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CLEANUP OF PLUTONIUM OXIDE REDUCTION BLACK SALTS

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R. E. Giebel and R. O. Wing

ABSTRACT

This work describes pyrochemical processes employed to convert direct oxide reduction (DOR) black salts into discardable white salt and plutonium metal. The laboratory work was performed in September 1981 and March and April 1982 in Chemistry Research and Development pyrochemistry facilities at the Rocky Flats Plant.

The DOR process utilizes calcium metal as the reductant in a molten calcium chloride solvent salt to convert plutonium oxide to plutonium metal. An insoluble plutonium-rich dispersion called black salt sometimes forms between the metal phase and the salt phase.

Black salts accumulated for processing were treated by one of two methods. One method utilized a scrub alloy of 70 wt % magnesium/30 wt % zinc. The other method utilized a pool of plutonium metal to agglomerate the metal phase. The two processes were similar in that calcium metal reductant and calcium chloride solvent salt were used in both cases.

Four runs were performed by each method, and each method produced greater than 93% conversion of the black salt.

INTRODUCTION

Between 1980 and 1982, development work was performed on DOR at Rocky Flats. Calcium metal reagent was used to reduce plutonium oxide to plutonium metal in a molten calcium chloride solvent salt. At times, a salt-insoluble dispersion, rich in plutonium, formed as part of the product. This dispersion, referred to as "black salt," collected between the metal phase and the salt phase. Impurities in the feed, moisture in the salts, improper stirring, or insufficient solvent salt may have contributed to the black salt formation. Black salt is a general term used to denote a dark or black-colored product salt, which usually has the following characteristics:

- Plutonium content greater than the economic discard limit
- Higher concentrations of calcium oxide than white salts
- Higher temperatures of fusion than those of white salt
- Higher density than white salt

No attempt was made as a part of this work to further characterize black salt.

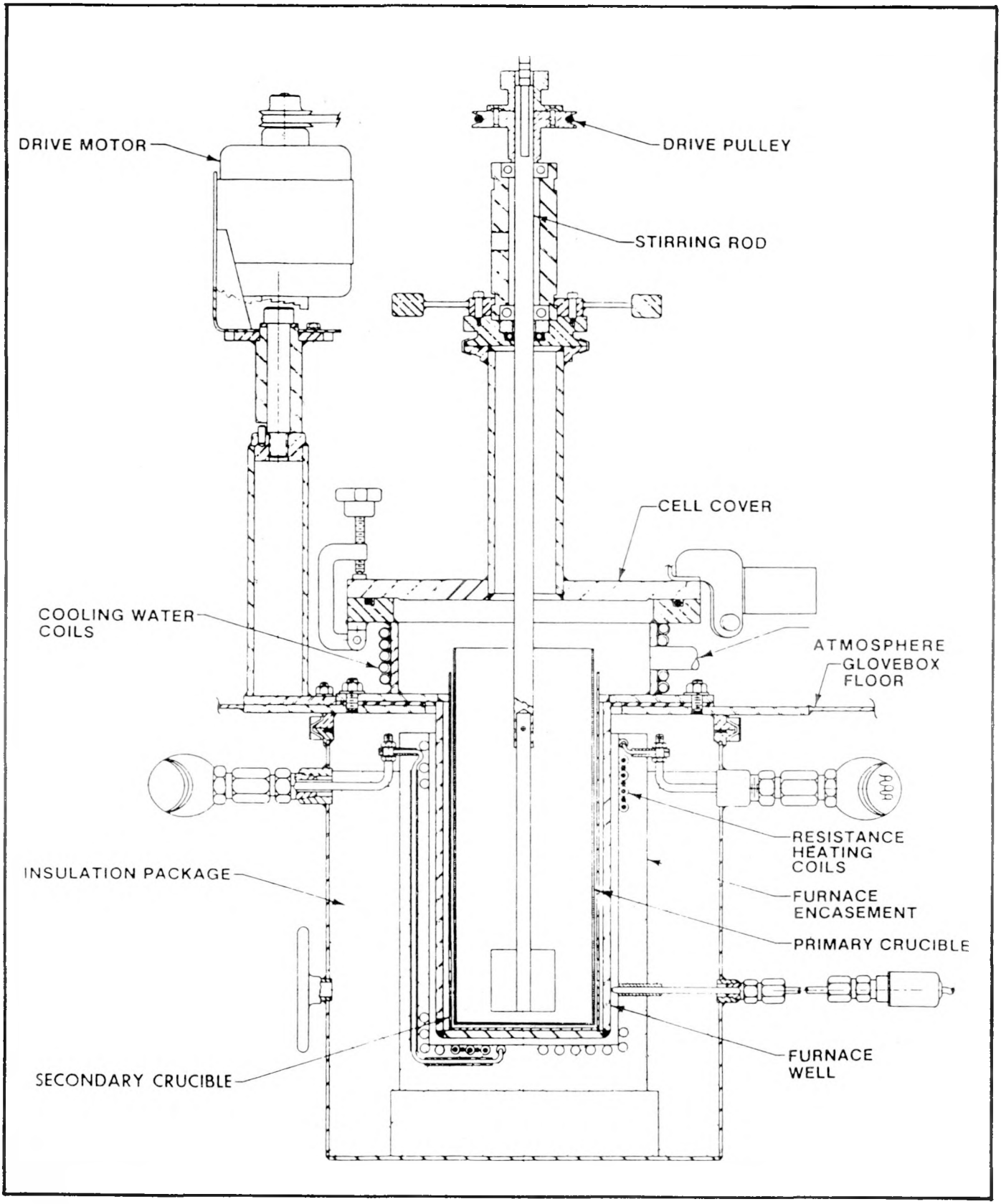
This report describes efforts to process black salt pyrochemically. The ideal product of processing is discardable white salt and a metal button. The black salt for this effort originated from DOR experiments performed both in stationary furnaces and a tilt-pour furnace. Without pyrochemical processing, the black salt would have been stored for eventual treatment by aqueous methods.

