Milestone Report
Evaluation of Co-precipitation Processes for the Synthesis of Mixed-Oxide Fuel Feedstock Materials

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Introduction

The focus of this report is the evaluation of various co-precipitation processes for use in the synthesis of mixed oxide feedstock powders for the Ceramic Fuels Technology Area within the Fuels Cycle R&D (FCR&D) Program's Advanced Fuels Campaign. The evaluation will include a comparison with standard mechanical mixing of dry powders and as well as other co-conversion methods. The end result will be the down selection of a preferred sequence of co-precipitation process for the preparation of nuclear fuel feedstock materials to be used for comparison with other feedstock preparation methods.

A review of the literature was done to identify potential nitrate-to-oxide co-conversion processes which have been applied to mixtures of uranium and plutonium to achieve recycle fuel homogeneity. Recent studies have begun to study the options for co-converting all of the plutonium and neptunium recovered from used nuclear fuels, together with appropriate portions of recovered uranium to produce the desired mixed oxide recycle fuel. The addition of recycled uranium will help reduce the safeguard attractiveness level and improve proliferation resistance of the recycled fuel. The inclusion of neptunium is primarily driven by its chemical similarity to plutonium, thus enabling a simple quick path to recycle. For recycle fuel to thermal-spectrum light water reactors (LWRs), the uranium concentration can be ~90% (wt.), and for fast spectrum reactors, the uranium concentration can typically exceed 70% (wt.). However, some of the co-conversion/recycle fuel fabrication processes being developed utilize a two-step process to reach the desired uranium concentration. In these processes, a 50-50 "master-mix" MOX powder is produced by the co-conversion process, and the uranium concentration is adjusted to the desired level for MOX fuel recycle by powder blending (milling) the "master-mix" with depleted uranium oxide.

In general, parameters that must be controlled for co-precipitation processes include (1) feed solution concentration adjustment, (2) precipitant concentration and addition methods, (3) pH, temperature, mixing method and time, (4) valence adjustment, (5) solid precipitate separation from the filtrate "mother liquor," generally by means of centrifugation or filtration, and (6) temperatures and times for drying, calcination, and reduction of the MOX product powder. Also a recovery step is necessary because of low, but finite solubility of the U/TRU metals in the mother liquor. The recovery step usually involves destruction of the residual precipitant and disposal of by-product wastes. Direct denitrations of U/TRU require fewer steps, but must utilize various methods to enable production of MOX with product characteristics that are acceptable for recycle fuel fabrication.

The three co-precipitation processes considered for evaluation are (1) the ammonia co-precipitation process being developed in Russia, (2) the oxalate co-precipitation process, being developed in France, and (3) the ammonium-uranyl-plutonyl-carbonate (AUPuC) process being developed in Germany. Two direct denitration processes are presented for comparison: (1) the 'Microwave Heating (MH)" automated multi-batch process developed in Japan and (2) the "Modified Direct Denitration (MDD)" continuous process being developed in the USA. Brief comparative descriptions of the U/TRU co-conversion processes are described below. More complete details are provided in the references.

Ammonium Hydroxide Co-Precipitation

The process steps for the ammonia co-precipitation process are illustrated in Figure 1 and the uranium-plutonium co-precipitation curves are shown in Figure 2.

