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**PRODUCTION-SCALE DIRECT
OXIDE REDUCTION DEMONSTRATION**

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Rockwell International

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OXIDE REDUCTION DEMONSTRATION

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P. O. BOX 464
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PRODUCTION-SCALE DIRECT OXIDE REDUCTION DEMONSTRATION

T. J. Humiston, D. J. Santi, and J. L. Long

ABSTRACT

A detailed, statistically valid, examination of the direct oxide reduction parameters affecting process yield and purity was planned and executed. Guidelines for attaining yields approaching 100% are presented. Feed oxide, percent excess calcium, and stirrer design affected yield and product purity. Experiments were performed in production-scale equipment utilizing 800 grams of plutonium dioxide per charge.

INTRODUCTION

Pyrochemical Operations at Rocky Flats has performed Direct Oxide Reduction (DOR) routinely since 1982 when the technology was transferred from Los Alamos National Laboratory. The process reduces foundry-generated plutonium dioxide waste to an electrorefinable product. It performs well when using $\geq 85\%$ plutonium oxide as feed. Overall average yield is 97%. DOR is not a purification process; any impurities in the plutonium oxide, calcium chloride, and (to some extent) the reaction vessel contaminate the metal product.

DOR is a batch process that reduces non-pyrophoric plutonium dioxide to metal using calcium metal as the reducing agent in a molten calcium chloride salt flux. The fundamental chemical reaction is:

The calcium oxide product readily dissolves into the salt to a maximum of 17 mole %. The reaction is spontaneous (free energy of formation equal to -47 kcal/mole PuO_2) and is probably controlled by the rate at which the calcium metal and plutonium dioxide are contacted. After the reaction

and completion of stirring, the reaction products separate into distinct phases according to their relative specific gravities.

Although DOR has been a production process for several years, little effort has been expended to obtain pure metal from purified plutonium oxide. Because DOR will be used as a primary pyrochemical metal producing process, the Plutonium Recovery Project (PRP) requires detailed process design information. The DOR Demonstration was initiated to provide this information. Phase I provided information about the operating conditions, product yields, and product quality of the DOR process using purified plutonium dioxide. Phase I showed that metal produced by DOR requires electrorefining before being usable by the foundry. It also identified areas that could be improved, ultimately reducing the fraction of DOR product metal requiring electrorefining.

Phase II was initiated to:

1. Determine the fraction of DOR product metal that requires electrorefining prior to foundry use for blending.
2. Locate and verify a commercial source of acceptable reagent salt.
3. Define the DOR operating parameters that affect product metal yield and quality from purified plutonium dioxide.

Development work consisted of: Small-Scale Salt Examination (Phase IIA), Small-Scale Parameter Study (Phase IIB), and Production-Scale Parameter Verification (Phase IIC). This report describes Phase IIC.

The experimental plan for phase IIC was based upon the recommendations included in the report on the small-scale investigation of DOR.¹ Seven recommendations resulted:

1. Use fused (cast cakes) calcium chloride salt because it increases yield and reduces moisture absorption.
2. Use 4:1 salt-to-oxide ratio to reduce the salt waste generation without sacrificing yield.
3. Use 10% and 20% excess calcium because 25% excess calcium worked well in Phases IIA and IIB.
4. Use the historical positioning of loading the calcium above the oxide.
5. Further study the stirring speed and stirrer design because it had a significant effect on yield.
6. Consider hold time after reaction as a variable because of the scale dependency potential.
7. Consider "stirring in" versus "stirring out" of the metal because stirring in produced magnesium inclusions in the metal product and increased calcium in the button.

The variables to be investigated were selected from the small-scale studies on the basis of product yield, purity, and possible scale effects.

EXPERIMENTAL PROCEDURE

Six parameters were selected for further study in Phase IIC.

1. Feed plutonium dioxide
2. Percent excess calcium
3. Stirrer design
4. Stirrer speed
5. Stirrer position
6. Hold time after stirring.

Variable and constant parameters are given in Table 1.

