

97  
2-11-92 JS (2)

RFP-4128  
December 9, 1991

RFP-4128  
December 9, 1991

**DIRECT OXIDE REDUCTION DEMONSTRATION,  
SMALL-SCALE STUDIES**

*J. L. Long*  
*D. J. Santi*  
*D. C. Fisher*  
*T. J. Humiston*



Rocky Flats Plant  
P. O. Box 464  
Golden, Colorado 80402-0464

U.S. DEPARTMENT OF ENERGY  
CONTRACT DE-AC04-90DE62349

## **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The view and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

Printed  
December 9, 1991

RFP--4128

DE92 006617

8  
Y  
i)

## DIRECT OXIDE REDUCTION DEMONSTRATION, SMALL-SCALE STUDIES

*J. L. Long*  
*D. J. Santi*  
*D. C. Fisher*  
*T. J. Humiston*

### SUBJECT DESCRIPTORS

Calcination  
Calcium/Magnesium Dist.  
DOR  
DOR Demonstration  
Elemental Mapping  
Product Leaching  
Small Scale

EG&G ROCKY FLATS, INC.  
ROCKY FLATS PLANT  
P. O. BOX 464  
GOLDEN, COLORADO 80402-0464

PREPARED UNDER CONTRACT DE-AC04-90DE62349  
FOR THE  
ALBUQUERQUE OPERATIONS OFFICE  
U.S. DEPARTMENT OF ENERGY

**MASTER**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *EB*

## ACKNOWLEDGMENTS

We wish to thank the following Laboratory personnel for their assistance. Many times we requested and received services above and beyond the normal scope of Laboratory operations.

Beth Bell	Amy Miller
Ed Brovsky	Dana Portlock
John Fraser	Len Sanculi
Carol Gies	Reuben Sironen
Keith Grossaint	Dot Stuit
Rene Hoatson	Jan Watson
Carl Jensen	Collins Whitehead
Judy Laurent	

The following people helped us with the special equipment, services, and supplies necessary for pyrochemical experiments:

Dave Adamak	Jim Mosler
Werner Buntrock	Mike Nelson
Dirk Conover	Don Rouze
John Dezzutti	Don Schlosser
Carl Edstrom	John Skufca
Gordon Fergus	Ed Sellman
Bill Ferguson	Mike Simmons
Jan Krankota	Mary Ellen Trujillo
Doug Krause	

## CONTENTS

Abstract .....	1
Introduction .....	1
Experimental Plan and Procedures .....	1
Phase IIA .....	3
Recalcination Experimental Procedure .....	3
Reagent Handling Phases IIA and IIB .....	3
Small-Scale DOR Experimental Procedure .....	4
Sample Analyses .....	4
Phase IIB .....	5
Screening Test Parameters .....	5
Screening Test Experimental Procedure .....	8
Screening Test Sample Analysis .....	8
Fine-Tuning Test Parameters .....	8
Fine-Tuning Test Experimental Procedure .....	9
Fine-Tuning Test Sample Analyses .....	9
Results and Discussion .....	10
Salt Examination .....	10
Screening Experiments .....	13

Fine-Tuning Experiments .....	15
Yields .....	15
Impurities .....	20
Physical Metallurgy Analysis .....	23
Aqueous Recycle Technology Analysis .....	23
Conclusion .....	25
Recommendations .....	28
References .....	29
Appendices (A Through G) .....	31

## DIRECT OXIDE REDUCTION DEMONSTRATION, SMALL-SCALE STUDIES

*J. L. Long, D. J. Santi,  
D. C. Fisher, and T. J. Humiston*

### ABSTRACT

A detailed, statistically valid investigation of the direct oxide reduction process was planned and completed, utilizing 100 grams or less of plutonium dioxide per experiment. Conditions were established for obtaining 95%+ yields. Conclusions drawn from the results of the experimental work were utilized to make recommendations for future large-scale investigative and confirmative work as well as large-scale production demonstration work.

### INTRODUCTION

This project was initiated to provide process design information to the Plutonium Recovery Project (PRP). Although direct oxide reduction (DOR) has been operated in a production mode both at the Rocky Flats Plant (now operated by EG&G, Inc.) and Los Alamos National Laboratory, many aspects of the process are ill-defined. Because the PRP plans include significant DOR capability, a well-defined process should minimize capital cost and maximize productivity. Reduced radiation exposure may also be realized.

Rudiments of the DOR process are well known. Plutonium oxide is reduced by calcium metal to form plutonium metal and calcium oxide. Unless removed, the calcium oxide forms a barrier to further reaction. Current practice utilizes a molten salt, calcium chloride, to remove the reaction barrier. Calcium metal is always added in excess of stoichiometric requirements, and some form of agitation is used. Within these broad constraints, there were many questions on interactions of the process variables. To provide answers, a new facility was placed on line to permit operation on a

small scale and allow the numerous experiments required by the many variables.

The small-scale work evolved into two parts: small-scale salt examination (Phase IIA) to evaluate calcium chloride from four sources (choosing one for use in subsequent experiments), and a small-scale parametric study (Phase IIB) to evaluate the effect of changes in operating conditions on product metal yield and quality. The small-scale parametric study was further broken into two parts: small-scale screening experiments (Phase IIB-1) to perform an evaluation of 12 variables for screening purposes, and small-scale fine-tuning experiments (Phase IIB-2) to focus on selected variables for further examination (as suggested by the first two phases). The design of each phase and the operating procedures for each set of experiments are presented in the Experimental section.

### EXPERIMENTAL PLAN AND PROCEDURES

The equipment used for recalcination (full scale) and direct oxide reduction (small scale) in Phases IIA and IIB was installed just prior to the Phase II work. Figure 1 shows the small-scale furnace assembly. A Fisher Iso-Temp Ashing Furnace was used for recalcination.

Small-scale furnaces incorporated newly designed furnace elements, heads, and safety features. During installation of the small-scale furnaces, much time was spent on sealing the equipment, which enabled the exclusion of moisture and air from reaction vessels and materials. A higher quality reaction chamber atmosphere than that delivered by existing equipment can be maintained.