EXPERIMENTAL

Equipment

The equipment for this project was a resistance-heated stationary furnace equipped with a tantalum stirrer (Figure 1). For the first four runs, a flat-bladed stirrer provided washing-machine-type agitation. For the second four runs, a stirrer with two sets of opposing impellors operated in a single direction. High-density magnesium oxide (MgO) crucibles manfactured by either Honeywell or Norton served as the primary containers. This was the same type equipment used for DOR experiments.

FIGURE 1. Molten Salt Furnace

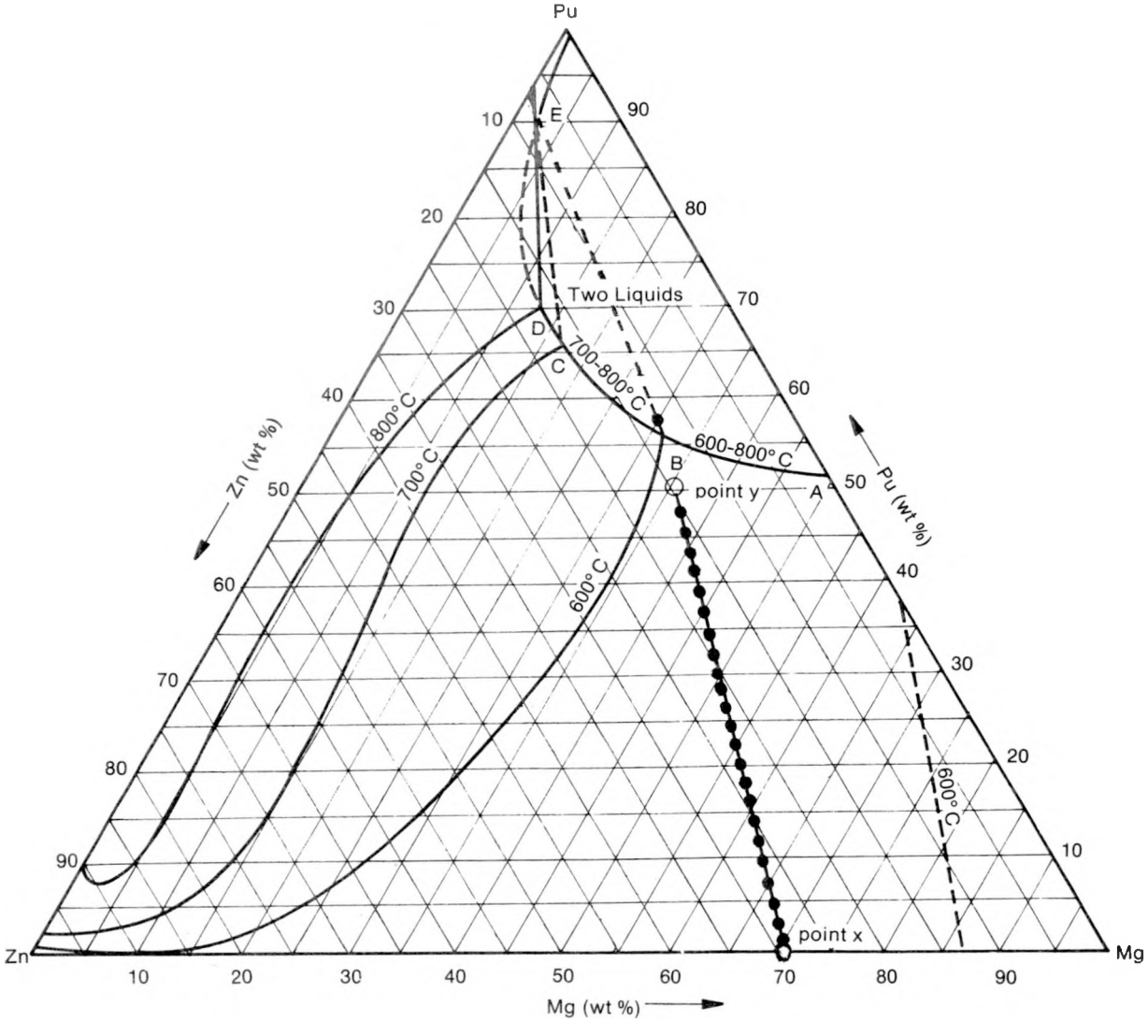


Reagents

As cleanup reagents for the first four runs, we used calcium metal, calcium chloride salt, and a scrub alloy of 70 wt % magnesium and 30 wt % zinc. This alloy composition is shown as Point x of the magnesium-zinc-plutonium ternary phase diagram (Figure 2). As plutonium is loaded into the alloy, the composition moves up line x-y toward Point y. The diagram suggests the alloy can contain more than 50% plutonium before solids form. The first black salt to be processed contained sufficient plutonium to load the alloy to about 50%, so we chose not to reuse that alloy in another run. A new magnesium-zinc alloy charge was used for the second run, and the metal product was recycled to the third and fourth runs to increase the plutonium content of the alloy.

For the last four runs, magnesium and zinc were excluded to obtain a more concentrated plutonium metal product for processing. To compensate for the lack of a scrub alloy, plutonium metal added to the last four runs provided a pool of metal into which reduced metal droplets could agglomerate. For this purpose, we added impure metal pieces and metal fines accumulated during DOR development work. We did not, however, evaluate black salt cleanup without a plutonium metal pool. The need for, or comparative effectiveness of, the plutonium metal pool was therefore not established.

FIGURE 2. Magnesium-Zinc-Plutonium Ternary Phase Diagram



After each run, a vise and hammer were used to break the plutonium/alloy product button into two pieces for recycle into the next cleanup run. The button increased in mass as more plutonium accumulated from the cleanup reductions.

Operations

The procedure for loading the magnesium oxide crucibles is listed below:

1. Place magnesium-zinc or plutonium metal in the bottom of the MgO crucible.
2. Add calcium metal and the black salt to be processed.
3. Place a cake of dried, fused calcium chloride salt on top of the load.

Often, the salt cake overfilled the crucible; but when the contents melted, the cake settled into the crucible.