TABLE 1. Phase IIC Parameters

Variable Parameters Studied				Constant Parameters	
Plutonium dioxide feed source	Process Simulation Laboratory (PSL), producing <i>batch</i> peroxide precipitated oxide			Recalcination temperature	1000 °C
	Line 16, producing <i>continuous</i> peroxide precipitated oxide			Recalcination time	6 hours
Excess calcium percentage	10%	Plutonium dioxide particle size			As received
	20%				
Stirrer design	Paddle	Salt-to-Oxide ratio			4:1
	Impeller				
Stirrer Program	10 min	5 min	5 min	Melt temperature of initial stirring	780 - 800 °C
	←-----rpm-----→				
	(slow) 100	300	600		
	(fast) 300	450	600		
Stirrer position	In the metal				
	Out of metal				
Hold time after stirring	15 min				
	60 min				

Feed type was included as a variable because of potential oxide supply problems and need for more information about the two types of oxide. The two types of plutonium dioxide of interest at Rocky Flats are from continuous peroxide precipitated oxide utilized in the current production process (Line 16) and batch peroxide precipitated oxide from the Process Simulation Laboratory (PSL).

An experimental matrix was developed to analyze the six variables. It was a Resolution Five fractional factorial experimental matrix of 32 runs to estimate the effect of the variables on process variation as well as the mean. Process variation is the "spread" or scatter in the data around the mean value. A Resolution Five plan does not confound (cause to be inseparable) main effects and two-way interactions, but does confound two-way interactions with three-way interactions.

The plan was then randomized to eliminate potential for confounding the variable effects with

the processing order. For example, when one operator performs experiments and another completes the tests, are the differences in results caused by variations of the experiment or handling by the operators? Randomization greatly reduces potential effects of outside factors.

Salt Preparation and Handling

Because the small-scale investigation¹ determined that Fisher anhydrous (C-77) calcium chloride salt had fewer impurities and less water content than other salt supplies, it was used for Phase IIC. The salt was dried in a convection oven at 225 °C, cast into salt cakes, and stored in a vacuum drying oven at 225 °C. One cake for each run was cast with a large center cavity and the other was cast as a solid cake. The combined weight of a two-cake charge was approximately 3200 grams. The cake with the cavity was loaded with calcium metal, providing distinct separation between the calcium and plutonium dioxide. See Figure 1. Before

FIGURE 1. Calcium Chloride Salt Cakes and Calcium Metal Granules 36806-17

loading a DOR charge, the cakes were taken from the drying oven and placed into a desiccator to cool, then weighed, bagged, and sealed under positive-pressure argon.

Calcium Metal Handling

The calcium metal supply was kept in a sealed pressure vessel at approximately 20-30 psig argon to prevent reaction with moisture. Two levels of calcium excess (10 and 20% by stoichiometry) were used in the DOR experiments. Calcium granules are shown in Figure 1.

Crucible Treatment

High-density magnesium oxide crucibles are used as the primary reaction chamber for DOR. The crucibles (Figure 2) were approximately 12 inches high by 5 3/16 inches inner diameter with a 3-3/4-inch spherical radius bottom; they were stored in a vacuum drying oven. Before use, the crucibles were baked at 225 °C (at least 24 hours,

usually seven or more days), placed in a desiccator to cool, and then bagged in positive-pressure argon.

Plutonium Dioxide Preparation and Handling

The plutonium dioxide was produced via peroxide precipitation. Precipitation occurs when hydrogen peroxide solution is added to concentrated plutonium nitrate solution, producing solid plutonium peroxide. To enhance filtration by enlarging particle size, a sulfate solution is added with the peroxide. The peroxide precipitation acts as a purification process because the peroxide selectively precipitates plutonium while the impurities are washed through with the filtrate. However, if the wash (with nitrate solution) at the end of filtration is incomplete, some impurities stay with the peroxide compound. Any impurities not removed in calcination remain in the DOR product metal. After filtration, the plutonium peroxide was calcined at 450 °C, producing plutonium dioxide containing varying amounts of sulfates, nitrates, water, and carbon.

FIGURE 2. Crucible and Back-up Can Assembly

36806-01

The oxides were calcined again at 1000 °C. After recalcination, the oxide was sent for calorimetry. Then, it was heated to 210 °C in the same calcination furnace, weighed, and stored in a 16-ounce wide-mouth glass jar with a vinylite lined screw cap.