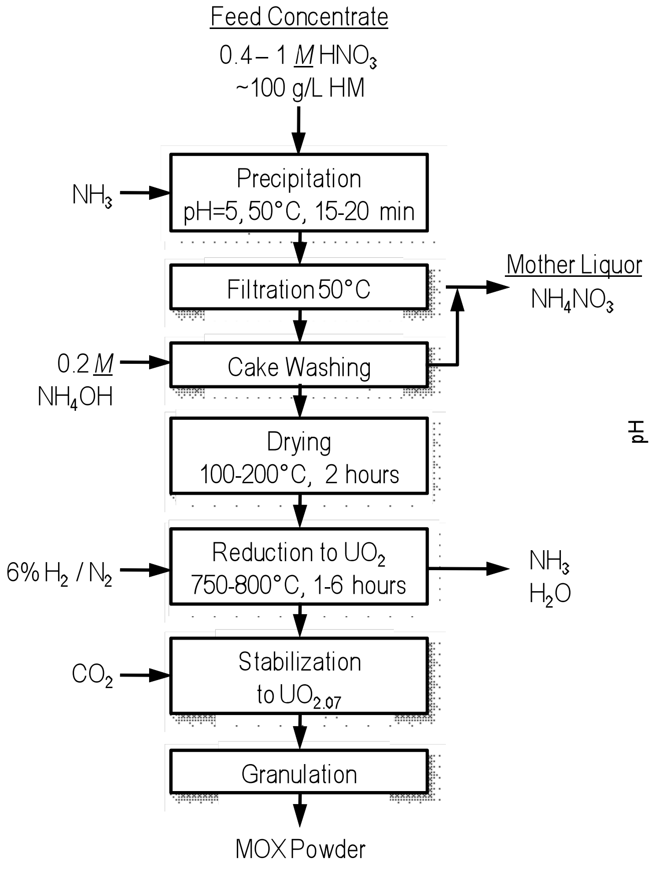


Fig. 1. Ammonium co-precipitation.

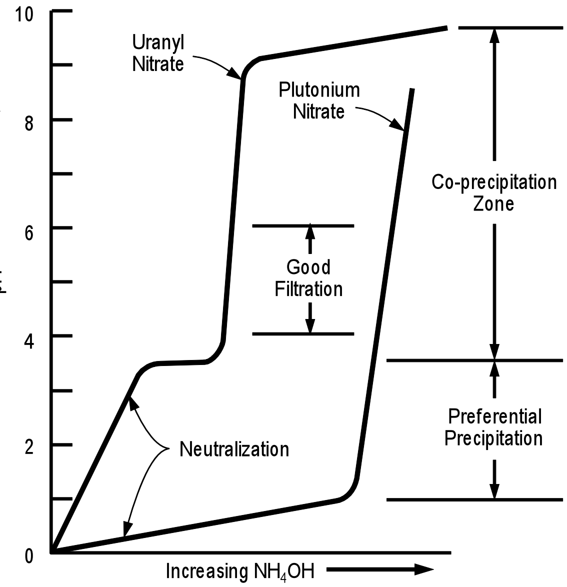


Fig. 2. U-Pu Co-precipitation curves.

This process is similar to the ammonium diuranate precipitation process which is widely used for making fuel-grade UO_2 in current fuel fabrication plants. The co-precipitation process, with carefully controlled precipitation conditions (illustrated in Fig. 2) and with avoidance of higher temperature calcination is capable of producing a "very homogeneous" MOX powder, with respect to plutonium distribution. However, the by-product ammonium nitrate produced in the mother liquor requires a complex treatment for waste disposal, as illustrated in Fig. 3.

As with the other co-precipitation methods, the ammonia hydroxide co-precipitation process is only in the R&D stage, thus powder properties may differ widely depending on various control parameters during the critical steps of precipitation and calcination. In some cases, processing is difficult because the preparations are gelatinous with the final reduction producing irregularly shaped particles with a small fraction of fines. Comparison of powder properties with other co-conversion methods is difficult because very little data is available on the surface area (SA), particle size (PS), and morphology of mixed actinide oxides prepared by ammonia co-precipitation.

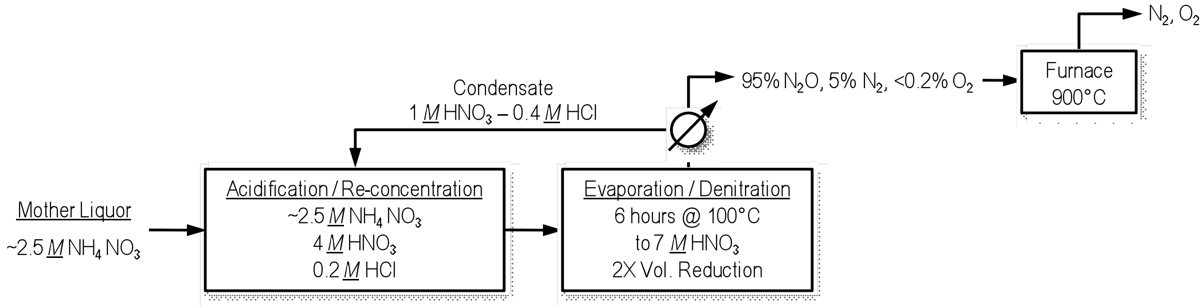


Fig. 3. Mother Liquor from Ammonium Hydroxide Co-Precipitation Ammonium Nitrate Decomposition Russian Process.

