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AUTHOR(S): H. A. Dayem

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LOS ALAMOS SCIENTIFIC LABORATORY
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A COMPARISON OF MATERIALS ACCOUNTING IN CONVERSION AND COCONVERSION PROCESSES

Hassan A. Dayem
Safeguards Systems
Los Alamos National Laboratory
Los Alamos, New Mexico

ABSTRACT

Materials accounting systems performances are compared for plutonium nitrate-to-oxide conversion [Oxalate (III)] and uranium-plutonium coconversion (Coprecal and modified Coprecal). These processes have the same design basis plutonium throughput and achieve this throughput in parallel operating lines. However, the process line configurations differ. In comparing the materials loss detection sensitivities for the three processes, we find better materials loss detection sensitivity for the Oxalate (III) process than for either of the two Coprecal processes, better single-balance detection sensitivity for the original Coprecal than for the modified Coprecal, and better long-term detection sensitivity (> 1d) for the modified Coprecal than for the original Coprecal. Sensitivity differences result from differences in in-process inventories, feeding arrangements, and scrap generation.

I. INTRODUCTION

Conceptual designs of near-real-time accountability (NRTA) systems have been developed for plutonium nitrate-to-oxide conversion and uranium-plutonium nitrate-to-oxide coconversion. Three processes were examined: plutonium (III) oxalate,[1] Coprecal,[2] and modified Coprecal. These studies were performed in support of the Savannah River Laboratory's (SRL) Alternative Fuel Cycle Technology Program. They invoke materials measurement, control, and accountability technology that has been demonstrated or can be projected in a time frame consistent with the construction schedule of future fuel-cycle facilities. The studies were intended to define systems concepts, to develop methods for evaluating safeguards systems and the data they produce, and to stimulate further development of the facilities, processes, systems, and instrumentation needed for improving nuclear materials accountability.

This paper compares NRTA in these three processes. A brief description of the processes and a comparison of process parameters is given first. NRTA using identical unit process accounting areas (UPAA) and measurements in each process are then compared. The results point to some process design features that impact materials accountability.

II. THE REFERENCE PROCESSES

Each of the three processes converts the nitrate received from a chemical separations facility to an oxide suitable for use in fuel fabrication. The design basis throughput (~117 kg of plutonium/day) is achieved in three parallel operating lines. A short description of each process is given below, followed by a comparison of the operating characteristics.

A. Oxalate (III)

The reference facility for the first study was a conceptual design of a plutonium nitrate-to-oxide conversion process developed by SRL and Savannah River Plant (SRP).[4,5] The process is based on precipitation and calcination of plutonium (III) oxalate.

Figure 1 shows a block diagram of a single process line in the Oxalate (III) process. Plutonium-nitrate solution from the chemical separations facility is fed to a receipt tank. The receipt tank is air-sparged and mechanically agitated, and an accountability sample is taken before three 47-L batches are metered to three different valence adjustment tanks of three independent process lines. The last batch dispensed completely empties the receipt tank. Hydrazine and ascorbic acid are added to each valence adjustment tank to reduce the plutonium to the trivalent state. The adjusted solution is transferred to a precipitator and digested with oxalic acid to produce an oxalate slurry, which is vacuum-filtered through sintered-metal filter boats. The wet oxalate cake is then washed. The filtrate and cake wash solution is transferred to recovery operations. The boat is fed into a furnace for drying and calcining, and the calcined product in each boat is transferred to a container for sampling and storage. The filter boat is flushed and rinsed before being