Calcination

A second, high-temperature, calcination step is required to remove carbon, remaining sulfates, nitrates, water, and other impurities after calcinations at 450 °C. The plutonium dioxide was recalcined at 1000 °C for six hours in an air atmosphere and stirred at least hourly. Recalcination was performed in a Fisher Isotemp Ashing furnace Model 495 equipped with microprocessor control (Figure 3). Air is preheated and exchanged through the chamber three times per minute, producing high-temperature uniformity and extra air for good reaction kinetics. The chamber is made of molded alumino silicate ceramic with low thermal mass and self-insulating chamber walls for fast heatups and cooldowns. Because of their

construction, the chamber walls have less potential for partial disintegration, thus eliminating aluminum-silicon addition to the plutonium oxide during calcination.

In Phase I, an Inconel boat held the oxide; and iron, nickel, and chromium were introduced during the recalcination process. The plutonium dioxide corroded the boats to the extent that the Inconel flaked into the oxide. Results from previous studies indicated that platinum remains inert to the plutonium dioxide and its contaminants at high temperatures. A platinum recalcination vessel (boat) along with platinum coated tongs for stirring (Figure 3) were used for recalcination in Phase IIC.

Direct Oxide Reduction Equipment

The DOR experiments were performed in stationary furnaces (cells) with 5-3/4-inch inner diameter Inconel wells as the reaction chambers. The outer furnace cans containing the heating coils included a water-cooled copper heat sink in case of reagent

FIGURE 3. Fisher Calcination Muffle Furnace

36806-18

leakage from the Inconel well. See Figure 4. The outer furnace can is vented to the glovebox. Thus, in the event of inner can failure, pressure would be relieved into the glovebox.

The cells were equipped with typical Rocky Flats DOR cell heads and stirring apparatus. The cell heads seal the inner reaction chamber from the glovebox atmosphere (flow-through nitrogen system) by an O-ring machined into the furnace top flange. Figure 5 shows a cell head in the loaded configuration (DOR charge in the furnace) before the reagents have melted. Notice the optical encoder on the motor pulley. Encoders register the revolutions per minute of the stirrers. They are slipped over the top of the steel stirrer shafts like a bearing after the salt becomes molten and the

stirrers are lowered. The electronics that drive the motor and receive the encoder signals provide precise speed and time control for this step-type stirring program. Speed is actuated through the stirrer by an O-ring used as a belt coupled with pulleys on the motor and stirrer shaft.

The tantalum stirrers are screwed into 3/4-inch stainless steel shafts. The steel shaft penetrates the cell head through an oil seal contained within a bearing retainer flange. Two types of stirrers were used: Flat paddle and opposing-pitch impeller. The paddles are approximately 3 3/4 inches at the widest point. The 2-inch-diameter impeller stirrers are 12 to 13 inches long. Figure 6 shows both types.

FIGURE 4. Lower Half of Stationary Furnace

36806-14

FIGURE 5. DOR Cell Head

36806-11

Impeller Type

Paddle Type

36806-03

FIGURE 6. Stirrers

Direct Oxide Reduction

Prior to each experiment, the equipment was cleaned and checked. The tantalum stirrers were leached after each run in 1N HCl to remove holdup material and salt residue.

Figure 2 shows the crucible and back-up cans before assembly.

The back-up can assembly containing the crucible was moved to the stationary cell area along with the plutonium dioxide and reagents. The assembly without reagents was placed in the cell, and the stirrer was lowered and positioned to the proper height, less than 1/4 inch from the bottom for an "in-the-metal" run; for an "out-of-metal" run, the flat paddle was positioned 3/4 inch from the bottom. The reagents were kept in bags under argon pressure in the glove line before being loaded.

First, the plutonium dioxide was poured slowly (to minimize dusting) from a water-tight jar into the crucible. A salt cake (with cavity) was carefully lowered onto the oxide, and calcium metal was dropped into the cake cavity. A solid salt cake was then placed on the calcium/salt cake. The entire can assembly with reagents was lowered into the stationary furnace and the cell head was sealed to the furnace. The chamber was evacuated to approximately two millibar and backfilled with argon to approximately 1100 millibar three times before heating.

A conservative heating program was used to avoid crucible failure during heatup.

Approximately 45 minutes after the furnace coil reached 1000 °C, the salt became molten, the stirrer and thermocouple were lowered, and one of the two stirring programs was initiated.