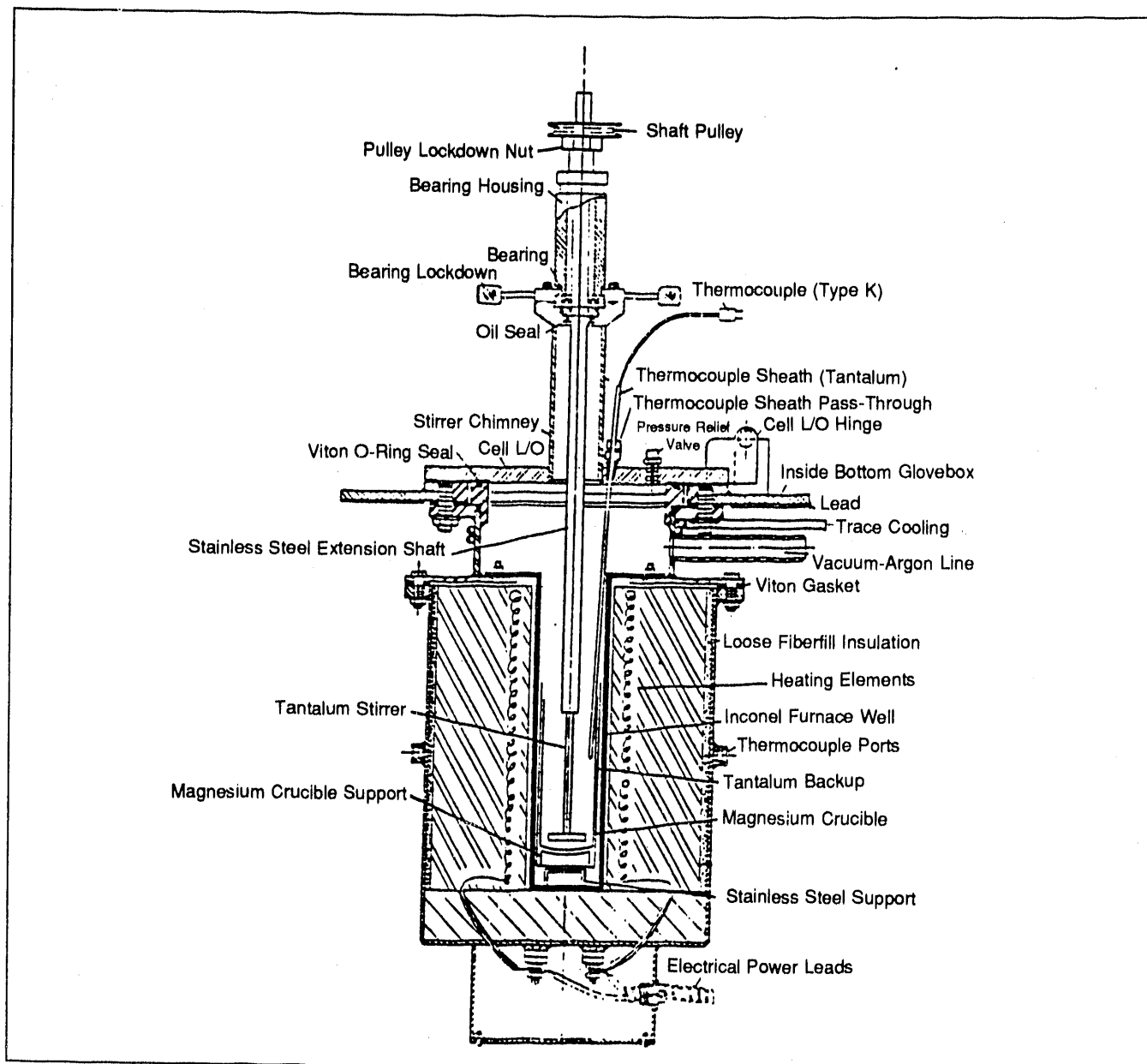


FIGURE 1. Small-Scale Stationary Furnace Assembly

The oxide recalcination was performed in the Fisher Iso-Temp Ashing Furnace. The ashing furnace incorporates a microprocessor for accurate temperature control, linear heating rates, and program duration. The heating chamber and door liner are molded from alumino-silicate ceramic fibers and low-density insulating material, which allows faster heating and cooling and is cleaner than conventional fire-brick construction. In

addition, the furnace has a dispersion tray for preheating any incoming reaction gases and a fan that pumps ambient air through the dispersion tray at a rate of three chamber volumes per minute.

Small-scale experiments have numerous advantages over large scale. Small-scale experiments produce less waste, use less fissile material (70 grams of plutonium oxide per DOR experiment), and reduce



experiment time. Operational flexibility permits varying parameters to an extent not possible in the old large-scale equipment.

## Phase IIA

Phase IIA objectives were to analyze several sources of calcium chloride salt, determine their purity, and use them as the reaction medium in small-scale DOR experiments. Four were selected for this phase: a cast salt supplied by Los Alamos National Laboratory, Fisher Anhydrous Powder C-77, Baker Dihydrate Crystals, and Sharpe (currently used by production). Each salt was dried in a convection oven at 230 °C and then cast in a tantalum mold. Oxygen analysis by neutron activation proved that insignificant amounts of oxygen-containing species were in the calcium chloride after air drying at 230 °C. The results are detailed in Appendix A.

The salt source was the only parameter that was varied in Phase IIA. All other parameters were held constant throughout this phase. Following is the list of parameters for Phase IIA DOR experiments and their respective values:

Recalcination Time	6 hours
Salt-to-Oxide Ratio	5 to 1
Melt Temperature	~790 °C
Stir Speed	200, 350, 500, 650 rpm
Recalcination Temperature	850 °C
Excess Calcium	25%
Hold Time before Cooling	15 minutes
Position of Calcium Metal	Above oxide separated by salt
Feed Oxide	Line 16
Stirrer Design	DOR Impeller
Oxide Particle Size	As Is
Salt Entry	Cast

The values for each parameter were chosen using past experience in DOR and represented a first approximation of optimum conditions.

Eight experiments were planned for Phase IIA. Each salt was used in two DOR experiments. Any

failures that could be explained by equipment or operator problems were repeated. Two recalcination experiments supplied the oxide necessary for these DOR experiments.

## Recalcination Experimental Procedure

The oxide used in these small-scale DOR experiments was recalcined to remove any volatile components (water, sulfates, and nitrates). The feed oxide was obtained from Line 16, a continuous peroxide precipitation process. One batch of oxide was used for this phase. It had a plutonium content of 82.16%. (The theoretical percentage of plutonium in pure PuO<sub>2</sub> is 88.20%.)

Approximately one kilogram of oxide was sampled, weighed, and loaded into a platinum tray for each recalcination experiment. One kilogram of oxide correlated to an approximate one-inch depth in the platinum tray. The tray and its contents were placed into a stainless steel support tray and the entire assembly was put into the Fisher Ashing Furnace. The furnace was programmed to heat to 850 °C in one hour, held at 850 °C for six hours, and turned off allowing the contents to cool. Starting one hour after the furnace reached 850 °C and each hour thereafter, the oxide was stirred with platinum-tipped tongs. The oxide was allowed to cool to approximately 200 °C before it was sampled and split into 105-gram batches. Each 105-gram batch of oxide was stored in a glass vial (designed for storage of hygroscopic materials) until the subsequent DOR experiment.

## Reagent Handling Phases IIA and IIB

Great care was taken to ensure that reagents in these experiments were handled properly and didn't absorb moisture during storage. Any moisture in the oxide or salt produce detrimental effects on the metal yield from DOR.

To prevent moisture pickup, the oxide was removed from the calcining oven at approximately 200 °C. Typical Thermogravimetric Analysis

(TGA) traces showed that essentially all weight loss occurs and moisture is expelled at 200 °C. Once the oxide was removed from the oven, it was sampled and divided into batches. Each batch was placed into a Wheaton "800" brand glass vial with a tight-fitting special cap to keep moisture out. These vials were tested both before and during each phase. After several weeks of oxide storage in these glass vials, no moisture pickup was measured by TGA.

In Phase IIB, two forms of Fisher-brand reagent-grade calcium chloride salt were used: pelletized and cast. Powdered Fisher salt was pelletized by an outside vendor (Cargilles Laboratory). The pelletized salt was dried and stored in a Blue M convection oven at 230 °C prior to use. When an experiment required pelletized salt, a beaker of salt was removed from the oven, sampled, and a portion weighed out. This portion was placed in a plastic bag, purged with argon, and sealed at a positive pressure of argon. The cast salt produced by Foundry Operations was cast in a tantalum crucible, removed while still hot, placed in a produce can, and sealed until used. Before each experiment, each cake was sampled, weighed, and packaged the same way as the pellets.

Both the pellets and cast cakes showed up to 2% weight loss as measured by TGA prior to introduction into the line. Special TGA work showed that moisture pickup during routine TGA could have accounted for the weight loss. Subsequently, up to 2% weight loss was accepted.