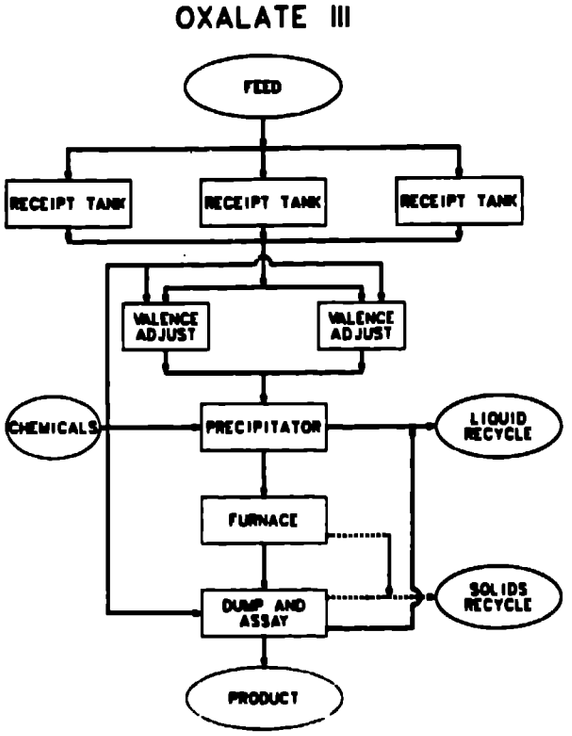

Fig. 1 Oxalate (III) block diagram.

returned to a filter station. The flush and rinse solutions are transferred to recovery.

B. Coprecal

The reference facility for the second study was a preliminary design of a coprecipitation and calcination (Coprecal) process developed by General Electric. It was designed for the continuous coprecipitation and calcination of a blended uranium- and plutonium-nitrate solution.[6]

Figure 2 is a block diagram of a single process line. Uranium-plutonium solution is received from the solvent-extraction facility and blended with a natural-uranyl-nitrate solution to obtain a 10% plutonium solution. Three parallel feed-blend tanks are required for each process line to permit the continuous processing of large homogeneous batches. One feed-blend tank continuously feeds the precipitator where ammonium hydroxide is added to produce a slurry of ammonium diuranate and plutonium hydroxide. The entire slurry from the precipitator is fed continuously to a fluidized-bed calciner system, which produces mixed uranium-plutonium-oxide powder.

The four calciners discharge into a single primary filter. Powder collected on the filter is removed by periodically blowing back portions of the filter. The powder collects in the bottom of the filter chamber and is discharged through a valve to a batch-transfer container. The batch-transfer container is removed and sent to a reduction-stabilization station. Gas from the calciner primary filter is discharged through a secondary filter to an off-gas treatment system. The batch-transfer container from the secondary filter is removed only once every operating campaign. From this point the process line operates in batch mode.

The batch-transfer container filled with mixed UO_3-PuO_2 powder is transferred from the primary filter to one of four parallel reduction-stabilization stations. Gas from the primary reduction-stabilization filter is discharged through a final filter to the off-gas treatment system. At the completion of the reduction-stabilization cycle, the batch-transfer container is removed and transferred to the screening station. The transfer container on the reduction-stabilization final filter will probably be removed at each physical inventory.

At the screening station, the stabilized powder is removed from the batch-transfer container and passed through a screen system to remove any foreign particles and oxide agglomerates. The powder passing through the screen is collected in a tared storage can. When all powder from a transfer container has been screened, material on the screen is dumped into a scrap container, which is sent to scrap recovery after filling. The product storage can is removed, sampled, weighed, sealed, and transferred to a storage vault.

C. Modified Coprecal

Several materials accountability and process design problem areas were identified in the preliminary Coprecal design. SRL, SRP, and duPont Engineering significantly modified the original Coprecal flow sheet to address these basic deficiencies. Figure 3 is a block diagram of a single process line of the modified Coprecal process. The most significant modifications from a materials accountability viewpoint are as follows:

- Adding 12 aliquot tanks to feed the co-conversion process lines.
- Replacing the primary and secondary filters in each process line. In the original design, four calciners are manifolded to a single primary filter and a single secondary filter. In the modified design, a primary secondary filter were included for each calciner. Each new filter is approximately half the size of the original filter.
- Raising the calciner operating temperature from 400°C to a range of 500°-600°C.
- Raising the reduction-stabilization operating temperature from a range of 550°-650°C to as high as 800°C.