After stirring and proper hold time, the furnace was cooled at a controlled rate of 200 °C per hour to 600 °C outside temperature (inside temperature = 700 °C).

After cooling to a safe temperature, the contents were sent to the breakout area where the backup cans were separated from the crucible and set aside. To aid breakout, the stainless steel backup cans were made with a three- to five-degree taper.

When a ceramic crucible broke during a run, the entire charge was tipped upside down and slammed against the glovebox floor. The taper in the backup can along with the steel crucible support weighing more than two kg helped force the contents from the can.

The crucible was broken from the charge, leaving the salt and plutonium button. The button normally rested on the salt's bottom surface. Any

salt or other residues were either brushed or hammered from the button.

The button was sampled three times. The first was a 10- to 15-gram drill sample from the top surface. The second was from the bottom. The last sample was pie shaped, weighing 5 to 35 grams. It was hack sawed from the edge and used for metallography data. Photomicrographs were taken at the top, middle, and bottom of the latter sample. After sampling, the button and salt samples were sent for non-destructive assay.

RESULTS AND DISCUSSION

General breakouts of the Phase IIC experiments were simple. The crucibles rarely failed unless the cool-down rate exceeded 200 °C per hour. See the Crucible Failure section of this report. Figure 7 depicts a typical DOR charge after reaction; it is shown in the inverted position with the bottom of the crucible broken away. Notice the distinct phases of salt and button. The top surface is shown in Figure 8. The impressions left by the salt are clearly visible.

Yield

Yield was calculated by multiplying the product button's weight by its purity (determined by

FIGURE 7. DOR Charge After Experiment

36805-5

FIGURE 8. DOR Product Button Top Surface

36805-14

calorimetry) and then dividing by the oxide feed weight and purity. A linear least squares regression analysis was performed. Plutonium oxide type, percent excess calcium, and stirrer design were shown to affect the yield. Other variables and their interactions did not influence yield at the 95% confidence level.

Overall, the yield for the entire set of experiments averaged 86.1%. Table 2 shows the variables used in each experiment and corresponding yields. The three variables that affected yield at the 95% confidence level are:

1. Line 16 (continuously precipitated) oxide performed better than PSL (batch precipitated) oxide.
2. 20% excess calcium demonstrated higher yields than 10% excess calcium.
3. The paddle stirrer achieved higher yields than the impeller stirrer.

A statistical least squares analysis is provided in Table 3. For the main effects, if the overall average yield of 86.1% is subtracted from the

