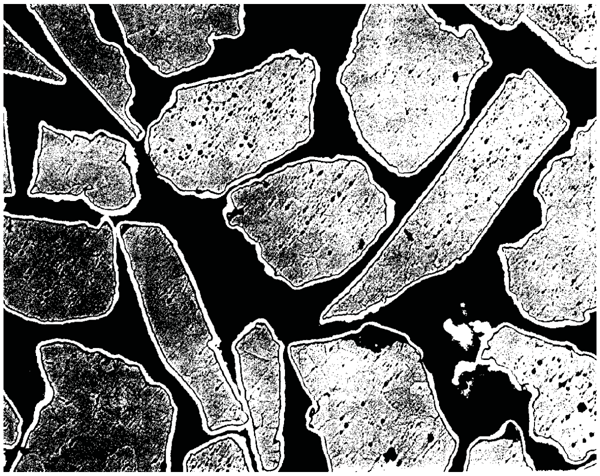


Fig. 12. Pu-238 oxide shards produced by hydroxide precipitation.

Plutonium-nitrate feed stream added to ammonium hydroxide allows direct precipitate formation and is a straightforward process. One disadvantage of the process involved handling and filtering of the Pu hydroxide cake material. The hydroxide is a sticky, gelatinous precipitate with a chemical formula of $Pu(OH)_4 \bullet xH_2O$ that is difficult to handle and filter. On the other hand, once the dried plutonium oxide cake was formed, handling, crushing, and sizing of the product was straightforward and dust free. The plutonium oxide shard-shaped granules had an open porosity, a TD of approximately 90% and a reasonable packing density. After heat treatment, the granules were suitable for direct pressing. The plutonium nitrate stream must be of high purity as the hydroxide precipitation process is nonselective.

IV.D. Denitration

A number of denitration processes were evaluated for granule production. The processes evaluated were developed for UO_2 fuel pellet fabrication[33]; therefore, they are not directly applicable to the Pu nitrate conversion to $^{238}PuO_2$ without further development. Some of the various denitration methods include the following:

1. NITROX, a freeze-drying method where denitration occurs under vacuum, was developed in France.[34]
2. Microwave decomposition, a batch denitration process, was developed by the Power Reactor and Nuclear Fuel Development Corporation of Japan.[35]
3. The modified direct denitration (MDD), developed at ORNL,[36] involves addition of an ammonium nitrate additive to form a 'double salt' precipitate, followed by conversion to oxide using a rotary kiln.

Of the various denitration processes described above, the MDD method using a rotary kiln appears to be the most applicable to conversion of Pu-238 nitrate solution to the oxide. The MDD is a very simple process and is easily applied at the scale needed for granule production. As discussed below, the process has also been demonstrated for mixed actinide (U/Np/Pu) conversion and with pure Pu with positive results.

The MDD process is shown in Figure 13. The MDD method involves adding ammonium nitrate (NH_4NO_3) to the Pu-238 nitrate stream to form the tetranitrate salt slurry. The slurry is then fed to a rotary kiln where the complex is decomposed and converted to the oxide in four distinct steps:

- Dehydration at 50°C
- Decomposition of the tetranitrate salt at 270°C
- Decomposition of the trinitrate salt at 300°C
- Conversion to the oxide at 500°C.

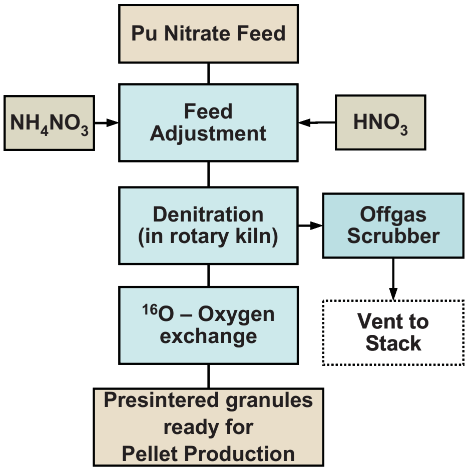


Fig. 13. Process flow for denitration.