#### Small-Scale DOR Experimental Procedure

The furnaces were cleaned before each DOR experiment by vacuuming or wiping with a moist rag. The DOR stirrers were cleaned before each experiment to remove the material holdup by leaching in 200 ml 1N HCl.

The backup can, ceramic adapter, and crucible were placed into the furnace so the stirrer could be adjusted 1/16 to 1/8 inch from the bottom of the crucible before the reagents were loaded. The corresponding batch of recalcined oxide was

sampled and weighed. Both salt cakes were sampled before being loaded. The reagents were loaded into the crucible in the following order: approximately 100 grams of oxide, one half of the salt (one salt cake), the calcium charge, and the remainder of the salt. The salt cakes were cast so they would fit into the crucible with a minimal gap between the cake and the wall, minimizing the amount of calcium that would contact the oxide.

Once the furnace was loaded, it was sealed and evacuated to approximately 23 inches of mercury and backfilled three times with argon. An argon atmosphere of 3 psi was maintained during each experiment. The furnace controller was programmed for a linear heating rate of 333 °C per hour to a furnace element temperature of 1000 °C. A slow heating rate was necessary because of the low thermal shock resistance of the magnesium oxide ceramic crucibles. The furnace element temperature was held at 1000 °C during the experiments.

When the salt was molten, the stirrer was lowered and started at 200 rpm. When the temperature began to stabilize, stirring speed was increased to the next level. Once the temperature leveled at 650 rpm, stirring was continued 15 minutes. After completion of the stirring program, the stirrer assembly and thermocouple were pulled from the melt and the furnace element temperature was held at 1000 °C 15 minutes before turning off furnace power.

After cooling to a safe temperature, the contents were removed and each item or phase was separated and sampled.

#### Sample Analyses

Many different methods were used to analyze for impurities in the various phases of each experiment:

Feed CaCl<sub>2</sub> Salt:

Inductively Coupled Plasma Emission (parts-per-million levels of Al, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Th, Ti, U, V, Zn, Lu)

Atomic Absorption Spectroscopy (parts-per-million level of K)

Thermogravimetric Analysis (wt. loss of water)

#### DOR Oxide:

Plutonium Chemistry (parts-per-million levels of C and U)

Emission Spectroscopy (parts-per-million levels of Ta, W, Zr)

Photographic Emission Spectroscopy (parts-per-million levels of Al, B, Be, Ca, Cr, Cu, Fe, Ga, Mg, Mn, Mo, Ni, Pb, Si, Sn, and Ti)

Infrared Spectroscopy (weight percent of  $\text{NO}_3$  and  $\text{SO}_4$ )

Radiochemistry (g/g Am, g/g Pu)

Thermogravimetric Analysis (wt. loss of water)

In addition to the chemical characterizations described above, selected physical properties of the oxides were also determined. These include lattice parameter and crystallite size by X-ray diffraction, particle size and distribution by sieve analysis and particle analyzer techniques, morphology as determined from photomicrographs, and bulk density. These determinations were performed for both the unrecalcined and recalcined oxides.

#### DOR Product Button:

Atomic Absorption Spectroscopy (parts-per-million levels of Al, Ca, Cr, Fe, Ga, Mg, Ni)

Plutonium Chemistry (parts-per-million levels of C, Pu, U)

Emission Spectroscopy (parts-per-million levels of B, Be, Cu, Mn, Mo, Pb, Si, Sn, Ta, Ti, W, Zr)

Radiochemistry (g/g Am, g/g Pu)

#### DOR Product Salt:

Emission Spectroscopy (parts-per-million levels of Ag, Al, As, B, Ba, Bi, Ca, Cd, Cr, Cu, Fe, Ga, Ge, Hg, In, K, Mg, Mn, Mo, Nb, Ni, P, Pb, Sb, Si, Sn, Sr, Te, Ti, Tl, V, Zn, Zr)

Radiochemistry (g/g Am, g/g Pu)

#### Stirrer Leach Solution:

g/l Pu, g/l Am, pH,  $\text{Cl}^-$  concentration

#### Button Leach Solution:

Atomic Absorption Spectroscopy ( $\mu\text{g}/\text{ml}$  of Ca and Mg)

### Phase IIB

There were two parts associated with Phase IIB of the DOR Demonstration Project. The first was the screening experiments. These experiments were designed to qualitatively investigate all 12 parameters believed to have an effect on DOR yields and button purities. The objectives of the screening experiments were to: (1) determine which of the 12 parameters had an effect on DOR and (2) define the parameters to be investigated in the second half of Phase IIB, the fine-tuning experiments. The fine-tuning experiments would further define operating ranges of the selected parameters for later large-scale verification experiments.

#### Screening Test Parameters

Following are specific parameter values and the rationale used in the screening tests of Phase IIB of the DOR Demonstration.

1. Calcination time — 4, 6, and 8 hours. Six hours is the current production calcination time. Two hours either side of that value was assumed to indicate the effect of calcination time on DOR.
2. Salt-to-oxide ratio — 3:1, 4:1, and 5:1. This represents the ratio ranges that are practical in our current furnaces. The 3:1 ratio was

perceived as the lowest that would produce a successful run.

3. Melt temperature — 780, 800, and 820 °C. The current production procedure calls for an outside furnace temperature calibrated to give an inside temperature of 840 °C. Calcium metal melts at 839 °C. At lower temperatures, the reaction between the calcium and magnesium oxide crucible would be a solid-solid reaction, which is far slower than a liquid-solid reaction. Therefore, the upper limit was set below this temperature.
4. Stir speed — Phase IIA used a stirrer program based on operator interpretation of the thermal trace. This produces an uncontrolled variable. Therefore, a stirring program was conceived that would effectively eliminate the operator dependence.
 

<u>Low</u>	<u>Midpoint</u>	<u>High</u>	<u>Time</u>
100	200	300	10 min
150	300	450	5 min
200	400	600	5 min
5. Calcination temperature — 650, 850, and 1050 °C. Here again, the midpoint was chosen and is currently used in production. The upper limit is as high as the calcining furnace consistently achieves. This upper limit, along with the midpoint, also defines the lower temperature.
6. Excess calcium — 5, 25, and 45%. Phase IIA achieved satisfactory yields using 25% excess calcium. Production uses 50% excess calcium. It was felt that 25% would be a good midpoint, but 0% excess calcium would be too low. Therefore 5% was chosen as the low value with 45% as the high.
7. Hold time before cooling — 15 min, 1 hr 22 min, and 2.5 hr. Fifteen minutes was determined as a minimum hold time, and production currently uses 2.5 hours. This dictated the mid-point.

8. Position of calcium metal in the charge — calcium midway up the salt charge; calcium and oxide as close as possible without touching; oxide half way up the salt charge. Very little is known about relative positioning effects of the reactants. These values were selected as the most radical possible and, therefore, most likely to show an effect.
9. Feed oxide — Process Simulation Laboratory (PSL) and Line 16. PSL oxide is produced by batch peroxide precipitation and is the process selected for the Plutonium Recovery Project design. Line 16 oxide is produced in a continuous peroxide precipitation process.
10. Stirrer design — Opposing-pitch dual impeller or flat paddle. The opposing-pitch dual impeller (DOR stirrer) is the current "standard" DOR stirrer (Figure 2). The impellers were bent by hand without fixturing so the pitch was by visual comparison. The flat paddle stirrer was chosen so there would be a significant design difference (Figure 3).
11. Particle size — as is or <120 mesh. It was originally planned to use as is and <20 mesh. (Los Alamos screens all its oxide to <20 mesh.) However, it was discovered there was very little oxide >20 mesh during the oxide characterization work. Approximately half the oxide was <120 mesh; therefore, this size was chosen as the cutoff point.
12. Salt entry — cast cakes or pelletized. Fisher brand calcium chloride salt was cast by Foundry Operations. Cargilles Laboratory pelletized this salt in time for these experiments. Pelletized salt was preferred over powdered salt by Plutonium Recovery Operations.