TABLE 2. Phase IIC Parameters and Yield Results

DOR EXP.	Oxide Type*	Hold Time (min)	Stirrer Design	Stirrer Position	Stirring Program	Excess Ca (%)	Button (g)	Button Purity (%)	Oxide (g)	Oxide Purity (%)	Yield** (%)
1	PSL	60	PAD	Out	Slow	20.00	685.00	0.9955	799.40	0.8847	96.42
2	L16	60	IMP	In	Fast	10.00	674.20	0.9988	800.00	0.8720	96.53
3	PSL	60	IMP	In	Slow	20.00	525.90	0.9820	800.00	0.8758	73.71
5	PSL	15	PAD	Out	Fast	20.00	700.00	0.9810	800.00	0.8821	97.31
6	PSL	15	PAD	In	Slow	20.00	609.00	0.9847	800.00	0.8837	84.83
7	PSL	60	PAD	In	Fast	20.00	690.80	0.9943	800.00	0.8818	97.37
8	L16	60	IMP	Out	Slow	10.00	596.50	0.9859	800.00	0.8775	83.77
9	PSL	15	IMP	In	Fast	20.00	630.80	0.9680	800.10	0.8773	86.99
10	PSL	15	PAD	Out	Slow	10.00	674.80	0.9961	800.00	0.8848	94.96
11	PSL	15	PAD	In	Fast	10.00	614.40	0.9135	800.00	0.8830	79.45
13	L16	60	IMP	Out	Fast	20.00	536.40	0.9751	800.00	0.8788	74.40
14	L16	15	IMP	In	Fast	20.00	723.10	0.9946	800.00	0.8825	99.90
15	L16	60	IMP	In	Slow	20.00	654.70	0.9879	800.00	0.8772	92.17
16	L16	60	PAD	Out	Slow	20.00	695.20	0.9881	800.00	0.8781	97.79
17	PSL	60	IMP	In	Fast	10.00	568.40	0.9318	800.00	0.8806	75.18
18	PSL	15	IMP	In	Slow	10.00	395.50	0.9437	800.00	0.8792	53.06
19	L16	15	IMP	Out	Fast	10.00	570.20	0.9872	800.00	0.8819	79.79
20	L16	15	IMP	In	Slow	10.00	674.90	0.9733	800.10	0.8744	93.89
21	L16	15	PAD	Out	Slow	10.00	545.80	0.9909	800.00	0.8740	77.35
22	PSL	15	IMP	Out	Fast	10.00	544.70	0.9547	800.00	0.8778	74.05
23	L16	15	PAD	In	Slow	20.00	703.60	0.9868	800.00	0.8906	97.45
24	L16	15	PAD	Out	Fast	20.00	700.00	0.9999	800.00	0.8758	99.90
25	L16	60	PAD	In	Fast	20.00	702.50	0.9892	800.00	0.8680	99.90
26	PSL	15	IMP	Out	Slow	20.00	611.20	0.9838	800.00	0.8772	85.68
27	L16	60	PAD	Out	Fast	10.00	663.90	0.9852	800.00	0.8747	93.47
28	PSL	60	IMP	Out	Slow	10.00	440.40	0.9534	800.00	0.8794	59.68
29	PSL	60	PAD	In	Slow	10.00	646.70	0.9929	800.00	0.8762	91.60
30	PSL	60	PAD	Out	Fast	10.00	622.40	0.9909	800.00	0.8782	87.78
31	PSL	60	IMP	Out	Fast	20.00	498.40	0.9692	800.00	0.8742	69.07
32	L16	60	PAD	In	Slow	10.00	646.90	0.9892	800.00	0.8789	91.01
33	L16	15	PAD	In	Fast	10.00	673.00	0.9797	800.00	0.8754	94.15
34	L16	15	IMP	Out	Slow	20.00	547.20	0.9887	800.00	0.8810	76.76

Average Yield = 86.11

*Line 16, continuous peroxide precipitated.

PSL, batch precipitated.

**Yield = $\left\{ \text{button weight} \times \text{button purity} \right\} / \left\{ \text{oxide feed weight} \times \text{oxide purity} \right\}$.

TABLE 3. Yield Comparison - Main Effects

L16 Oxide (%)	PSL Oxide (%)		Impeller Stirrer (%)	Paddle Stirrer (%)		10% Excess Ca (%)	20% Excess Ca (%)
96.53	96.42		96.53	96.42		96.53	96.42
83.77	73.71		73.71	97.31		83.77	73.71
74.40	97.31		83.77	84.83		94.96	97.31
99.90	84.83		86.99	97.37		79.45	84.83
92.17	97.37		74.40	94.96		75.18	97.37
97.79	86.99		99.90	79.45		53.06	86.99
79.79	94.96		92.17	97.79		79.79	74.40
93.89	79.45		75.18	77.35		93.89	99.90
77.35	75.18		53.06	97.45		77.35	92.17
97.45	53.06		79.79	99.90		74.05	97.79
99.90	74.05		93.89	99.90		93.47	97.45
99.90	85.68		74.05	93.47		59.68	99.90
93.47	59.68		85.68	91.60		91.60	99.90
91.01	91.60		59.68	87.78		87.78	85.68
94.15	87.78		69.07	91.01		91.01	69.07
76.76	69.07		76.76	94.15		94.15	76.76
90.51	81.70	a	79.66	92.55	a	82.86	89.35
8.82		b	13.09		b	6.49	
4.41		c	6.54		c	3.25	

$$\text{Yield} = [(\text{button weight}) \times (\text{purity})] / [(\text{oxide feed weight}) \times (\text{oxide purity})]$$

^a Average yields calculated from the columns above.

^b Difference between the two average yields in (a) above.

^c Differences in (b) divided by two.

average yield of the individual parameter, an estimate of that parameter's effect on the process yield can be calculated. For example, comparing Line 16 with PSL oxide:

Line 16 90.5 - 86.1 = 4.4%
(continuous peroxide precipitated)

PSL 81.7 - 86.1 = -4.4%
(batch precipitated)

This means the process yield of 86.1% could be increased approximately 4.4% by using only Line 16 oxide or that a decrease of 4.4% would be realized by using PSL oxide. The same holds true for the other main effects. Using the paddle stirrer would improve the 86.1% yield 6%, and 20% excess calcium would increase the yield 3%.