The general reaction formula for this process is:

$$2NH_4NO_3 + Pu(NO_3)_4 \rightarrow (NH_4)_2Pu(NO_3)_6 \rightarrow PuO_2 + 2N_2O + 4H_2O + 4NO_2 + O_2 \qquad (6)$$

The decomposition and oxide conversion occurs continuously within the rotary kiln. The converted PuO_2 exits the kiln as a free-flowing powder.

The MDD process has been developed for UO_2 fuel pellet fabrication, which aims to produce small oxide particles with large surface areas for enhanced sintering, resulting in high density, low porosity pellets. The oxide powder characteristics needed for $^{238}PuO_2$ heat-source pellet are quite different; therefore the MDD process will need to be tailored for this application. Because most development and demonstration activities have not been directed toward PuO_2, current literature does not fully evaluate the conversion process for application to $^{238}PuO_2$ heat-source fabrication. However, considering the various parameter components associated with the denitration process, it seems reasonable that larger particles could be produced.[37] Current investigations on MDD production of $^{239}PuO_2$ show good particle size distributions with the majority of material in the 180 μm particle size range and approximately 10% of particles below 38 μm (see Table 2). The MDD produced $^{239}PuO_2$ powder had a tap density of 3.0 g/ml and a bulk density of 2.2 g/ml, and a high active surface area of 5 to 15 m^2/g. A micrograph of the MDD produced $^{239}PuO_2$ is shown in Figure 14.

Table 2

Particle size distribution of Pu-239 and cerium oxide powders produced by MDD.[38]

	Weight %		
Particle size, μm	Sample P01 (SEM)	Sample P02 (SEM)	Cerium run (sieved)
≥ 710	29	26	37
180	57	52	40
75	7	9	14
≤ 38	7	13	9

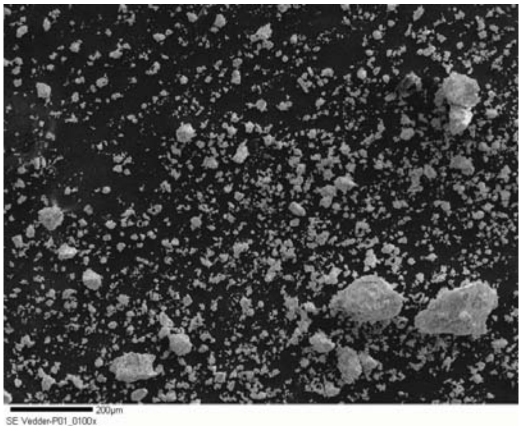


Fig. 14. Scanning electron micrograph of Pu-239 oxide produced by MDD.[38]

A favorable process characteristic associated specifically with the MDD is use of a rotary kiln to produce a free-flowing powder that can be directly pressed into a pellet. Specialized and commercially available rotary kilns used specifically for fabricating ceramic oxides have multiple heating zones with atmospheric control that allow for the dehydration, decomposition, and oxidation to the final PuO_2 product in a single process. This ability to convert the initial liquid Pu nitrate state to the final Pu oxide state in a single process instrument with no intermediate handling has significant advantages in simplifying the conversion process of Pu-238 oxide production. However, current investigation of the MDD process has focused primarily on uranium oxide production with very few PuO_2 studies.

IV.E. Granat Flocculation

The Granat method for manufacturing MOX fuel pellets, named after the pilot commercial plant in PA Mayak, was developed in Russia as a “safe, very simple, efficient and reliable” method to prepare MOX feed powder granules that can be used directly in a standard cold press and sinter operation.[39] The method was developed as a continuous process wherein uranium and plutonium are coprecipitated from a mixed nitrate solution through formation of ammonium diuranate and plutonium hydroxide precipitates with ammonia addition, and subsequently controlling granule formation using a flocculating agent. The resulting granules are converted to oxide MOX feed powder and prepared for fabricating MOX fuel pellets. All development was done up to pilot scale, and the design of a full-scale continuous production plant was also completed. Several successful irradiation tests were completed to validate the in-reactor performance of fuel fabricated with the Granat method.

The following Granat operations are set up in cascade arrangement so that material can be easily fed in a continuous manner. Figure 15 illustrates the basic Granat production plant process.