The operating cycle began by heating the crucible 200 to 250 ° C per hour. A vacuum pump removed any water vapor, until the temperature reached 500 °C. At 500 °C, the pump was turned off and the furnace was backfilled with argon. When the contents of the crucible melted, a stirrer was lowered and the contents were agitated for 20 minutes at 650 to 700 rpm at a temperature ranging from 875 to 930 °C. For the last three runs, following this 20-minute cycle, we attempted to mix the salt-metal interface by raising the stirrer in 1/4- to 1/2-in. increments, stirring rapidly and then slowly. This may have helped break up salt-metal dispersions and to remove metal from the blades. After incrementally raising the stirrer about 1 1/2 in., we lifted it from the melt and allowed the furnace to cool.

The cooled ceramic crucible was removed from the tantalum backup crucible, the ceramic was broken away, and the white salt, black salt, and metal button were separated from each other. Then, each product was weighed. Any black salt in the product was recycled into the next run as black salt feed.

RESULTS AND DISCUSSION

The objectives of this effort--to convert black salt into discardable white salt, to recover plutonium in a concentrated metal phase, and to avoid expensive aqueous processing--were generally met. Recalling that any black salt residues in the products were always recycled to the next run, 325 g of black salt heel from the last (eighth) run remained for either pyrochemical or aqueous processing.

Table 1 summarizes the feed and product data for the first four runs in which magnesium-zinc scrub

TABLE 1. DOR Salt Cleanup, Four Runs in Stationary Furnaces (Includes Recycle)

	Feed						Product		
				Alloy Metal					
Run No.	Black Salt (g)	$CaCl_2$ Salt (g)	Ca Metal (g)	Mg (g)	Zn (g)	Recycle (g)	Alloy Metal (g)	White Salt (g)	Black Salt (g)
1	1575	500	52	71	30	–	362[a]	1855	–
2	1514	493	16[b]	112	51	–	184[c]	1567	365[c]
3	2004[d]	409	9[b]	–	–	184	224[c]	2298	64[c]
4	1548[d]	492	58[b]	–	–	224	306	1541	421[e]
Total	6641[d]	1894	135	183	81	–	668	7261	–

a. This alloy contained about 50% plutonium; it was not reused or recycled.
b. This was not reagent calcium, but was low-density, floating metal spheres recovered from discardable DOR white salt.
c. Recycled to the next cleanup run.
d. Includes recycle of black salt heels from the previous run (429 g total).
e. Recycled as part of feed to Run 5.

alloys were used. These runs processed 6212 g of feed black salt and 429 g of recycle from which 5232 g of discardable white salt was formed.*

Table 2 summarizes the feeds, and Table 3 summarizes the product data for the second four runs. During the runs (in which no magnesium or zinc was added), most of the black salt was converted to white salt and a metal product. From 5035 g of black salt processed, 4043 g of white salt was formed. Plutonium metal fines and pieces, which were added for consolidation and to provide a pool of metal, weighed 1112 g. The plutonium metal pool gained 406 g.

Plutonium content of the feed and product materials from all eight runs is shown in Table 4. Figures 3 and 4 summarize the data from the tables. The two magnesium-zinc alloys, which gained a total of 404 g, contained 188 and 120 g plutonium, respectively (total, 308 g). The plutonium button from Run 8 weighed 1519 g and contained 1308 g plutonium. Emission spectroscopy analyses of two samples taken from the button show major impurities (in parts per million) to be: iron—1500, nickel—360, carbon—1200, calcium—2500, and magnesium—2000.

*To estimate the quantity of white salt that formed from the black salt, subtract the quantity of new calcium chloride salt (1894 g) plus calcium metal (135 g) added to the runs from the amount of white salt recovered in the product (7261 g).

TABLE 2. DOR Salt Cleanup, Feed (Second Four Runs)

	Feed								
	Pu Metal		$CaCl_2$	Ca	Black Salt		MgO		
Run No.	New (g)	Recycle (g)	Salt (g)	Metal (g)	New (g)	Recycle (g)	Crucible (g)	Stir Rod (g)	Total
5	889	–	502	92[a]	1767	–	856	612	4718
6	223	1086	501	31	1087	552[b]	755	627	4862
7	–	1426	443	31	2181	42	752	583	5458
8	–	1358	502	25	–	1022	764	576	4247
Total	1112	–	1948	179	5035	–	–	–	19,285

a. Light metal spheres recovered from previous runs (assumed to be calcium).
b. 77 g of black salt from Run 5 breakout was diverted to a special project.