The superior performance of Line 16 oxide versus PSL oxide is difficult to explain. The only major difference is that Line 16 oxide has a larger crystallite size after recalcination. Both oxides were

produced via peroxide precipitation, one continuous, the other batch. Either there is a direct correlation between crystallite size and yield, or there are other differences in the two oxides. This should be resolved before deciding which to use. The yield difference may be suspect because some of the PSL oxide contained a small amount of water, which could have depressed the yields. See Thermogravimetric Analysis, this report.

A 13% greater average yield performance of the paddle stirrer over the impeller stirrer can be explained by the physical design difference. The paddle stirrers had blades nearly double those of the impeller stirrers.

Twenty percent excess calcium performed better than 10% excess calcium, probably because the latter was inadequate to reduce the full amount of plutonium oxide and other undesirable oxides. The numbers of calcium buttons produced and when they were produced support this argument. For the 16 runs performed with 10% excess

calcium, seven produced calcium buttons. This compares with 14 calcium buttons produced in 16 runs using 20% excess calcium. A calcium button present at the end of a run indicates: (1) inadequate contact between oxide and calcium or (2) more than the required amount of calcium. For the seven runs that produced calcium buttons using 10% excess calcium, six were performed with impeller stirrers. This suggests the impeller stirrer provides insufficient agitation and supports the superior yield performance of the paddle stirrer.

A model based on the results of the linear least squares regression was calculated as follows:

$$\begin{aligned} \text{Yield} &= 86.1 \text{ (average yield)} \\ &- 4.4 \cdot (\text{feed oxide}) \\ &+ 3.2 \cdot (\text{excess calcium}) \\ &- 6.5 \cdot (\text{stirrer design}) \end{aligned}$$

This equation summarizes the quantitative yield results stated previously about Table 3. Theoretically, the quantitative effects are additive, so more than 14% could be added to the 86.1% overall average yield if the best parameters are selected from those that affect yield. Other factors, such as water in the reagents, glovebox atmosphere, and argon, tend to decrease the yield slightly. A yield greater than 100% is not possible, but yields approaching that value can be achieved by choosing the best parameters according to the model.

Based on the results of the least squares regression, two experiments were selected from the experimental plan with the "best" parameters: Line 16 continuous precipitated oxide, 20% excess calcium, fast stirrer program, and a paddle stirrer. Yields for both experiments were 99.9%.

Additional verification of the additive principle was supported by two experiments performed after the completion of Phase IIC. These runs used the best parameters available based on preliminary results of Phase IIC. Yields of 99% and 98% were achieved. The same fixed parameters were used as in Phase IIC. Following is a listing of the parameters not fixed in Phase IIC used to achieve the respective yields:

<u>99% Yield</u>	<u>98% Yield</u>
← Paddle stirrer →	
← <1 min. ramp to 600 rpm stirring →	
Line 16 oxide	PSL oxide
50% Excess calcium	25% Excess calcium
← 15 min. hold time →	
← Stirred "in the metal" →	

Crucible Failure

No crucibles failed in Phase IIC from heat of reaction thermal shock. Four crucibles did fail for other reasons. Two occurred with a cooling rate exceeding 200 °C per hour. Faster cooling rates should be used only after the reaction products are frozen at ≤700 °C inside temperature. Two failures occurred because of operator error. Yield was not affected by any of the failures.

DOR crucibles can fail from heat of reaction thermal shock. Figure 9 illustrates this phenomenon, which occurred in a run performed after Phase IIC. Most likely, failure was caused by a short stirring ramp to 600 rpm, whereby most of the heat of reaction was transferred to the crucible producing stresses above the limits of the magnesium oxide. The crucible shown was separated into two halves; the right half is the bottom of the charge showing the frozen salt, and the left is the top of the crucible. Looking carefully at the left half, notice a ring of salt pointing to the center of the crucible just below the top, indicating the salt level at the highest rate of stirring. Crucible failure occurred just below this ring (top edge).