- Prepare a mixed uranium-plutonium nitrate solution with a heavy metal concentration of 100 g/L
- Introduce a concentrated ammonia solution for a one-stage coprecipitation of U and Pu hydroxides
- Flocculate by adding a 6% solution of polyacrylamide
- Form strong dense granules
- Separate granules from liquor using a vibration separator
- Dry granules at 100ºC in air
- Calcine granules in air to form stable oxide
- Size through vibration sifter.

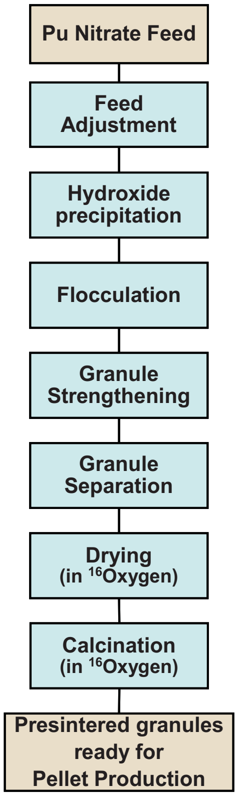


Fig. 15. Process flow for Granat flocculation.

The calcined powder produced by the Granat process consists of large granules that are rounded in appearance and thus flowable, and has proven to be excellent automated press feed powder (see Figure 16). It contains no small particles <10 µm and is therefore clean to work with. Table 3 contains a summary of some of the final calcined powder characteristics.

Table 3

Granat calcined powder characteristics

Parameter	Value
Bulk density (settled)	3.52 g/cc
Average agglomerate size	387 µm
Granule size (µm)	Fraction distribution
+ 350	61.7%
+212	13.4%
+150	6.4%
+90	10.5%
+53	5.5%
+38	1.5%
<38	1.0%

Fig. 16. Calcined granules of MOX powder produced by the Granat process. (scale in cm.)

The Granat process was designed to produce a mixed uranium-plutonium oxide. Its applicability to plutonium oxide, and specifically to Pu-238 oxide production, is unknown. However, for plutonium applications, the Granat method essentially simplifies to an enhanced plutonium hydroxide precipitation process using flocculation aids to ensure uniform, dense precipitates that can be dried and calcined without production of dust. So far, all of the testing of this specific process has been conducted in Russia. Testing with surrogates and ultimately with plutonium and Pu-238 would be required to optimize the process for producing GPHS and to quantify the purported advantage of the process – production of free-flowing, low-dust feed.

IV.F. Resin-bead Loading and Calcining

The resin bead loading and calcination process has been demonstrated with transuranics, including both curium[40] and Pu-238.[41,42] The process has also been used to produce fuel kernels for high-temperature gas-cooled reactor coated-particle fuel.[43,44] The process has two advantages that warrant its consideration, simplicity and generation of a dust-free product. Plutonium is loaded from nitrate solution onto ion exchange resin beads. The beads are then emptied from the column, dried, and calcined into PuO_2 beads, whose size are determined by the size of the precursor resin beads. Two types of resin loading are distinguished by the use of anionic or cationic exchange resin. Cationic exchange was successfully demonstrated with Pu-238 and is currently used for curium target fabrication, but anionic exchange was also determined to be potentially feasible for Pu-238 applications. Its use would seamlessly mesh with the current purification process.

The process diagram for cationic exchange is shown in Figure 17. The plutonium nitrate feed stream arising from the precursor anion exchange purification undergoes a valence adjustment to ensure high-efficiency loading onto the resin. The nitrate is then fed into an exchange column containing cationic resin. Both the Pu-238 experience and current curium operations the process is based on use DOWEX 50W resin beads that have been previously sized and washed. However, other resins including nonsulfonated resins may prove more suitable for Pu-238 GPHS applications. A simple fractionation technique has been used to size the resin before introduction to the column, so that sizes of the final oxide beads can be controlled either as a mono-size or as a distribution within a controlled range. However, the resin is manufactured with a specific size range, which necessarily limits the variability in the final product.