Oxalate Co-Precipitation

The process steps for the oxalate co-precipitation process are shown in Figures 4 and 5. This process is being developed in France by the CEA and Areva, and will be operated in a continuous manner, using equipment similar to that used in the La Hague plant for plutonium conversion. However, to adapt the process to co-precipitation of uranium, the uranium valence must be reduced from the normal hexavalent state in nitric acid solution to the tetravalent state to minimize the uranium solubility in the mother liquor. The pre-reduction step can be done electroytically by established methods, but in order to maintain uranium in the tetravalent state, a "holding reductant" (hydrazine) must be present to preferentially react with nitrous acid as it is generated in the nitric acid solution.

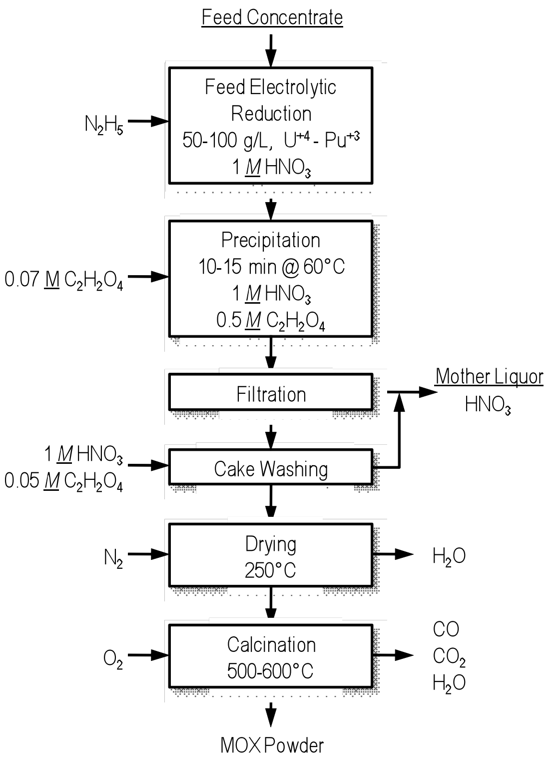


Fig. 4. Oxalate Co-precipitation Flowsheet.

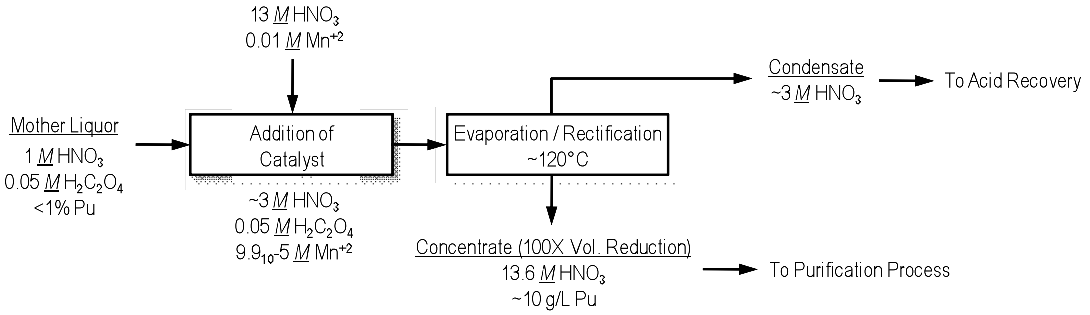


Fig. 5. Mother Liquor from Oxalate Co-Precipitation.

The presence of hydrazine facilitates reduction of the plutonium valence to the trivalent state, such that the oxalate salt that is co-precipitated is $U^{+4} – Pu^{+3}$. During the subsequent calcination step, the plutonium is re-oxidized to the tetravalent state and homogeneous MOX powder is produced. Since the $U(NO_3)_4$ is directly converted to UO_2 in the MOX powder, no further reduction step is required.