The primary difference between experiments in Phase IIC and the subsequent experiment where the crucible failed from heat of reaction was the stirring program. During Phase IIC, the reactants were stirred 15 minutes at less than 600 rpm before reaching the maximum speed. In contrast, the stirring program of the failed crucible experiment consisted of a step-like jump to 600 rpm from the

FIGURE 9. Crucible After DOR Showing Reaction Thermal Shock

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static condition. By gradually increasing speed over a few minutes to the maximum, the heat of reaction can be spread out, thus reducing the shock to the crucible.

Theoretically, approximately 141 kcal are released to the system. This corresponds to a 151 °C temperature increase given the conditions of charge size and salt composition- -in this case, 800 grams plutonium oxide, 3200 grams 99.2% pure calcium chloride, and 284 grams calcium metal (20% excess). This energy release should be spread out over several minutes to prevent crucible failure.

Identifying the type of crucible failure is accomplished by examining the cracks. Typically, cracks caused by improper equipment or reagent handling or from an overly aggressive heating or cooling ramp appear as a single, vertical, non-symmetric crack. In contrast, evidence of heat of reaction thermal shock failure shows a single, uniform, circumferential crucible crack just below the maximum salt height.

Thermogravimetric Analysis of Feed Oxide

As part of the experimental procedure, a five-gram control sample of the feed oxide was taken just

before loading into the crucible. It was submitted for Thermogravimetric Analysis (TGA) to determine whether the oxide had absorbed any water during storage after recalcination.

Five of the 32 samples exhibited moisture pickup; those five samples used PSL oxide as feed. The moisture pickup could have resulted from:

1. Improper handling of oxide during packaging.
2. Poor storage container seal.
3. Excessive time sampling the oxide.
4. Improper handling/splitting of the sample.

Statistically, there was an average 8.8% difference in yield between PSL oxide and Line 16 oxide. In two experiments using PSL oxide, the difference in yields from two corresponding Line 16 experiments is far greater than the 8.8% average. It appears that an outside effect, probably water, depressed the yields. Therefore, proper handling is essential.

Impurities

DOR product buttons produced in Phase IIC were sampled and analyzed for 23 elements. These

elements are of interest to the foundry and can have an impact on down-stream processes such as electrorefining. See Appendix A. Like the statistical yield calculations, a linear least squares regression analysis was performed pertaining to impurities.

The analysis showed that six impurities were affected by the DOR process: Aluminum, gallium, iron, nickel, chromium, and carbon. Calcium and magnesium were excluded from analysis because of high variability in the data. The main effects on impurities in the metal product were caused by the same parameters that affected yield: feed oxide, stirrer design, and excess calcium. Feed oxide was the most dominant, showing an effect on all six of the impurities above. PSL oxide increased the average concentration of aluminum and carbon in the product metal, whereas Line 16 increased concentrations of aluminum, gallium, iron, nickel, and chromium.

CONCLUSIONS

Yield for the 32 experiments in Phase IIC averaged 86.1%. Three main effects affected yield: feed oxide type, percent of excess calcium, and stirrer design. A statistical model was developed; it predicts with 95% confidence that best yields can be attained with the following main effects:

1. Line 16 (continuously precipitated) plutonium oxide as feed
2. 20% excess calcium
3. Flat paddle stirrer

Hold time, stirrer position, and stirring program did not affect yield. All other parameters should be used at the levels specified in the Experimental Procedure. The model predicts that yields approaching 100% can be obtained by using the best conditions specified above.

Heat of reaction did not cause thermal shock failure of crucibles in this study. Evidence suggested the DOR reaction temperature release can be controlled by stirring rate. This may be beneficial if crucible failure becomes a problem in the future.

There is some evidence that any moisture depresses yield. In two of five experiments where water was absorbed by the plutonium oxide, yields were much lower than the average as predicted by the statistical model for the conditions used. It has been theorized that moisture can cause foaming. No evidence of foaming was observed in these experiments. Considerable effort was put forth to provide careful handling of reagents to ensure minimal moisture absorption. This will be essential in subsequent DOR work to produce maximum yields.

Foundry specifications for metal purity were satisfied for all impurities analyzed except carbon, calcium, magnesium, and the aluminum, silicon, and gallium combination. Carbon failed to meet foundry specifications in only one of the 32 product buttons and is not considered a problem.