After loading the plutonium onto the resin, the resin beads are emptied from the exchange column, dried, calcined, and subjected to oxygen exchange. Carbon residue from the resin itself can be removed through controlled oxidation during the calcination step. The oxygen exchange and granule seasoning operations should be possible in the same furnace.

The current curium target process and the previous Pu-238 work include sintering at >1000°C, which produces dense, spherical particles with low ceramic activity. Based on conversion processes for sol-gel derived particles, carefully controlled drying and calcination at lower temperatures up to about 700°C should result in lower density spherical particles that retain internal porosity and ceramic activity. If successful, the two-part mixture used in the current reference pelletization process could be produced through appropriate control of the

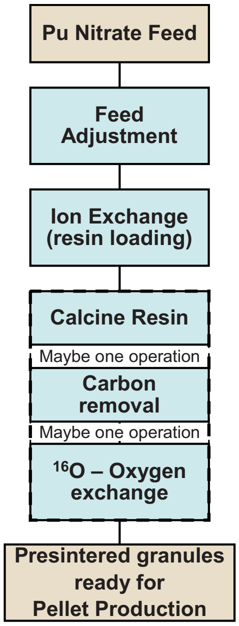


Fig. 17. Process flow for Granat flocculation.

calcination and sintering conditions. The final oxide is essentially dustless; the only fine material results from particles either broken during handling or “popped” during calcination. The current curium product retains impurities originating in the resin at levels above those allowed in the Pu-238 GPHS. A key question for applying this process to Pu-238 GPHS production is whether a suitable resin and calcination/heat-treatment can be defined that achieves the desirable product purity while retaining adequate ceramic activity.

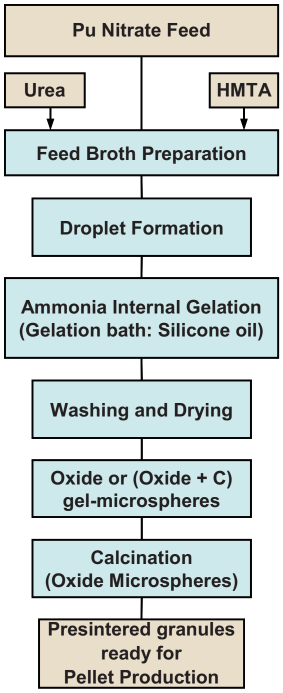
The ability to size the precursor resin beads allows control of the final oxide particle size, either as monomodal, bimodal, or continuous distributions as desired. The key concerns with the resin bead process for Pu-238 applications are selection of optimum resin, chemical impurities in the final product resulting from the resin itself, and retention of adequate ceramic activity in the oxide product.

IV.G. Sol-gel Method

“Sol-gel” refers to a group of related processes for producing microspheres. Sol-gel processes have been used extensively for producing nuclear fuel and target materials, including oxides, nitrides, and carbides of various actinides and actinide mixtures. A sol-gel process was also used early in the RPS program at Mound for fabricating DART and SNAP Pu-238 fuel forms.[45,46,47,48] The process was changed in the late 1960s from sol-gel to hydroxide cake precipitation and crushing to fabricate PuO_2 shards into molybdenum cermet fuel.[49] Among the variations, two classes are generally considered – internal and external gelation – the two differing principally in the source of ammonia used to gel a plutonium nitrate broth.

The most directly applicable sol-gel experience, including all of the Pu-238 work conducted at Mound, used an external gelation process developed by ORNL.[50] However, for the current GPHS ceramic pellet production, internal gelation may prove to produce the better ceramic feed product. A generic flowsheet for an internal sol-gel process is shown in Figure 18.

As shown in Figure 19, sol-gel products are typically uniform spheres that are essentially dust free. Because many of the applications of sol-gel derived microspheres require a fully dense, low-porosity product, drying and calcination conditions have often been optimized accordingly. Such products have essentially no ceramic activity. However, sol-gel derived microspheres have also been used to a limited extent for producing pellets.[51,52] For these applications, the drying and calcination temperatures are limited such that a fine-grained microstructure and internal porosity are maintained. The relatively soft and porous microspheres can be handled without damage, but break apart during pressing operations such that they lose their independent identities. Carbon, dispersed uniformly into the gel spheres, has been successfully used as a pore former during the drying/sintering step.