TABLE 3. DOR Salt Cleanup, Product (Second Four Runs)

	Products						Material Balance				
Run No.	Pu Button (g)	White Salt (g)	Black Salt (g)	MgO Crucible (g)	Stir Rod (g)	Total	Δ Pu Metal (g)	Δ[a] White Salt (g)	Δ Black Salt (g)	Δ Stirrer (g)	Δ Crucible (g)
5	1090	1471	629	878	627	4695	+201	+ 877	-1138	+15	+22
6	1426	1998	42	818	583	4867	+117	+1466	-1597	-44	+63
7	1353	1695	1022	805	576	5451	- 73	+1221	-1201	- 7	+53
8	1519	1006	359[b]	780	579	4243	+161	+ 479	- 663[b]	+ 3	+16
Total	–	6170	–	–	–	19,256	+406	+4043	-4599	-33	+154

Total Δ = -29

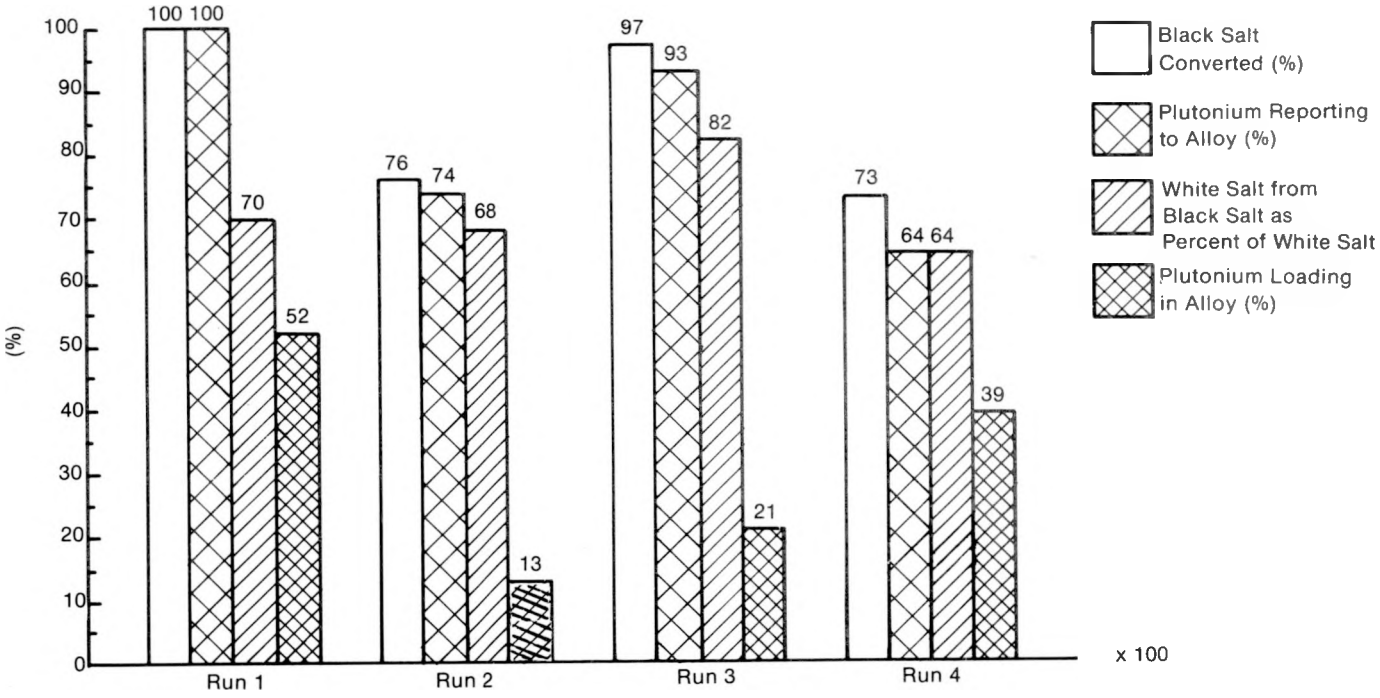
a. Grams of white salt in the product minus the sum of grams $CaCl_2$ salt plus grams calcium metal in the feed.
b. 34 g of calcium (as spheres) were removed from the top of the white salt and combined with 325 g of black salt.