To efficiently analyze 12 parameters, an experimental design was developed by the Statistical Applications Group; it is a Resolution Three design, which allows estimation of main effects with the assumption that all interactions are negligible. The design enabled evaluation of each

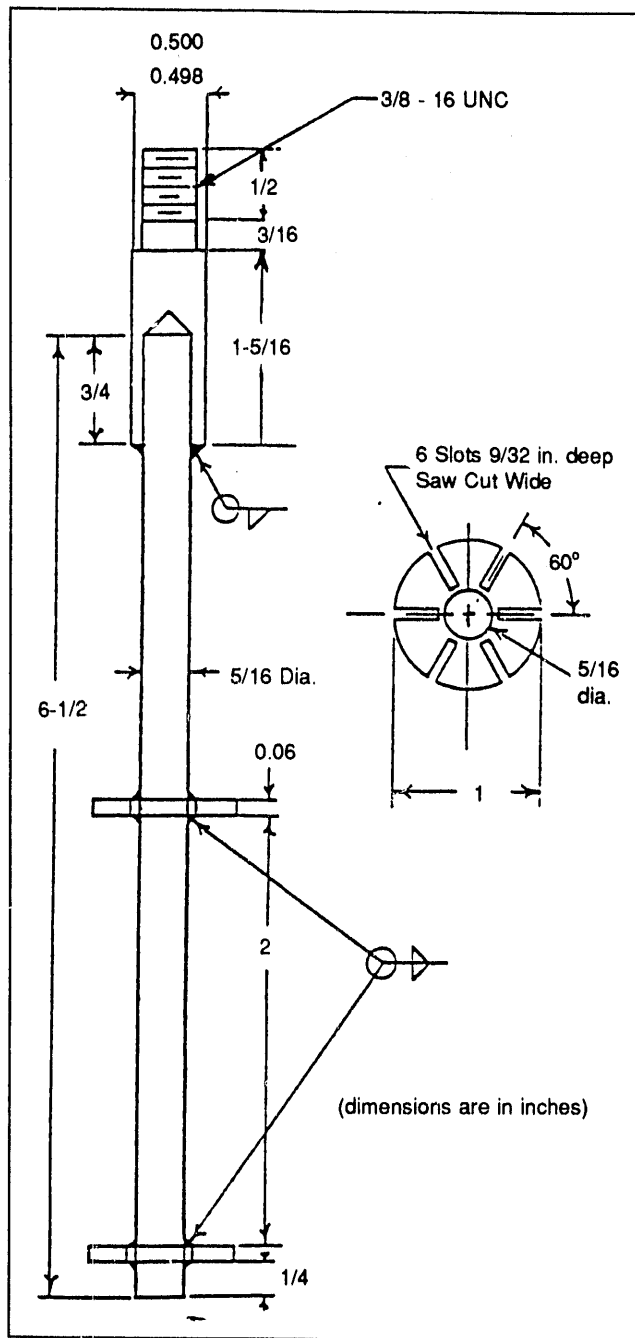


FIGURE 2. Small-Scale DOR Tantalum Stirrer

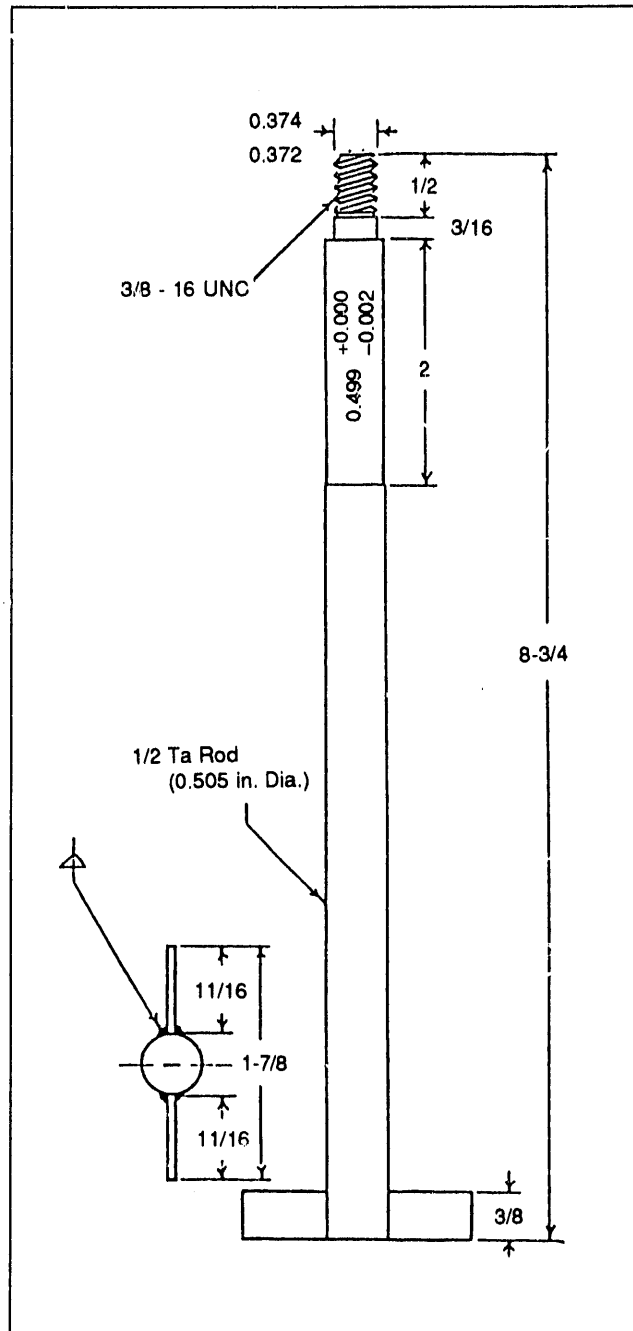


FIGURE 3. Small-Scale DOR Tantalum Flat Paddle

parameter with a minimal number of experiments. Eighteen randomized runs were needed for the screening tests.

### Screening Test Experimental Procedure

Experimental procedures for the screening tests are similar to Phase IIA procedures. For the recalcination experiments, the oxide was recalced at the statistically assigned calcination temperature (650, 850, and 1000 °C) and time (4, 6, and 8 hrs). Sufficient oxide was calcined in each batch to supply two DOR experiments, one with <120 mesh oxide and the other with as-is oxide. The remainder of the oxide was returned to production.

For DOR experiments, oxide was reduced to 75 grams to allow sufficient room in the crucible for the pelletized CaCl<sub>2</sub> salt at a 5-to-1 salt-to-oxide ratio for use without opening the furnace to add salt. A set stirring program was implemented in addition to raising the stirrer 1/4 to 3/8 inch from the bottom of the crucible. This was to ensure that the stirrer was above the metal product button. The DOR product buttons were not leached, but the stirrers were immersed in 2N HCl. This was to prevent any residual plutonium metal or compound from affecting the yield of the next experiment.