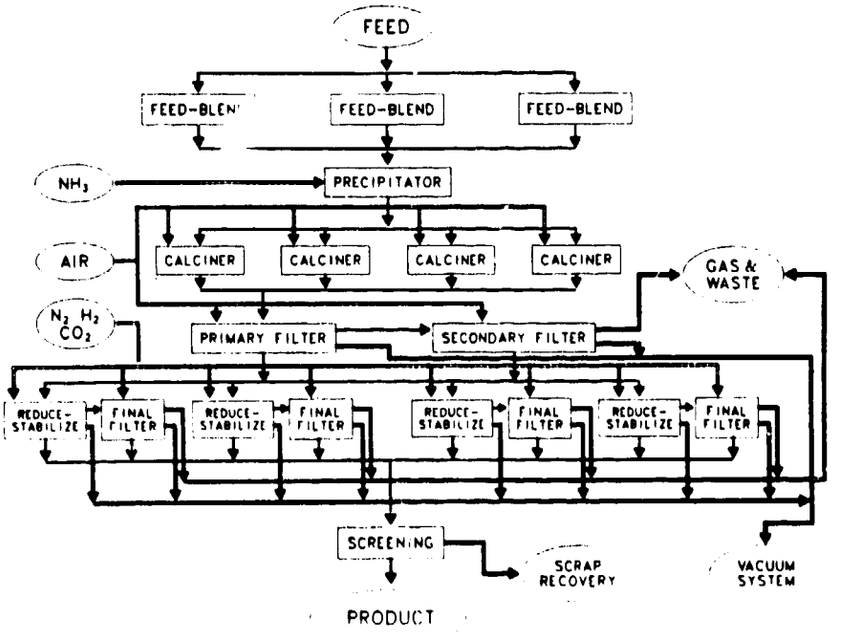

Fig. 2. Original Coprecal block diagram.

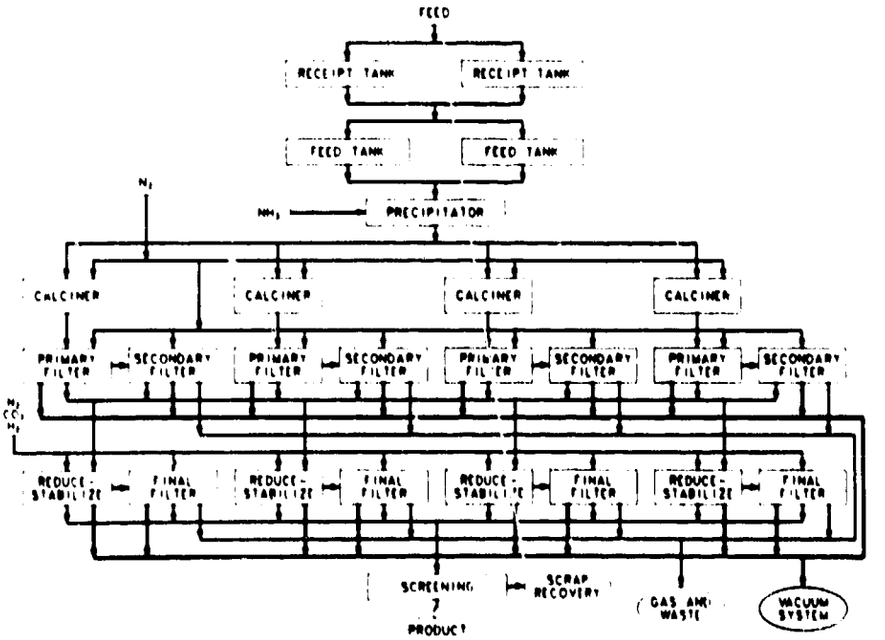

Fig. 3. Modified Coprecal block diagram.

- Increasing the oxide storage capacity from 2-wks to 2-months production.
- Providing for periodic (between daily and weekly) acid flushing of the precipitator.
- Providing for easy replacement of plugged slurry lines and nozzles.