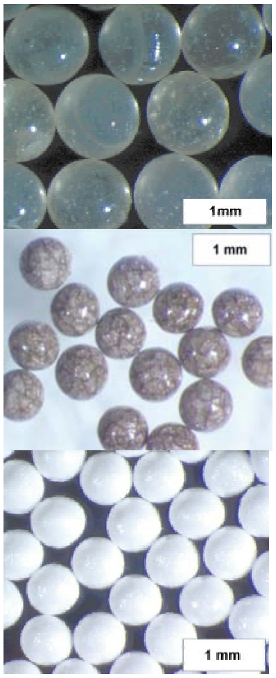


Fig. 18. Process flow of internal sol-gel process

Fig. 19. From top to bottom: Drip-casting microsphere formation of ZrO_2/Y_2O_3 spheres obtained by dropping Zr and Y nitrate solution into NH_4OH solution and drying; ZrO_2/Y_2O_3 spheres calcined 3 hours at 500°C; ZrO_2/Y_2O_3 spheres sintered 2 hours at 1600°C.[53]

Sol-gel processes appear complex, but have been routinely used at pilot and production scale with actinides. In Mound's previous work with external gelation, the Pu-238's generation of internal heat was actually used as part of the drying process, and was determined to have no deleterious effect on the process or the product; however, pure plutonium oxide pellets, such as the GPHS, have not been fabricated from the sol-gel process. For GPHS applications, the key uncertainties relate to defining the optimum press-feed characteristics and adjusting the process to produce the desired product. Mixed-waste generation must also be considered and minimized; CCl_4 has typically been used to wash residual silicon oil from the green microspheres.

IV.H. Suspension/Temporary Binder Method

As with the sol-gel method, plutonium oxide spheres are produced. The size of the oxide spheres can be controlled precisely and spheres can be produced from tens of microns to millimeter size. The difference with the suspension/temporary binder method is that the feed stream is an aqueous slurry of fine particle PuO_2 and organic binder. Droplets are produced that fall into a hardening solution. After that, spheres are then collected, dried, and sintered.

Fine plutonium oxide powder (less than 20 µm) is mixed with an aqueous solution of sodium alginate to form homogeneous slurry. Alginate is the salt of alginic acid, an organic, unbranched binary copolymer that after cellulose is the most abundant biopolymer. The alginate binder is nontoxic and used worldwide in numerous processes for the pharmaceutical and food industries. The slurry is dispensed through an orifice, the size of which determines the dimension of the droplet. The orifice may be the tip of a syringe needle for manual production, or a vibrating single nozzle or multiple nozzles for automated production. The round droplets fall into a hardening solution of calcium chloride where the droplets harden into spheres. The spheres harden, owing to the ion exchange of Na alginate (water soluble) to Ca alginate that is insoluble in water. The metal oxide is not involved in the alginate ion exchange reaction. The spheres are cured in the solution, collected, and washed with alcohol to remove water and excess alginate and $CaCl_2$. As with the sol-gel process, washing is very important to maintain the integrity of the spheres and produce a pure product. Spheres are air dried at ~150°C to evaporate the wash fluid, calcined in air at ~550°C to fully decompose the organic binder. Actinide oxide spheres are then typically sintered in reducing conditions to form high-density spheres of PuO_2.

This process produces PuO_2 spheres with precisely controlled size distributions. Microsphere diameter dimensions are determined primarily by the drop orifice diameter ranging from tenths of a millimeter to tens of millimeters. Typically, the microspheres are sintered at high temperature to produce high-density spheres of 96 to 99% TD, but conditions can be altered or pore formers added to decrease the sphere density with increased porosity. With sufficient sphere washing and calcining methods, impurities in the bulk spheres typically range from 10 to 500 ppm residual carbon and less than 150 ppm Ca and Cl.