After Phase IIA, the sampling of every salt charge was stopped for these reasons:

1. Salt purity was consistent between each run.
2. Increased handling of the salt led to greater potential for moisture pickup.
3. Sampling the cakes generally caused the cake to shatter, increasing the surface area of the cake.

### Screening Test Sample Analysis

Sampling and analyses for the Phase IIB Screening Tests were the same as in Phase IIA, except that in some experiments there was an unreacted oxide and calcium button phase after the reduction. These product phases were analyzed as follows:

### Semi-Quantitative Emission Spectroscopy:

Parts-per-million levels of Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, In, K, Mg, Mn, Mo, Nb, Ni, P, Pb, Sb, Si, Sn, Sr, Te, Ti, Tl, V, Zn, and Zr

### Radiochemistry:

g/g Am and g/g Pu

### Fine-Tuning Test Parameters

Fixed parameters for fine-tuning tests are listed below:

Recalcination Time	6 hours
Melt Temperature	780 °C
Stir Speed	300, 450, and 600 rpm
Recalcination Temperature	1000 °C
Hold Time Before Cooling	15 minutes
Feed Oxide	Process Simulation Laboratory
Stirrer Design	Flat Paddle
Particle Size	as-is

Only four of the original twelve parameters were selected for further investigation:

Salt-to-Oxide Ratio	4:1 and 5:1
Excess Calcium	10%, 25%, and 40%
Position of Calcium Metal	Below oxide and Above oxide
Salt Entry	Pelletized and Cast

With only four parameters, a more detailed study was possible. The Statistical Applications Group along with Pyrochemistry Technology, developed a statistical experimental plan consisting of 26 experiments. This plan allowed all main effects and estimation of two-way interactions with the assumption that all three-way interactions were negligible. Duplicate experiments were included in the original 26. This enabled determination of DOR experiment reproducibility in small-scale furnaces. Table 1 contains the statistical experimental plan for the fine-tuning tests.

TABLE 1 DOR Experimental Plan for  
Phase IIB Fine-Tuning Experiments

Experimental Runs in Order Performed				
Run	Excess Calcium	Salt-to-Oxide Ratio	Calcium Position	Salt Type
1	40	5:1	Above	Pell
2	40	4:1	Below	Pell
3	25	5:1	Above	Pell
4	40	5:1	Above	Pell
5	10	5:1	Below	Pell
6	10	4:1	Above	Pell
7	25	5:1	Above	Cast
8	40	4:1	Above	Cast
9	25	5:1	Above	Cast
10	25	4:1	Below	Cast
11	25	4:1	Below	Pell
12	10	4:1	Below	Cast
13	25	4:1	Above	Cast
14	40	4:1	Below	Pell
15	10	5:1	Above	Cast
16	40	5:1	Below	Cast
17	10	5:1	Above	Cast
18	25	5:1	Above	Pell
19	25	5:1	Below	Cast
20	10	4:1	Below	Cast
21	40	4:1	Above	Cast
22	10	4:1	Above	Pell
23	25	4:1	Above	Pell
24	10	5:1	Below	Pell
25	25	5:1	Below	Pell
26	40	5:1	Below	Cast

### Fine-Tuning Test Experimental Procedure

The DOR procedure used for screening experiments was also used for fine-tuning tests.

Changes were made in material handling of the Phase IIB screening tests. These changes incorporated the oxide sent to the calorimeter for analysis after recalcination. Once the oxide was analyzed, it was placed into the calcining furnace and heated to 200 °C for one hour to remove any moisture the oxide picked up during shipment to and from the calorimeter. After eliminating the moisture, the oxide was removed from the furnace and divided into batches for the DOR experiments. Each batch of oxide was placed into a vial as in the Phase IIB Screening Tests.

### Fine-Tuning Test Sample Analyses

Sampling and analysis of the feed and product residues were modified only slightly. Only three recalcination runs were necessary to provide the required quantity of oxide because the recalcination temperature and time were fixed. Four samples were taken before and after calcining to better characterize the oxide before DOR. Oxide analyses before and after recalcination were changed to the following:

#### Atomic Absorption Spectroscopy:

Parts-per-million levels of Al, Be, Cr, Fe, and Ni

#### Plutonium Chemistry:

Parts-per-million levels of C, Pu, and U

#### Emission Spectroscopy:

Parts-per-million levels of Ta, W, Y, and Zr

#### Photographic Emission Spectroscopy:

Parts-per-million levels of B, Ca, Cu, Ga, Mg, Mn, Mo, Pb, Si, Sn, and Ti

Oxide samples taken just before the DOR experiments were analyzed for weight percent water, nitrate, and sulfate only because there was essentially no difference between results of the

sample taken after recalcination and the sample taken before DOR. The only change that could occur during storage was moisture absorption.

## RESULTS AND DISCUSSION

### Salt Examination

The initial task for this phase was a survey of calcium chloride from different sources. Sharpe

was the current supplier of calcium chloride to the production DOR process. Sharpe salt has a high concentration of boron (Table 2). Any plutonium metal product made with this salt would exceed the boron foundry specification of 50 ppm (Appendix B) if only a fraction of the boron reported to the product button. This did occur, as evidenced by analysis of the metal product (Table 3). Sodium and potassium were also concerns because of their potential to create waste handling problems by

TABLE 2. Impurities in Calcium Chloride

Source	Form	Al	B	Cr	Fe	K	Mg	Na	Ni	Si	Zn
		ppm									
Sharpe	Pellet	<2.7	122	<2.1	9	14,800	53	6300	30	<4	<1
Baker	Dihydrate Powder	<2.7	<5.4	<2.1	<0.8	5	17	92	<9	7	<1
Baker	Anhydrous 4-8 Mesh	<2.7	78	<2.1	32	15,800	38	5100	<3	<4	<1
Fisher	Anhydrous 4-20 Mesh	<2.7	84	2.6	11	14,600	44	4840	<3	<4	<1
Fisher	Anhydrous Powder	<2.7	<5	<2.5	4	260	98	600	<3	<4	<1
Fisher	Dihydrate	<2.7	<5	<2.5	<2	15	110	44	<3	<4	<1
Los Alamos	Fused	<2.7	159	<2.5	9	12,300	71	6900	<3	<4	<1
Sargent Welch	8 mesh	<2.7	160	<2.1	5	16,100	45	7300	<3	<4	<1

TABLE 3. Impurities-Product Metal Versus PuO<sub>2</sub> by Salt Source

	Al	B	C	Cr	Fe	Ga	Ni	Si	U	Ta	Salt Source/Type
	ppm										
Impurities in PuO <sub>2</sub>	43	<1	119	65	65	150	-	28	398	-	Baker Dihydrate
Impurities in Corresponding Metal Product	99	12	176	54	245	68	35	275	80	115	
Impurities in PuO <sub>2</sub>	30	<1	75	23	50	100	-	28	549	-	Fisher Anhyd. Powder
Impurities in Corresponding Metal Product	136	16	157	66	277	78	41	213	72	70	
Impurities in PuO <sub>2</sub>	25	<1	130	38	50	200	-	5	211	-	Los Alamos Fused
Impurities in Corresponding Metal Product	83	449	176	40	225	57	<27	297	70	30	
Impurities in PuO <sub>2</sub>	250	<1	106	43	20	138	-	750	426	-	Sharpe Salt
Impurities in Corresponding Metal Product	173	436	200	36	335	63	<24	290	72	15	