TABLE 4. Plutonium Content of Feed and Products

Run No.	Feed				Product				
	Black Salt (g)	Mg-Zn Alloy (g)	Pu Metal (g)	Stirrer (g)	Black Salt (g)	White Salt (g)	Mg-Zn Alloy (g)	Pu Metal (g)	Stirrer and MgO (g)
1	162	0	–	32	0	a	188[b]	–	6
2	27	0	–	6	7	0	23	–	3
3	28	23	–	3	2	0	48	–	4
4	118	48	–	4	42	0	120[b]	–	8
5	168	–	852	92	46	5	–	965	96
6	92	–	215 + 961[c]	95	4	6	–	1276	77
7	105	–	1276[c]	76	102	10	–	1275	70
8	102	–	1275[c]	69	9	9	–	1308	68

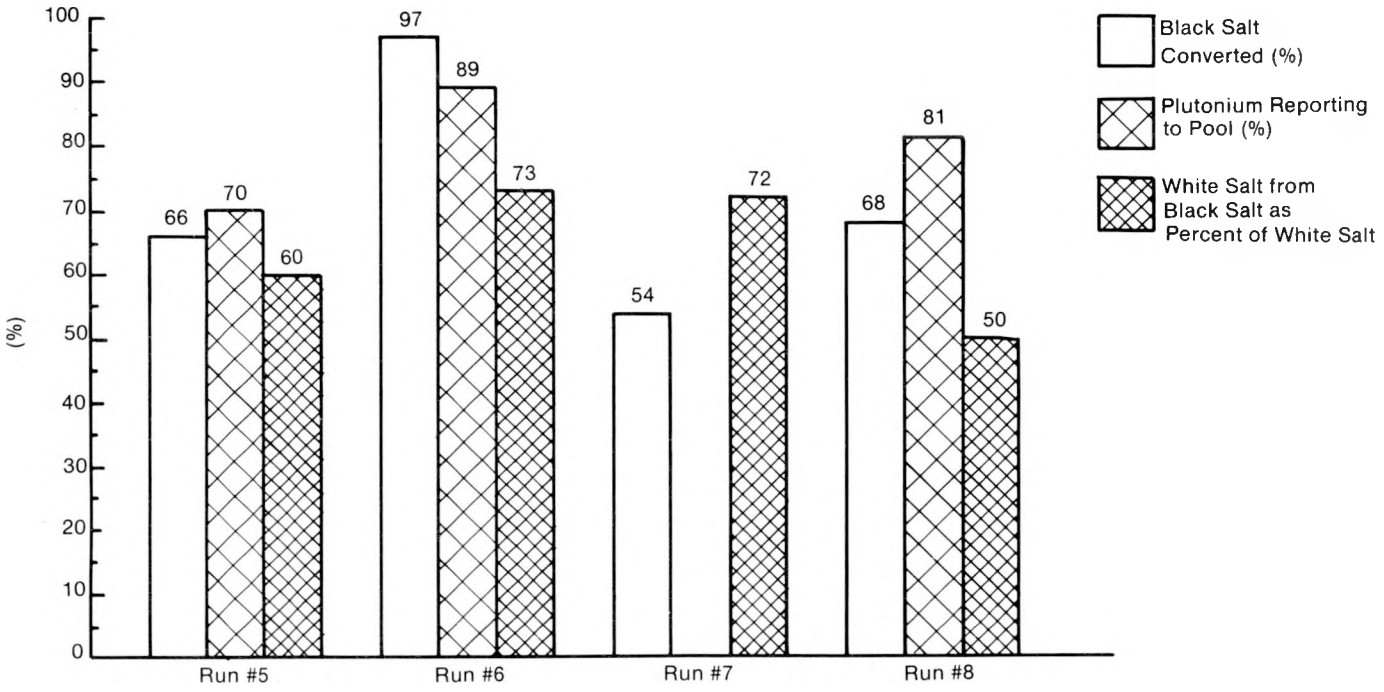
a. Not determined
b. Not reused
c. Recycle