D. Process Comparison

The three processes have many similarities. All three convert nitrate solutions to oxide powders and use precipitation and calcination process steps. They also have the same design-basis throughput and achieve this throughput in three parallel operating lines. However, Oxalate (III) processes plutonium while Coprecal processes uranium-plutonium (10% Pu); to achieve the same plutonium throughput Coprecal processes ten times as much material as does Oxalate (III). Other process differences are described below.

Feed tanks for the processes are compared in Table I. The original Coprecal process line is fed continuously for ~16.5 days from a large tank. The Oxalate (III) and modified Coprecal processes are batch fed from aliquot tanks.

The precipitators in the processes are also operated differently. In the Coprecal processes, a relatively short precipitator residence time is sufficient to produce a finely divided slurry, thus a small precipitator is used (40 L, ~1 kg of plutonium). In the Oxalate (III) process, the precipitator has a relatively large working volume (90 L, ~2 kg of plutonium) to provide a residence time sufficiently long to promote crystal growth.

The calcination systems for each process also differ. In the modified Coprecal process, each of four parallel calciners discharges continuously into a separate filter system. In the original Coprecal process, four parallel calciners in each process line discharge continuously into one large filter. In the Oxalate (III) process, batches are transferred through a single tunnel furnace for each process line.

In all coconversion processes, reduction and stabilization are required after calcination to reduce and stabilize the UO_3 to UO_2. These extra steps significantly increase the residence time of material within the process and the in-process plutonium inventory.

As shown in Table II, the Coprecal processes produce fewer and larger batches per day than the Oxalate (III) process. The Coprecal processes have ~10 times the mass throughput of the Oxalate (III) process for the same plutonium throughput.

The Coprecal processes are generally more complicated and have more process equipment than the Oxalate (III) process (excluding any recycle). Special instrumentation problems are also encountered in Coprecal because of the geometry and size of some process vessels, such as the large calciner primary filters (annulus 7.6-cm thick, 3.5-m o.d., 1.2-m tall), and the high operating temperatures of the calciners and filters.

III. NEAR-REAL-TIME ACCOUNTING

A. Accounting Strategies

In each of the studies, materials accounting strategies were applied independently to each process line. Two accounting strategies were formulated and evaluated for the Oxalate (III) and the modified Coprecal processes. Four accounting strategies were formulated and evaluated for the original Coprecal process. In each accounting strategy, materials balances are formed from periodic measurements of transfers and in-process inventories. The materials balance frequency and the PPAA structure are dictated by process logic. The accounting strategies are as follows.

Oxalate (III) Process:

Strategy 1—each process line from the receipt tanks to the product loadout station is treated as a single PPAA, PPAA 1.

TABLE I

FEED TANK CHARACTERISTICS

	Oxalate III	Original Coprecal	Modified Coprecal
Number of tanks	1 for the entire facility	1 per line	2 per line
Normal working volume (L)	2[illegible]	1[illegible]	1[illegible]
Pu concentration (g/L)	[illegible]	[illegible]	[illegible]
Pu tank content (kg)			
Full	[illegible]	[illegible]	[illegible]
Heel	[illegible]	[illegible]	[illegible]
Feeding time (h)[a]	[illegible]	[illegible]	[illegible]

[a] In the Coprecal processes, a single feed tank feeds each process line. In the Oxalate (III) process, a feed tank sequentially dispenses batches to three parallel lines.

TABLE II

PRODUCT BATCHES

	Oxalate III	Original Coprecal	Modified Coprecal
Batch frequency per line	1 every 1.[illegible] h	1 every 2.[illegible]	1 every 2.[illegible] h
Pu content (kg)	2.0	3.2	3.1
Total mass (kg)	2.1	30.4	35.1

Strategy 2--each process line is divided into two UPAAs. The first UPAA, UPAA 1, is bounded by the receipt tanks and the filter boat loading stations; the second UPAA, UPAA 2, is bounded by the filter boat stations and the product loadout station.