The suspension/temporary binder method requires a feed of fine PuO_2 powder of 20 µm or less. This somewhat defeats the dust-free requirements of the process. Once the PuO_2 powder is slurried with the binder solution, the process can be considered dust free as long as the powder remains wet. Once the spheres are produced in a well-controlled manner, very little fine powder is produced. The process can be performed either as a manual operation for small-scale sphere production or automated to produce kilogram quantities of spheres in a very short time as shown in Figure 20. The process is simple, with minimal equipment or chemical requirements. With the exception of the Pu-238, the chemical reagents are nonhazardous. Some residue contaminates from the process remain in the product.

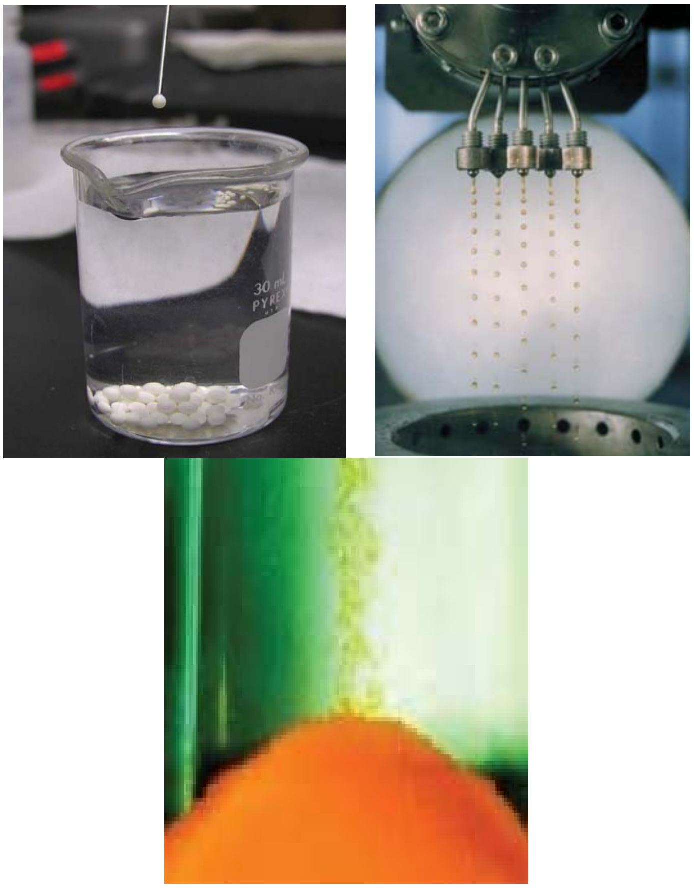


Fig. 20. Manual drip-casting of CeO_2 slurry with binder into $CaCl_2$ hardening solution[54]; Automated drip-casting of UO_2 slurry (bottom photograph).[55]

V. EVALUATION

A committee of subject matter experts convened to review and discuss the above alternatives for granule production. The committee members represented four national laboratories experienced in Pu-238 handling, universities and industry experts. The four laboratories involved were: Idaho National Laboratory, Los Alamos National Laboratory, Oak Ridge National Laboratory and Savannah River National Laboratory. The alternatives were evaluated by the DOE trade study process. To compare alternatives, criteria were developed and weighted. Then the alternatives including the current process were ranked relative to each other for each criterion.

The criteria and resulting weights were:

- **32%-Minimize the hazards**–Reduce radiation exposure, improve contamination control, and eliminate production of fine powder
- **23%-Simplify process**–Favor a robust process with fewer process steps and less equipment
- **19%-Minimize technical risk**–Reduce the probability of producing and qualifying flight-approved pellets
- **13%-Control granule process**–Control particle size distribution and ceramic activity and improve the consistency of granule quality
- **13%-Maximize chemical purity**–Maximize chemical purity of the granules.

The resulting ranking of the alternatives with relative numerical scores was:

- 39-Improved Oxalate Precipitation
- 35-Hydroxide Precipitation
- 31-Granat Flocculation
- 31-Denitration
- 30-Sol-gel Method
- 29-Resin-bead Loading and Calcining
- 27-Plutonyl Carbonate Precipitation
- 23-Current Process
- 21-Suspension/Temporary Binder Method

While the ranking grades the merit of the alternate processes in comparison to the baseline, the relative scores were so close that the committee acknowledged insufficient test data existed to determine the best solution. Alternatives were selected that merit further testing recognizing that all precipitation methods could be tested using the same equipment. The list of process alternatives that warrant further testing is prioritized in Table 4.