FIGURE 3. Method I, Magnesium-Zinc Scrub Alloy



$$\text{Black Salt Converted (\%)} = \frac{\text{Black Salt in Feed - Black Salt in Breakout}}{\text{Black Salt in Feed}}$$

$$\text{White Salt from Black Salt as Percent of White Salt} = \frac{\text{White Salt - } (CaCl_2 + Ca)}{\text{White Salt}} \times 100$$



$$\text{Black Salt Converted (\%)} = \frac{\text{Black Salt in Feed - Black Salt in Breakout}}{\text{Black Salt in Feed}} \times 100$$

$$\text{White Salt from Black Salt as Percent of White Salt} = \frac{\text{White Salt - } (CaCl_2 + Ca)}{\text{White Salt}} \times 100$$

FIGURE 4. Method II, Plutonium Metal Pool

A mass material balance was performed during the last four runs. A portion of Table 3 (material balance) shows the changes in mass between feeds and products. A gain in the tantalum backup crucible (not shown in the table) was 8 g. The total mass unaccounted for was 21 g [19,285 – (19,256 + 8) = 21 g]. Collections on the interior of the furnace after each run were removed using a brush and a vacuum cleaner. These cleanings could not be weighed.

The last run was stirred at a temperature of 875 to 890 °C. However, the product button showed the imprint of the bottom stir blade (Figure 5). This demonstrates that the metal phase was not completely molten, an indication of the presence of

FIGURE 5. Metal Button Showing Imprint of Stir Blade

impurities. It also suggests the need for a higher operating temperature.

The cleanup of DOR black salt with calcium metal, a pool of plutonium metal, and dry calcium chloride salt seems effective; but the resulting discardable white salt contained more plutonium than when the magnesium/zinc scrub alloy was used. This suggests that using the scrub alloy may be more effective for recovering plutonium from black salt than using a pool of plutonium.

Calcium metal reductant used in all cleanup runs provided insurance in case oxides and other reducible species were present. Since no runs were made without calcium, its necessity in the runs was not shown. A portion of the calcium dissolves in the calcium chloride salt because calcium metal has a significant solubility in calcium chloride.[1] Possibly, calcium also dissolves in the impure metal phase, although it has a very low solubility in pure plutonium. Light metal spheres, assumed to be undissolved calcium, were observed above the salt phase during breakout of three of the eight runs.

The ceramic crucibles of Norton manufacture, which were evaluated during the last four runs, performed satisfactorily. They were larger in diameter than the Honeywell crucibles used previously and were a snug fit in the tantalum backup crucible.

Black salt formed in a DOR run might be recycled to a subsequent DOR run. This procedure is practiced by the Los Alamos National Laboratory.[2] Black salt recycle could be evaluated at Rocky Flats during future DOR processing efforts.

RECOMMENDATIONS

Based upon the results of these eight runs, accumulated black salts from DOR runs can be processed using calcium metal, calcium chloride salt, and either a magnesium-zinc scrub alloy or a pool of plutonium metal. Temperature during stirring might be increased from 875 to about 950 °C inside the melt to ensure complete melting. If significant black salt residue remains after black salt processing, increasing the ratio of dry calcium chloride salt to black salt processed and increasing the quantity of calcium metal might be evaluated. We might recycle black salt to the next DOR run at the risk of jeopardizing the run. To decrease risk, the ratio of calcium chloride salt to feed oxide might be increased for DOR runs in which black salt is recycled. For best results, black salts that are to be processed pyrochemically should be accumulated free of extraneous materials (such as floor sweepings) and stored in a manner that excludes moisture.

In the future, there may be interest in pyrochemically processing black salts generated from DOR. It is recommended that investigators (1) have control and/or knowledge of the conditions under which the black salt was formed, collected, and stored, (2) attempt to characterize or define the components of black salt, and (3) choose a method of processing compatible with the disposition capabilities for the plutonium metal or alloy recovered.

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