After extensive analyses of impurities, it was determined that iron, chromium, and carbon reports to the product plutonium button from the oxide. Gallium and uranium may report to another product phase; but without better analyses on all the residues, this cannot be conclusively stated. To consider other elements, further analyses of all product phases are required to fully understand and characterize the origination and reporting pattern of each impurity.

If the entire concentration of aluminum, silicon, and gallium had reported to the product, the specification would not have been satisfied. DOR is not a purification process. Attempts to produce foundry-quality metal through DOR or reduction of the quantity of DOR product requiring electrorefining can be successful only if the feed reagents (including plutonium oxide) are relatively free of contaminants.

The results of Phase IIC show that the small-scale studies performed previously correlate very well to production scale. Stirring speed and oxide source were the only parameters that affected the small-scale yields differently than production scale.

Tapered stainless steel back-up cans were effective in making breakouts easier when crucibles failed.

RECOMMENDATIONS

It is recommended that future work in DOR continue in the refinement of stirrer design and optimization of calcium excess.

Following is a list of recommended parameters that can be used to attain the highest yields based on the results of this study:

1. Stirrer design: Paddle.
2. Percentage excess calcium: 20%.
3. Salt: Cast calcium chloride.
4. Salt-to-oxide ratio: 4:1 (to minimize salt residue).
5. Oxide feed type: Line 16 (continuously precipitated) plutonium oxide calcined at 1000 °C at least six hours and packaged at 200 °C in a water-tight vessel.
6. Stirring speed: 600 rpm (ramp to this speed in one to two minutes).
7. Stirring initiation: When the salt becomes molten.
8. Hold time after stirring: 15 minutes.
9. Calcium metal position on loading: Above the oxide.

Emphasis in the future should be placed on acquisition of the purest reagents possible. Any impurities contained in the reagents contaminate the product. Before foundry-quality metal can be produced by the DOR process, aluminum and silicon concentrations in both feed oxides must be reduced. If Line 16 oxide is used, the gallium concentration must also be reduced. The Fisher C-77 calcium chloride salt and the Pfizer calcium metal used had acceptable purities.

The data gathered in this study does not conclusively show that calcium and magnesium contamination of the product can be reduced by varying any of the parameters used. Since these

two elements were present in most of the products in quantities considerably above foundry specifications it is recommended that a batch of DOR buttons, produced under conditions similar to Phase IIC, be cast by the foundry to determine their effect on casting yield and quality. Calcium and magnesium concentrations in buttons produced by using 10 or 20% excess calcium may not be detrimental to the foundry casting process.

The results of this study showed that 10% excess calcium increased the average concentrations of gallium and nickel. Future work in DOR should verify this result and determine its cause.

Because water decreases yields, it is recommended that reagents be handled to minimize water absorption.

Further work should be done to characterize differences between Line 16 and PSL oxide.

Verification of the results of Phase IIC is recommended. After the stirrer design and excess calcium are refined, a baseline set of runs should be performed using a consistent set of parameters. This would include plutonium oxide batches produced under the same set of conditions. Inconsistent feed may provide inconsistent results.

In future DOR development efforts where large numbers of experiments are required, it is recommended that preliminary screening work be performed on a scale similar to one used in the small-scale studies. Performance on the small scale is similar to production scale, saves time and nuclear material resources, and reduces residues requiring further processing.

REFERENCE

1. J. L. Long, D. J. Santi, D. C. Fisher, and T. J. Humiston, *DOR Demonstration 1. Small Scale Studies*, RFP-4128, Rockwell International, Rocky Flats Plant, Golden, CO, April 1987.

APPENDIX A

Foundry Specifications for Plutonium Metal

<u>Element</u>	<u>Maximum (ppm)</u>	<u>Element</u>	<u>Maximum (ppm)</u>
Al	*	Mn	100
Am	200	Ni	**
B	50	Np	100
Be	3	Pb	100
C	200	Si	*
Ca	500	Sn	100
Cd	10	Ta	100
Cr	100	Th	100
Cu	100	Ti	100
Fe	**	U	100
Ga	*	W	200
Mg	500	Zn	100

*Each button must conform to the following limits:

4 (ppm Ga) + 10 (ppm Al) + 10 (ppm Si) <1300

**Fe plus Ni must be <400 ppm

RFP-4204

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