Oxalate co-precipitation of mixed oxides is generally isomorphous which facilitates the formation of solid solutions. In most cases, a complete solid solution is formed during calcination at temperatures 900°C, in any case, the solid solution is formed at sintering temperatures. Oxalate co-precipitation is a flexible process and allows modification of particle morphologies for optimization of powder properties for fuel fabrication. Powder agglomeration is typically small resulting in favorable bulk densities of >1.7. The PS and SA tend to be a strong function of calcination/reduction conditions. Oxalate co-precipitation of mixed oxides can produce PS and SA ranging from 1 to 40µm and 4 to 24 m^2/g respectively.

AUPuC Co-Precipitation

The process flowsheet for ammonia-uranyl-plutonyl-carbonate co-precipitation is shown in Fig. 6. The process involves conversion of mixtures of uranyl and plutonyl nitrate to mixed oxide by precipitation and calcination of their respective ammonium carbonates.

The initial process step involves heating a nitric acid solution of uranyl nitrate and plutonium nitrate to convert the plutonium from the tetravalent to the hexavalent state. This brings the U and Pu to similar chemical behavior in order to ensure preparation of a homogeneous product. The concentration of HNO_3 in the oxidized solution is then adjusted to 1*M* by distillation to dryness followed by redissolution in 1*M* HNO_3. Precipitation of ammonium uranyl/plutonyl carbonate is accomplished by feeding NH_3 and CO_2 gases to the nitrate solution in a reactor vessel. Precipitation occurs at a pH of 7-9. A particular advantage of this process is the ability to control grain growth and size during precipitation. This promotes the flowability of the powder. The precipitate is filtered, with its coarse nature allowing the filter cake to dry sufficiently during filtration to go directly into the calcination-reduction step. Decomposition and reduction of the AUPuC is accomplished in a single step at 600-650°C inflowing N_2-3%H_2.

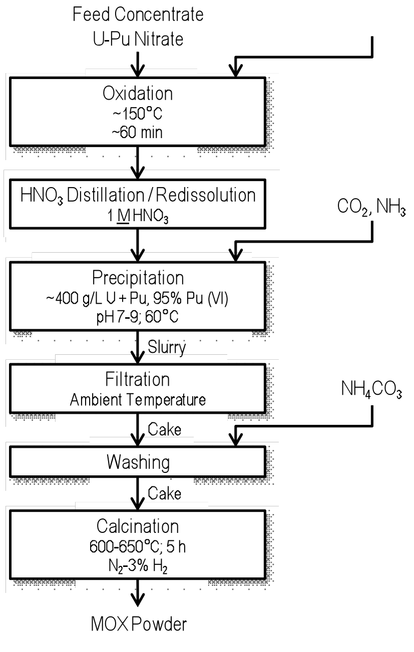


Fig. 6. Flowsheet for preparation of MOX powder by the ammonium uranyl plutonium carbonate (AUPuC) process (Germany).

Powders produced by this process are claimed to be ceramically active and flowable so that they can be directly pressed into pellets without milling, granulating, or pre-compaction. The AUC process typically generates powders with a larger mean particle size (30-400 µm with a mean of ~50 µm) and dense, rounded crystals with low porosity as compared to the ADU, MDD, or other synthesis techniques. As a result, the powders are free flowing with a tap density of > 1.5 g/cc and the powder is amenable to direct pressing without additional powder preparation such as milling or slugging and granulation. The nominal SA is low at ~5m^2/g but the driving force for sintering remains acceptable and sintered densities of >93% theoretical are achievable.

Direct Denitration

Flowsheets for the Microwave Heating (MH) and Modified Direct Denitration (MDD) processes are shown in Fig. 7. The MH process relies on controlled, uniform batch heating and evolution of NO_2 gas to avoid the undesirable properties of direct denitration processes. The MDD process uses the addition of ammonia to the nitric acid U/TRU feed solution to enable formation and decomposition of ammonium-metal nitrates in a continuously-operated rotary kiln denitrator to produce fine granular agglomerates of MOX requiring only pre-screening, prior to fabrication of highly sinterable MOX pellets.