Original Coprecal Process:

Strategy 1--each process line is treated as a single UPAA, UPAA 123.
Strategy 2--each process line is divided into two UPAAs. The first UPAA, UPAA 12, includes the feed receiving and blending, precipitation, and calcination; the second UPAA, UPAA 3, includes reduction/stabilization and screening.

Strategy 3--each process line is divided into two UPAAs. The first UPAA, UPAA 1, includes feed receiving and blending; the second UPAA, UPAA 23, includes precipitation, calcination, reduction/stabilization, and screening.

Strategy 4--each process line is divided into three UPAAs. The first UPAA, UPAA 1, includes feed receiving and blending, the second UPAA, UPAA 2, includes precipitation and calcination, and the third UPAA, UPAA 3, includes reduction/stabilization and screening.

Modified Coprecal Process:

Strategy 1--each process line, from the feed tanks to the screening station is treated as a single UPAA, UPAA 12.

Strategy 2--each process line is treated as two UPAAs in series; the first UPAA, UPAA 1, includes the precipitation and calcination processes and the second UPAA, UPAA 2, includes the reduction/stabilization and screening processes.

B. Measurements

A summary of measurements required for NRTA in the reference processes is given in Table III. Feed transfers in the Oxalate (III) and modified Coprecal processes are measured using the volume and concentration of each feed batch. Feed transfers in the original Coprecal are by flow meter and a single chemical analysis of a sample for each feed-blend tank batch. The NDA product measurements are required to close the materials balances in near-real-time and do not replace the normal weight and chemical analysis of a sample. Therefore, there will be continuous verification of the product measurements. All principal process vessels are instrumented using NDA techniques to determine their in-process inventory. These measurement systems have not been tested and evaluated on the type of materials, geometry, and operating environment that is planned for these processes.

C. Results

Let us first consider NRTA in the original Coprecal process because the large feed-blend tanks presented a materials accounting problem. Each tank contains ~625 kg Pu when full and ~6 kg Pu at its process heel. To find the best loss detection sensitivity that we could possibly achieve for these tanks, we assumed measurement uncertainties of 0.1% (1σ) for volume precision and calibration and 0.2% (1σ) for concentration precision and calibration. Materials balance standard deviations (σ_{MB}) for UPAAs that include the feed-blend tanks are given in Table IV. Results are given for 2-h accounting periods for a full and nearly empty tank. The campaign materials balance spans 16.5 d beginning when the feed-blend tank is full and ending when the heel volume is reached. The materials balance standard deviations are dominated by the uncertainty in determining the tank contents. These large uncertainties degrade materials accounting sensitivity in the process lines. To isolate the feed-blend tanks from the rest of the process line, a flow meter was added to measure the precipitator feed flow. In general, flow meter measurements are poor compared to volume measurements in small, well characterized tanks. The study in Ref. 2 recommended that the large feed-blend tanks be buffered from the process lines by aliquot tanks.

If we assume that the feed-blend tanks are dealt with in some satisfactory manner, then it is useful to compare Oxalate (III) UPAA 1, (whole line) with original Coprecal UPAA 23 or with modified Coprecal UPAA 12 (whole line). To isolate further the effects of process design and operating logic, we largely ignore the effects of processing 10 times as much material in the coprecipitation processes as in the precipitation process (see Table II).

The materials balance standard deviations (at the 2% level) for the three processes are compared in Table V. In comparing the detection sensitivities of the modified and original Coprecal processes:

1) The single-balance detection sensitivity for the modified process is not as good as that of the original process because the in-process inventory in the modified process is larger. The larger inventory results from the addition of a filter system for each calciner.

2) Detection sensitivities for accounting periods greater than 1 day are improved in the modified process because the input transfer measurements are improved by adding aliquot tanks.