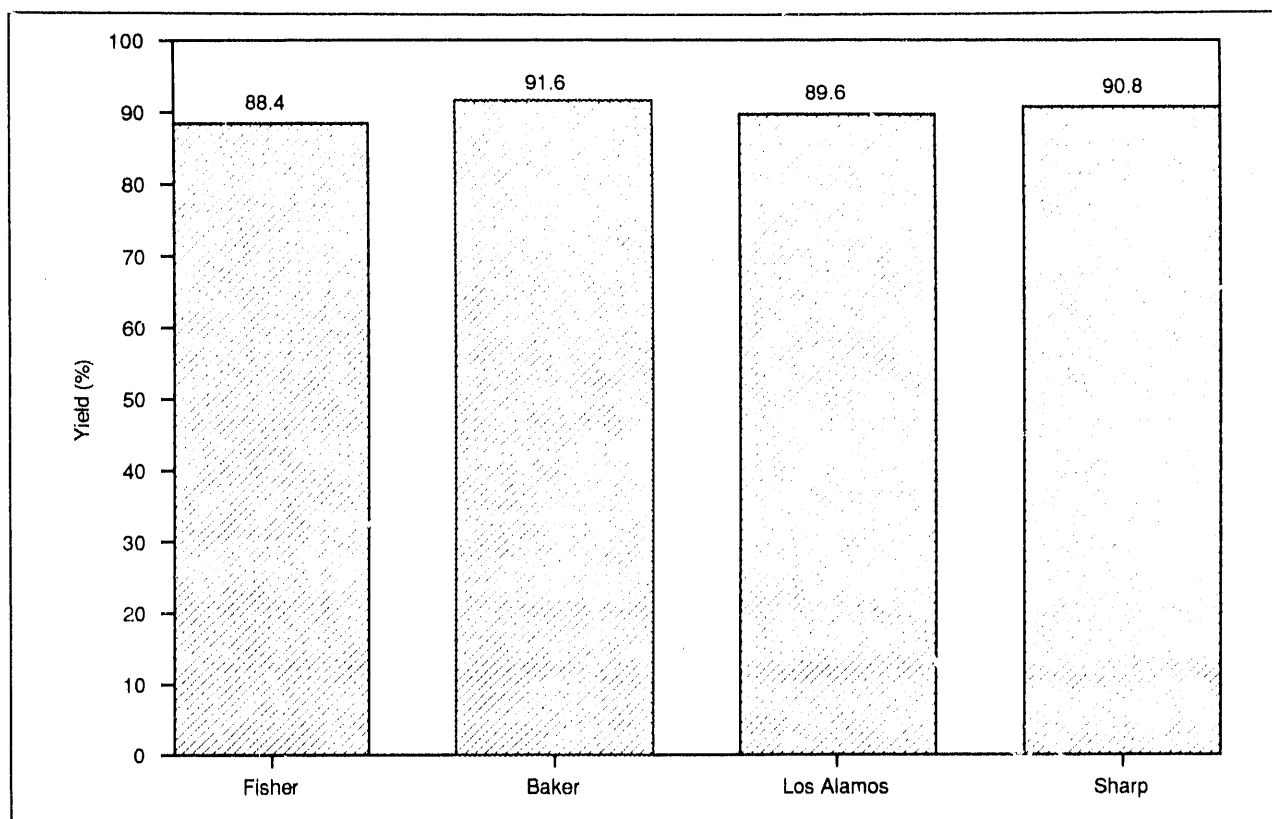


FIGURE 4. Yield as a Function of Salt Source

forming free alkali metals. These problems were foremost in selecting salts for experimental work.

The yields for these experiments versus salt type are shown in Figure 4. Each value is the average of two experiments, except the Sharpe salt where only one reduction is reported. Two reductions were made with the Sharpe salt, but one was ignored because of a <10% yield. This depressed yield could not be attributed to any mechanical or operator problems. All the yields are considered the same within experimental error. The yields were calculated as follows:

$$\text{percent yield} = \frac{(\text{grams of product metal})(100)}{(\text{grams of PuO}_2)(0.882)}$$

No evidence of alkali metal formation was observed.

The distribution of selected impurities is shown in Table 3. For oxides, all elemental analyses were

by emission spectroscopy except carbon (combustion method) and uranium (calorimetric method). For the product metals, carbon and uranium were analyzed in the same manner as oxides, silicon and boron analyses were by emission spectroscopy, and the remaining element analyses were by atomic absorption spectroscopy. Some anomalies appeared. An element-by-element evaluation follows:

A1 - It was suspected and subsequently demonstrated that aluminum results by emission spectroscopy on the oxide were biased low. Aluminum content in the metal is regarded as correct. In addition to the oxide, some aluminum could result from reaction of calcium metal with the 1 to 2 wt % aluminum oxide in the magnesium oxide reaction vessel.

B - Most of the boron in the salt reports to the product metal. The relative concentrations

are as expected from the salt data (Tables 2 and 3).

- C - Results are probably within the limits expected, considering inhomogeneity and analytical error.
- Cr - Results are consistent with the expectation (free energy data)<sup>1</sup> that chromium in the oxide will be reduced and report to the product metal.
- Fe - It was suspected and subsequently demonstrated that iron results by emission spectroscopy on the oxide are usually biased low. Therefore, iron content of the product metal was assumed to result from iron in the oxide.
- Ga - The gallium content of the metal products is substantially lower than expected. This means that most of the gallium remained with the salt phase or there was an analytical problem. It was not possible to obtain reliable analysis on the salt phase, so no material balance was done. The gallium problem was not resolved in Phase IIA.
- Ni - This element was low in the product metal. The oxide results were variable and not reported.
- Si - The calcium chloride was melted in quartz before pouring into a mold in the casting process. The high silicon content of the metal relative to the oxide (except that used in the Sharpe salt) is a consequence of the salt melting step.
- Ta - The use of a tantalum mold in the salt casting process did not introduce significant amounts of tantalum.
- U - If the analyses are correct, it is difficult to understand why the uranium did not report to the metal, considering the excess of calcium metal for reaction. Reduction of the uranium to the metallic state is expected based on the free energy data.<sup>1</sup> The inability to obtain

TABLE 4. Effect of Leaching on Calcium and Magnesium

Calcium (ppm)		Magnesium (ppm)	
Unleached	Leached	Unleached	Leached
490	578	999	1053
496	113	692	234
2379	53	720	167
336	53	1111	751
662	50	525	1686
507	50	866	596
292	320	5095	596
484	150	1893	1686
887	599	3032	751
627	459	22313	167

reliable analysis of the spent salt precluded a material balance so the uranium question was not resolved.

The calcium and magnesium values were excluded from Table 3 because consistent data could not be obtained on replicate samples from the same metal product. The problem was addressed as follows:

Ten samples selected arbitrarily from the plutonium metal products were analyzed for calcium and magnesium before and after water leaching. Each sample weighed approximately 10 grams and was leached with 5 to 8 ml of distilled water. After visual reaction ceased, the liquid was drained off and the metal sample was air dried. The results are presented in Table 4. With two exceptions, a value-by-value comparison shows a decrease in calcium and magnesium concentrations by leaching, within analytical error. A value-by-value comparison was necessary because there is no reason to expect the surface layer to be homogeneous from sample to sample.

The data support the general consensus that calcium and magnesium are distributed non-uniformly on the surface of DOR product metal.