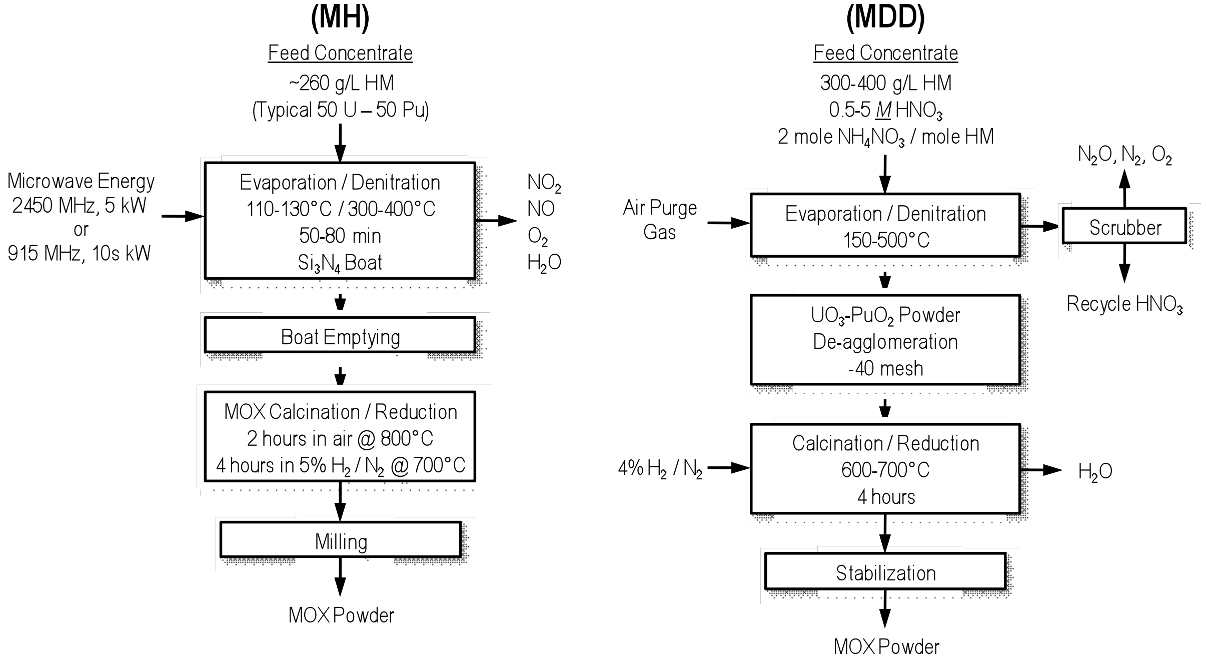


Fig. 7. Advanced direct denitration co-conversion processes.

The MH process has been extensively developed and operated at a 10 kg/day capacity level since 1983 at the Tokai Demonstration Plant, and will be operated at commercial scale in the Rokkasho Reprocessing Plant. Figure 8 shows the time-temperature steps in each batch denitration. Studies showed that, for denitration of uranyl nitrate, the crystal structure of the oxide product depends on temperature and heating rate, with the desired porous-structure UO_3 formed at faster heating rate. However, the oxide cake produced requires crushing prior to calcination and reduction to UO_2-PuO_2 and milling/blending of the MOX powder prior to pellet fabrication.