In examining the detection sensitivities, we find that the detection sensitivities for Oxalate (III) are significantly better than that of the Coprecal processes for all accounting

TABLE III

NRTA MEASUREMENTS

Measurement Point	Oxalate (III) Precision %(1σ)	Oxalate (III) Calibration %(1σ)	Original Coprecal Precision %(1σ)	Original Coprecal Calibration %(1σ)	Modified Coprecal Precision %(1σ)	Modified Coprecal Calibration %(1σ)
Precipitator feed						
Volume	0.2	0.1	0.1	0.1	0.2	0.1
Flow	-	-	1.5	1	0.5	0.3
Concentration	1	0.3	0.2	0.2	0.5	0.3
Product Cans	1	0.5	1	0.5	1	0.5
Wet Boat	2	5	-	-	-	-
Liquid Recycle						
Volume	0.2	0.1	-	-	-	-
Concentration	1-10	2-0.3	-	-	-	-
Solid Recycle	2	0.5	2	5	2	5
Precipitator Holdup	2	-	10	-	1	-
Vessel Inventory[a]	-	-	10	-	10	-

[a]The vessels are calciners, primary filters, secondary filters, reduction/stabilization filters, and final filters.

TABLE IV

ORIGINAL COPRECAL MATERIALS BALANCE UNCERTAINTIES IN ACCOUNTING STRATEGIES THAT INCLUDE FEED-BLEND TANKS

	Strategies 3 & 4 UPAA 1	Strategy 2 UPAA 1?	Strategy 1 UPAA 1??
In-Process inventory[a]			
Full	0.1	0.1	0.1
Heel	0.9	0.35	0.29
2-3 Accounting period			
Full			
Net transfer	0.05	0.07	0.05
Inventory change	0.0	0.0	0.0
Materials balance	0.0	0.0	0.0
Heel			
Net transfer	0.04	0.07	0.04
Inventory change	0.1	0.35	0.41
Materials balance	0.1	0.36	0.41
Campaign accounting period			
Net transfer	6.2	1.0	0.0
Inventory change	9.1	0.1	0.1
Materials balance	11.0	0.1	0.1

[a]A multiplicative measurement error model is used. Therefore, the absolute error is proportional to the amount of material measured.

TABLE V

DETECTION SENSITIVITY COMPARISON--
OXALATE (III), ORIGINAL COPRECAL, MODIFIED COPRECAL

Detection Time	Oxalate (III)		Original Coprecal		Modified Coprecal	
	Average per Balance (1.3 h) (kg Pu)	Total at Detection (kg Pu)	Average per Balance (? h) (kg Pu)	Total at Detection (kg Pu)	Average per Balance (4 h) (kg Pu)	Total at Detection (kg Pu)
1 balance	0.4	0.4	1.2	1.2	1.4	1.4
1 day	0.02	0.5	0.13	1.6	0.27	1.6
1 week	0.01	1.7	0.04	3.7	0.07	3.0
1 month	0.007	3.9	0.03	8.4	0.04	6.1

periods. There are two reasons for this: (1) the in-process inventory in the Oxalate (III) process is smaller; and (2) scrap generated in the Oxalate (III) process is better characterized (Coprecal scrap contains fragments from the fluidized bed of the calciners) and is much less than that generated by the Coprecal processes; scrap measurements contribute significantly to the materials balance uncertainty.

IV. CONCLUSIONS

The comparisons given in this paper should not be taken as an indictment of the basic Coprecal process or of coconversion in general. The less detection sensitivities calculated in this study are attributed to the particular process configuration and operating sequence chosen. The following conclusions may be drawn from this comparison.

- Generally, batch operation may facilitate the application of timely materials measurements and accountability.
- Materials transfers based on volume measurements may be of higher quality than those based on flow measurements.
- Large inventories within process lines should be avoided because large absolute uncertainties in measuring these inventories will degrade the process line materials accounting sensitivity.
- Methods of decreasing the amount of scrap that is generated should be investigated.
- The effect on loss detection sensitivity in processing 10 times the mass for the same plutonium throughput should be investigated.

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