TABLE 5. DOR Screening Test Data

DOR Exp. Number	Yield (%)	Al	B	C	Cr	Fe	Ga	Ni	Si	Ta	U
		(ppm)									
18	61	67	8	175	52	164	15	441	126	20	24
19	16	101	1	163	23	24	24	30	1000	10	16
20	4	*	1	*	63	327	49	42	250	10	*
21	19	469	1	162	35	97	19	22	5	10	39
22	65	5	5	76	5	236	5	34	500	20	38
23	24	94	7	136	53	213	96	40	223	10	56
24	92	224	3	189	163	229	60	39	30	10	17
25	64	27	3	162	39	41	19	25	34	2500	27
26	52	72	1	138	58	208	77	43	500	75	56
27	94	21	1	196	41	107	19	28	500	50	58
28	29	110	8	171	193	415	60	83	56	10	40
29	9	42	1	104	25	42	19	21	1200	200	51
30	50	56	8	215	67	162	43	34	75	10	35
31	59	29	6	132	257	188	143	2749	87	500	34
32	*	*	*	*	*	*	*	*	*	*	*
33	15	36	1	109	51	78	20	26	1200	10	47
34	33	143	7	233	32	176	19	42	115	20	39
35	67	161	1	165	39	83	19	25	625	55	44
Average	41	93	3	136	90	154	40	193	376	205	36
Std. Dev.	28	115	2	65	139	108	36	639	402	585	17

\*Not enough product metal for analysis.

With one inadvertent exception, no metal stirring occurred during this phase of work. Comparison of the photomicrographs and elemental maps of stirred and unstirred metal samples showed higher concentrations of silicon and magnesium in the stirred metal. The high silicon content is a consequence of melting the calcium chloride in a quartz mold. However, magnesium inclusions are in higher concentration in the stirred product metal.<sup>2</sup> Elemental mapping showed no detectable calcium in either case, so no photomicrographs were made. The magnesium data is significant in planning future work. It should be noted that present production practice is to stir the metal product.

### Screening Experiments

Eighteen DOR and ten recalcination experiments were completed for the screening section of Phase IIB. Table 5 lists the button purities and yields. The Statistical Applications Group performed a statistical analysis of these experiments.

Overall, the yields were low. Therefore, statistical results are based on experiments with an average yield of 41%. This may be due to the large range of variables. However, these statistics conflict with earlier results obtained under similar conditions. The disagreement could not be explained by the known chemical process. This presented a strong

possibility of an unknown factor not evident from the data in Table 5. The potential is illustrated by the spread in weight loss data for calcium chloride. Values ranged from a few tenths to nearly 10%. An unknown fraction of the loss (always occurring below 200 °C on the TGA traces) was due to moisture picked up during sampling, transport, and analysis. However, it is possible that moisture in the salt caused low yields. The statistics and results from previous small-scale experiments were used in determining whether to include the parameter in the fine-tuning experiments.

There were two main parameters in recalcination: recalcining temperature and time at temperature. Both parameters were studied for their individual effects on yield and purity. Neither had a statistically significant effect in these tests. These parameters were fixed in the fine-tuning experiments at 1000 °C and six hours (believed to be the optimum). These parameters are being further investigated in another more detailed project.

The next parameter was the salt-to-oxide ratio. Statistically, there were no significant effects, but there were potential interactions with other parameters that could not be estimated in the screening tests. Therefore, this parameter was retained in the fine-tuning tests to allow estimation of potential two-way interactions. The 3:1 ratio was thought to be too low for successful reduction in a production environment. The 4:1 and 5:1 ratios were therefore selected for further study.

Stirring was started at the melt temperature. Controlling this parameter was difficult. At 780 °C, salt melting was incomplete during some experiments; yet, at 820 °C, the reaction had already started, causing the temperature to rise quite suddenly before the operator could respond. Statistically, it had a slightly positive effect on yields starting at the lowest melt temperature. Because this parameter was difficult to control and early stirring was more reliable, this parameter was fixed at the lowest temperature possible.

Stirring speed and stirrer design are interdependent and highly scale dependent. The screening experiments were designed only to estimate single

variables, not interactions. Both the stirring speed and stirrer design had highly statistical significant effects on yield. The high stirring program proved the best of the three levels. The flat paddle was the simpler of the two designs. Taking into account the statistical significance of these two variables coupled with the scale dependency, it was decided that the best place to test these two parameters fully was in large-scale DOR experiments. The highest stirrer speed and the flat paddle stirrer were chosen, and no optimization was performed in this study.

The percent excess calcium had a positive effect on yield but a negative effect on purity. The higher the excess calcium, the higher the yield, but more calcium and magnesium collected on or in the button. Calcium and magnesium analyses were inconclusive and suspect, indicating need for further study. The general conclusion was that 5% was too low and 45% was too high. The 25% excess had worked well in Phase IIA, so it was selected again as the midpoint. Ten percent and 40% were chosen as the low and high levels in the fine-tuning tests.

The hold time was considered necessary for proper consolidation of the button. This parameter had no impact on product yield or purity. Product consolidation appeared to be unaffected by the hold time in small-scale DOR. Procedure-wise, the shortest hold time allowed experiment completion in a single shift. Therefore, this variable was fixed at 15 minutes in the fine-tuning tests.

There was no significant difference between pelletized and cast salts on DOR yields in this portion of the experimental program. There was some doubt about how well the calcium and oxide were separated by the cast cakes. As stated earlier, the cast cakes were sampled before each experiment. This sampling caused the cakes to shatter, increasing the surface area of the cast salt and greatly reducing ability of the large chunks of salt to provide the proper barrier. In addition, there were some potential interactions with the salt type that needed further investigation. Therefore, both the salt type and calcium position parameters were included in later tests.

After calcining, the oxide was split into approximately 80-gram batches of as-is and -120-mesh particle size. Originally it was thought that at least 50% of the oxide would pass through a 120-mesh screen, but this was not true for most of the oxide batches. Screening the oxide increased in-box handling of the oxide and exposure time of the operator. As no definite effect could be attributed to the particle size, the oxide was used without screening in the fine-tuning tests.

In summary, only four parameters were selected for further testing in the fine-tuning experiments. The screening tests results were used to identify which parameters to focus on in later DOR experiments.

## Fine-Tuning Experiments

### Yields

The yield data were sorted or grouped to facilitate comparisons regarding salt form, calcium excess, calcium metal position, and salt-to-oxide ratio. The yield data for all experiments in Table 6 have a relatively small standard deviation. The average yield for the entire sample population in Table 6 compares favorably with work done at Los Alamos on a somewhat larger scale.<sup>3</sup> The small standard deviation suggests that groupings of the data with relatively large populations will be needed to establish significant trends. When the data is sorted by calcium excess, the yield averages do not differ at a confidence level high enough to be of interest. One comparison of salt form was made by grouping the data as shown in Table 7. The 40% excess calcium data were excluded because water leaching of two product buttons from 40% excess exhibited weight losses with yields decreased much further than the standard deviation. (See the subsection entitled Impurities, this report.) Application of the "t" test (Appendix C) to the data in Table 7 showed that the means differed at the 94% confidence level. Thus, a significant increase in yield resulted with cast salt.

TGA traces made on all composite samples of calcium chloride were less than 2% weight loss

below 200 °C. A typical trace is shown in Figure 5. Although still subject to uncertainties in moisture pickup on the sample versus actual salt charge, the maximum is substantially less than observed for the screening experiments.

A comparison was made of cast versus pelletized salt for each of the three calcium excesses in Table 8. The basis was a hypothesis that moisture might be more detrimental to yields at a lower calcium excess by reducing the amount of free calcium for reaction with plutonium oxide. Although the sample populations are too small to expect a meaningful confidence level from the "t" test, there is a trend to higher yields with increasing calcium excess in pelletized salt. Pelletized salt has a much greater surface area than cast salt and would more readily pick up moisture. The trend is thus consistent with the observations.