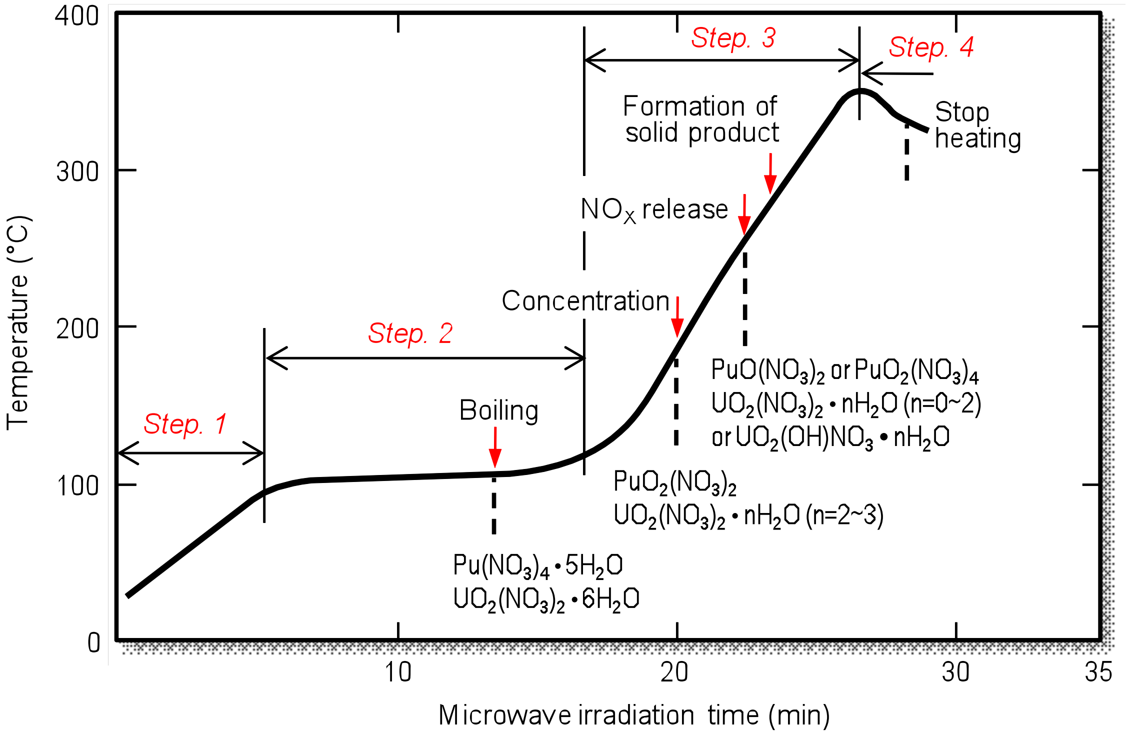


Fig. 8. MH Batch Processing Time is an important variable.

Based on TGA-DTA-EGA analyses, the MDD process operated with continuous feed and UO_3-PuO_2 production, proceeds rapidly through evaporation of water and nitric acid, decomposition of excess ammonia (from the diammonium–metal nitrate salt) the remaining ammonium-metal nitrate salt at ~ 280°C. The UO_3-PuO_2 and the final UO_2-PuO_2 powder have relatively low bulk density and high surface area. The agglomerated powder only requires a 40-mesh screening operation to prepare a free flowing powder that is suitable for making fuel.

Comparison of Feedstock Synthesis Methods

A qualitative comparison of the various feedstock synthesis processes is shown in Table 1. Mechanically mixing separate feedstock powders to achieve the desired composition is the process with the most industrial experience and technical maturity. Historically, this method has been used in the U.S. to fabricate MOX fuel for the Fast Flux Test Facility and it is still used today to make MOX fuel in Europe. The chief drawbacks with this process are that it is (1) a dry-powder process which requires multiple blending steps, and (2) the product fuel pellet is compositionally heterogeneous which can be a limiting factor with regards to high burn up fuel.

Each of the processes listed in Table 1 has some sort of recycle step in order to minimize process losses, however the explosive potential of an ammonium nitrate by-product stream, the labor intensive recovery of fine powder from the ammonium hydroxide and mechanically mixed processes, and the presence of hydrazine in the oxalate method present unique processing challenges.

The post-synthesis preparation of the product oxide is an important consideration. The flowsheet for synthesis and fabrication of nuclear fuel should be simplified as much as possible to reduce facility footprint and minimize powder hold-up and process losses. Product from MH tends to form hard agglomerates which requires additional process steps to break up and mill the powder prior to pressing. The oxalate co-precipitation and MDD methods generally produce fine, active powders however, the calcination/reduction process parameters required to create optimal powder properties has yet to be determined for a multi-component actinide oxide thus it is possible that some additional post-synthesis processing may be necessary.