Table 4

Granule production methods that merit testing

Precipitation methods
- Improved oxalate precipitation
- Hydroxie precipitation
- Granat flocculation
- Carbonate precipitation

Alternate Granule methods
- Denitration
- Sol-gel microsphere
- Resin bead loading and calcining

VI. CONCLUSIONS

VI.A. Findings

Finding 1 – The existing product specifications are essentially process specifications. Physical characteristics of the GPHS product are not specifically measured and controlled. Rather, the fabrication process and operating parameters are tightly controlled to ensure consistency between new batches and the original product, and thus tie to the flight-qualification database. The physical characteristics of Pu-238 in-process material require additional research if the current process is to be modified.

Finding 2 – Several processes potentially can achieve the objectives. The committee preferred improved oxalate precipitation granule production because it has the most developmental maturity and offers the lowest risk for flight qualification.

Finding 3 – Other alternative processes entail higher risk but offer potentially higher rewards. Further reduction in dust generation, simpler operations and improved stress distributions may be achieved.

VI.B. Recommendations

Recommendation 1 – Characterization should be performed on the current Pu-238 process to document the physical characteristics of GPHS in-process material and final products. Any development of a new process requires a more complete product specification.

Recommendation 2 – The committee recommends a staged test program, eliminating at each stage any processes that do not warrant further consideration. Final selection of a new Pu-238 process should be based on (1) test results from cold surrogate, Pu-239 surrogate, and Pu-238 testing, (2) optimized process parameters that produce the most repeatable product with the highest quality and (3) ability to produce GPHS pellets that can be readily qualified for space flight.

Recommendation 3 – Investigate the processes that were deemed viable alternatives. Investigation should include further literature reviews, testing, including impact testing, to answer key technical uncertainties; and further downselection of alternatives.

Numerous processes can be grouped and tested using the same equipment to reduce testing costs. For example, one precipitation system can be used to test all precipitation methods.

VI.C. Future Testing

Experimentation should progress through three phases of testing, with another down select evaluation at the end of each phase. Phase I testing will be performed with cold surrogates. Phase I should test all viable alternatives. Phase II testing will be performed with radiological material. Initially, Pu-239 may be used, followed by testing with Pu-238. Depending on the complexity of the process and the introduction of new hazards, preparation work Phase II may take 1 to 2 years. The Phase III testing is flight qualification testing. The extent of this testing will be determined by how significant the preferred alternative deviates from the current process.

Experimental evaluation of all precipitation methods can be accomplished using a single, multipurpose precipitator that will allow for precision process-parameter control and in situ particle growth analysis. Precipitation processes will be monitored in real time to determine the optimal processing conditions of: feed rate, temperature, agitation cycles, digestion rates, and particle size and distribution ranges. Product will be collected for further analysis to determine granule density, porosity, active surface area, crystal structure, surface morphology, and chemical purity. Initial questions that must be answered to determine the applicability of precipitation for GPHS granule production are:

- ***What is the particle size distribution in the precipitant and the granulate produced with the optimized process?***
- ***Are there any distinguishing characteristics, for example impurities, between the various precipitation methods?***

The MDD approach of producing granules has potential benefits above the improved oxalate precipitation approach. The direct denitration process is a simpler process requiring one system to go directly from liquid feed to a finished granule. The approach reduces material handling because it is self-contained. Initial questions that must be answered to determine the applicability of MDD for GPHS granule production are:

- ***What is the particle size distribution in the granulate that can be produced by the optimized MDD process?***

  Questions regarding the maximum granule size, the range of granule sizes and the type of size distribution, (Poisson, binomial, continuous uniform or other), are important to optimizing the packing density of granules for pressing. The denitration occurs in a rotary kiln. The evaluation committee's concern is that soft agglomerates will tend to break up, releasing 1-5 μm crystallites during the tumbling process.