The issue of compositional homogeneity is equally important. The FCR&D program has embarked on a campaign to increase the understanding of fundamental behavior of fuel materials during fabrication and in-pile performance. A key element of the experimental contribution to this effort is so called separate or single effects testing. These types of tests should be performed with compositionally pure and homogeneous samples; therefore, identification of preferred methods to synthesize homogeneous materials is paramount. The mechanical mixing route is least desirable because of the presence of micron-sized second phase “islands” in the microstructure. Methods in which the metal elements are mixed in the aqueous phase offer the best chance for achieving a homogeneously mixed feedstock material, provided that simultaneous precipitation is achieved. The degree of homogeneity however remains a question. In most cases, the co-precipitation or co-conversion product is heterogeneous on the sub-micron scale (hundreds of nanometers) but when the powders are pressed and sintered at high temperatures, cation interdiffusion leads to the formation of a complete solid solution with the second phase being resolved at the nanometer or sub-nanometer scale.

Table 1. Comparison of Co-conversion Methods to Synthesize Mixed Oxide Fuel Feedstock.

Oxalate	Ammonium Hydroxide	Ammonium Carbonate	Mechanically Mixed	MH	MDD
Well-developed process for single actinide or non-actinide mixed oxides.	Limited experience with mixed oxides.	Good experience with urania-thoria system.	Greatest industrial technical maturity and experience.	MH has greater experience and technical maturity than MDD.	Least experience.
Mother liquor recovery / purification and destruction of hydrazine required.	Undesirable ammonium nitrate by-product stream.	Ammonium carbonate recovery and recycle.	Dry-powder process. Recovery and recycle of fine powder required.	MH does not require addition of NH_4NO_3 modifier and corresponding safety evaluation.	Recycle of off-gas condensate.
Continuous operation demonstrated with Pu.	Automated multi-batch process.	Automated multi-batch process.	Automated multi-batch process.	Automated multi-batch process.	Continuous operation.
Milling may be required.	Post-synthesis powder preparation unknown.	Size reduction may be required.	Milling/blending required.	Oxide product requires crushing prior to calcination-reduction and milling afterward.	Oxide powder does not require crushing and milling – only screening through 20 or 40 mesh sieve to de-agglomerate larger agglomerates.
Liquid blending to final MOX composition.	Liquid blending to final MOX composition.	Liquid blending to final MOX composition.	Microstructure is compositionally heterogeneous with distribution of micron-sized grains of second phase.	MH process plan mechanical down-blending with UO2 powder.	Liquid blending to final MOX composition is planned .

With regard to the safety evaluation for use of NH_4NO_3 in the MDD process, studies show that, in the continually fed process with controlled feed rate, rapid decomposition is the goal. While some exothermic reactions are involved, the overall decomposition is endothermic. With a continuous purge of the vapor space and solids scraping and grinding bars in the rotary kiln, accumulation of reactive gases or solids is not likely.

Table 2 lists some key powder property data for the various oxide powder synthesis methods. Also shown are target values which were compiled from various nuclear fuel feedstock specifications. The values for each powder property are most accurately presented as a number range within which any specific number may be acceptable. This is because the final sintered density, microstructure, and mechanical integrity of the fuel pellet can be a function of all of these interrelated powder properties. For example, the bulk density is a function of the powder morphology, flowability, and the tendency for a powder to release entrained air during compaction. Flowability is a strong function of particle size. The smaller the particle size, the larger the specific surface area which increases the free surface to be acted upon by frictional and Van der Waals forces resulting in an increasing slope of the associated yield loci. One can conclude that the selection of a preferred co-precipitation process cannot be done using the properties of the powder product as the primary selection criteria. Other criteria such as process complexity, technical maturity, recycle or waste stream considerations, and engineering scale-up must be considered.

Considering the discussion above, an oxalate-type co-precipitation process was selected based on process technical maturity, demonstrated performance of the powder product, and the number of adjustable parameters. Experimental equipment for the oxalate co-precipitation processes will be set up and operated to produce MOX powder for comparative evaluation with traditional powder metallurgical mixing and direct conversion methods. Comparisons with other co-conversion processes will continue and may include future evaluation of the MH and AUPuC processes.

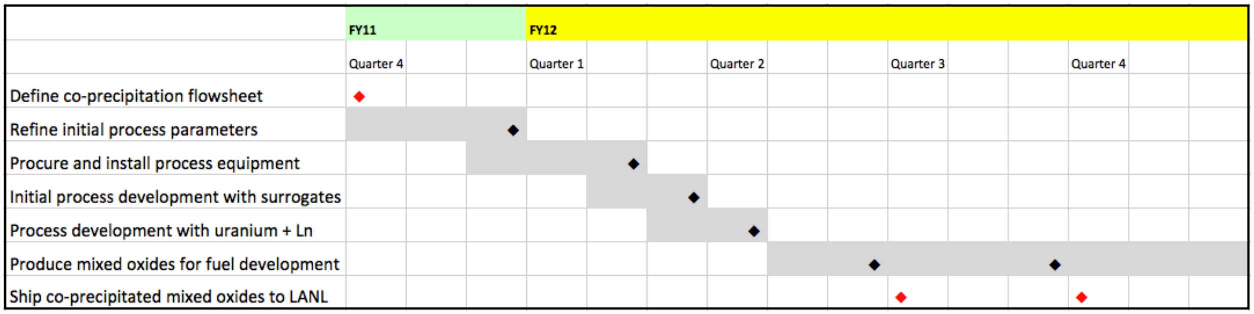
Co-precipitation Development Schedule

A Fiscal Year 2011 and 2012 schedule for the installation, startup, development, and the production of initial mixed oxide feedstock is shown in Table 3. The outline of a co-precipitation flowsheet is complete and the definition of initial process parameters will be finished by the end of FY11. Procurement of the process equipment will begin in FY11 and proceed in two phases. Phase I will focus on the electrolytic reduction of uranium to the tetravalent state. Phase II procurement will begin at the outset of FY12 and include the precipitation, filtration, washing, drying, and calcination equipment. Process development using surrogate material will precede the refinement of operational parameters for uranium-bearing compositions, and finally the production of the first U-Ln mixed oxide batches will commence during the second quarter of FY12.

Table 2 Comparison of MOX Product Characteristics.

Powder/Fuel Property	Target Values	Oxalate	Ammonium Hydroxide	Ammonium Carbonate	Mechanically Mixed	MH	MDD	Direct Denitration
Bulk density, g/cc	>1.5	>2.0	Not available	>1.5	>1.8	2.2	1.0	1.6-2.5
Surface area, m^2/g	2-30	4 to 24	Not available	5	UO2: avg. ~4.2 PuO2: avg. 10	4.5	7.5	0.1-1.6
Morphology	Rounded flowable particles or agglomerates without excessive internal porosity	Faceted geometry, rounded, relatively smooth agglomerates	Irregularly shaped particles	Rounded particles	UO2: rounded to egg-shaped particles with hedgehog agglomerate surface PuO2: monoclinic laths	Agglomerated porous structure	Fine granular agglomerates very porous internal structure	Hard glass-like chunks
Particle size, µm	99% > 100, 50% > 40, bi-modal distribution	1 to 40, wide bi-modal distribution	Not available	30 to 400, uni-modal distribution	UO2: mean 5.7 PuO2: mean 22	Requires crushing milling	5.5 (requires screening)	~43 (requires milling)
Sinterability % Theo. Density	>93%	>93%	>90%	>93%	>93%	>90%	>90%	~73%

Table 3 FY11/FY12 Co-Precipitation Process Schedule.



	FY11			FY12											
	Quarter 4			Quarter 1			Quarter 2			Quarter 3			Quarter 4		
Define co-precipitation flowsheet	◆														
Refine initial process parameters	▨	▨	▨ ◆												
Procure and install process equipment			▨	▨	▨ ◆										
Initial process development with surrogates					▨	▨ ◆									
Process development with uranium + Ln						▨	▨ ◆								
Produce mixed oxides for fuel development								▨	▨ ◆	▨	▨	▨ ◆	▨	▨	▨
Ship co-precipitated mixed oxides to LANL										◆			◆		

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