The resin bead approach of producing granules has potential benefits above the improved oxalate precipitation approach. The resin bead method can accurately control the size of granules produced. As discussed, the granule size distribution controls the packing (tap) density of granules before pellet pressing. By optimizing the granule size distribution, higher tap densities can be achieved. High tap densities require less compaction during pressing and improve stress distribution in the final pellet. The initial technical uncertainties with this approach can be answered with cold surrogate testing. These initial questions must be answered to determine if the resin bead method will work for GPHS granule production. They are:

- ***Can the required chemical impurity be achieved using this method?***

  One of the committee's concerns with the resin bead approach is residual chemical impurities left when reducing the resin material. Increasing the temperature to improve chemical purity will have a detrimental affect on the granule's ceramic activity. Alternate resin materials may reduce the chemical impurities left after resin calcination.
- ***What is the ceramic activity of the final granules produced by the resin bead method?***

  Because resin calcination is a thermal process, the committee's other primary concern is the unintentional sintering of granules during resin calcination. The finished granules must have sufficient activity for bonding during the pressing operation. As granule size increases, chemical impurity or the amount of sintering required to achieve chemical impurity may worsen.
- ***What is the particle size distribution in the granulate produced by this optimized process?***

  Experience has demonstrated the resin bead method does not produce fine powders. However, the broken microspheres from calcining will produce fine powder. Experimental data should be collected to confirm that powder production is minimal.

The Sol-gel approach of producing granules has potential benefits above the improved oxalate precipitation approach. The Sol-gel process is a simpler process requiring one system to go directly from liquid feed to a finished granule. The approach reduces material handling because it is self-contained. Preliminary testing could be performed with cold surrogate material. Initial questions that must be answered to determine the applicability of Sol-gel for GPHS granule production are:

- ***What is the particle size distribution in the granulate that can be produced by the optimized Sol-gel process?***
  Broken microspheres from calcining will produce fine powder. Experimental data should be collected to confirm that powder production is minimal.
- ***What is the ceramic activity of the final granules produced by the Sol-gel method?***
  Because the microsphere calcination is a thermal process, the committee's other primary concern is the unintentional sintering of granules during calcination. The finished granules must have sufficient activity for bonding during the pressing operation.
- ***Can the required chemical impurity be achieved using this method?***
  One of the committee's concerns with the Sol-gel approach is residual chemical impurities from the process chemicals.

VI.D. Final Conclusions

In this evaluation, eight different technologies were considered as alternatives to the current production method. All proposed alternatives meet the identified objectives to varying degrees. The unfortunate reality is that currently insufficient experimental data exists to select an optimal production method. Most of the techniques discussed have not been tested with plutonium and even fewer have been tested with plutonium-238. Therefore, any down selection from the available alternatives becomes professional judgment and is greatly influenced by the priorities of criteria used to make the selection.

For instance, if cost and technical risk are of greatest importance, as they are today in the U.S. economy, the improved oxalate precipitation is clearly the recommended alternative for enhancing the current granule production method. This alternative clearly improves the safety of operations by reducing the production of submicron fines. It also is the only production method that has actually been tested by successfully producing Pu-238 pellets. This solution though is only an incremental improvement over the current state of the art requiring many of the same operating steps as the current production system and having limited control over granule size. Easily half of the other alternatives offer greater benefits in simplicity, dose reduction and powder production. Therefore from a value approach, the improved oxalate precipitation may not be the best solution.

The one true insight of the evaluation is that an improved granule size distribution should decrease stress distributions in the pellet and improve pellet stability. Thermal stresses and shrinkage during sintering routinely causes pellet to crack and sometimes fracture. Two granule production alternatives; a) sol-gel microspheres and b) resin bead loading and calcining provide precise control of granule size. These granule methods could be used to produce optimal size distributions improving pour density and pellet stress distributions. As there are numerous process and waste issues with sol-gel, further testing with the resin bead method is recommended. Initial tests can quickly determine if the chemical purity and ceramic activity concerns are founded and if these issues can be overcome.

In summary, alternate technologies may potentially improve upon the current process used for GPHS pellet production. The degree of improvement is related to the technical risk and coincidently the research cost. As the United States wrestles with the cost of the Pu-238 program, advanced manufacturing methods should enhance the safety of this important national capability.

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