Considering the effects of excess calcium alone, Table 9 shows there is no difference in average yields for 25 and 40% excess calcium levels and that a slightly lower (approximately 1%) average yield was obtained using 10% excess calcium. Yield is calculated as follows:

$$\text{Yield} = \frac{\text{Button net weight}}{75 \text{ g oxide} \times 0.882 \text{ g Pu/g oxide}}$$

Whether the calcium metal was placed on the bottom of the crucible with the oxide above or the positions reversed made no significant difference in yields. The "t" test calculation is shown in Appendix D. The calcium metal and plutonium oxide were separated by 150 grams of calcium chloride. The cast salt was sized to reduce intermixing, compared with previous experiments.

When sorting according to salt-to-oxide ratio, there was no difference in average yield among total populations of 4:1 or 5:1 salt-to-oxide ratios. Dividing the populations of 4:1 and 5:1 into cast salt versus pelletized salt produces no difference between cast or pelletized salt at the 4:1 salt-to-oxide ratio. However, for 5:1, the average yield is 97.8% for cast salt versus 94.5% for pelletized salt. Applying the "t" test (Appendix E) to the cast versus pelletized salts for their average yields at a

TABLE 6. DOR Fine-Tuning Results

DOR Exp. Number	PSL Oxide	Excess Ca (%)	SLT to Oxide Ratio	Ca Pos.	Salt Entry	Wt. of Button (g)	Button Purity	Oxide Purity	*B Yield	Yield of Duplicate Exp.
47	C	10	5	B	Pell	61.0	0.993	0.882	91.7	92.5
62	A	10	4	B	Cast	64.1	0.998	0.882	96.6	97.9
48	C	10	4	M	Pell	59.6	0.995	0.882	89.7	98.2
*A 43	C	10	5	B	Pell	62.9	0.990	0.882	94.2	92.1
54	B	10	4	B	Cast	64.9	0.997	0.882	97.9	96.6
57	B	10	5	M	Cast	63.1	0.994	0.882	94.8	98.0
64	C	10	4	M	Pell	65.2	0.998	0.882	98.3	89.7
59	A	10	5	M	Cast	65.0	0.998	0.882	98.0	94.8
66	B	10	5	B	Pell	61.5	0.995	0.882	92.5	91.7
52	B	25	4	B	Cast	64.8	0.995	0.882	97.5	*C
67	B	25	5	B	Pell	65.9	0.997	0.882	89.3	97.8
45	C	25	5	M	Pell	58.4	0.991	0.882	87.4	96.6
53	C	25	4	B	Pell	64.6	0.998	0.882	97.4	*C
69	B	25	5	B	Pell	64.8	0.999	0.882	97.8	99.3
55	B	25	4	M	Cast	63.0	0.989	0.882	94.2	*C
60	B	25	5	M	Pell	64.3	0.994	0.882	96.6	87.4
51	B	25	5	M	Cast	66.0	0.998	0.882	99.7	98.6
65	B	25	4	M	Pell	62.6	0.998	0.882	94.5	*C
49	B	25	5	M	Cast	65.7	0.994	0.882	98.6	99.7
61	A	25	5	B	Cast	65.4	0.986	0.882	97.5	*C
56	C	40	4	B	Pell	64.5	0.995	0.882	97.1	98.4
50	B	40	4	M	Cast	62.7	0.998	0.882	94.6	95.6
46	C	40	5	M	Pell	63.0	0.995	0.882	94.7	96.1
58	A	40	5	B	Cast	66.0	0.993	0.882	99.1	96.9
63	A	40	4	M	Cast	63.4	0.998	0.882	95.6	94.6
41	C	40	5	M	Pell	64.0	0.993	0.882	96.1	94.6
68	A	40	5	B	Cast	64.2	0.999	0.882	96.9	99.1
42	C	40	4	B	Pell	65.6	0.992	0.882	98.2	97.1
Avg.						63.8	0.995	0.882	95.9	
Std. Dev.						1.8	0.0032	0.0001	2.8	
Foundry Specs										

\*A Different stirring program used.

\*B Button weight/(75 g)(Oxide Purity)

\*C No Duplicate Experiment

A PSL 44303

B PSL 44304

C PSL 44305

TABLE 6. DOR Fine-Tuning Results (Concluded)

DOR Exp. Number	Al	Am	B	C	Cr	Fe	Ga	Ni	Si	Ta	U	W	*D	*E	
	(ppm)														
47	47	47	9	220	480	840	21	768	47	10	31	<10	1026	1609	
62	68	52	10	99	52	164	33	28	38	262	33	<10	1199	193	
48	42	50	6	249	309	749	20	139	32	17	37	<10	832	888	
*A 43	64	44	7	394	225	1207	20	160	68	137	46	<10	1410	1368	
54	91	52	11	84	34	138	26	32	109	1550	35	<10	2116	171	
57	96	45	11	126	440	506	19	96	80	1750	30	<10	1836	603	
64	85	50	8	261	321	701	19	102	57	10	33	<10	1501	803	
59	55	56	9	75	46	150	30	33	19	75	33	<10	870	184	
66	71	50	6	193	401	511	19	2708	58	130	41	<10	1368	3219	
52	158	48	10	174	130	188	19	58	50	512	34	<10	2166	247	
67	223	38	17	201	93	227	20	589	66	17	34	<10	2980	817	
45	197	42	10	209	572	947	19	892	41	10	34	<10	2468	1839	
53	46	52	7	190	295	719	19	129	45	25	29	<10	996	849	
69	201	48	5	315	93	251	19	51	61	150	35	<10	2696	303	
55	132	41	5	161	178	175	19	52	28	75	32	<10	1676	228	
60	217	43	6	371	98	280	18	40	11	17	33	<10	2359	320	
51	218	42	3	134	203	233	18	45	28	750	34	<10	2542	279	
65	127	55	4	201	98	264	19	33	25	10	35	<10	1601	297	
49	218	36	6	118	178	208	18	37	41	10	21	<10	2667	246	
61	53	82	8	88	37	144	30	35	5	150	33	<10	700	180	
56	103	54	8	300	298	722	19	132	73	17	33	<10	1841	854	
50	66	55	3	123	165	204	18	54	44	1000	28	<10	1177	259	
46	267	122	8	214	352	917	25	159	35	10	30	<10	3125	1077	
58	50	40	20	120	82	270	36	2226	68	375	24	<10	1329	2497	
63	85	59	15	115	80	115	19	41	16	100	27	<10	1091	157	
41	304	86	7	386	344	873	20	123	30	30	39	<10	3420	996	
68	172	47	17	66	74	258	17	32	52	375	29	<10	2308	290	
42	317	28	10	276	409	901	20	143	47	10	18	<10	3720	1044	
Avg.	132	52	9	194	225	470	21	329	46	263	32	<10	1893	779	
Std. Dev.	82	17	4	91	154	320	4	628	22	444	5	0	819	743	
Foundry Specs	*D	200	50	200	100	*E	*D	*E	*D	100	100	200	<1300	<400	

\*D Al, Ga, Si: 1300&gt; [4 (ppm Ga) + 10 (ppm Al) + 10 (ppm Si)]

\*E Fe, Ni: 400&gt; [(ppm Fe) + (ppm Ni)]

**TABLE 7. Yield Data for Cast Versus Pelletized Salt (40% excess calcium experiments excluded)**

	Cast	Pelletized
	(%)	
	98.7	94.2
	99.7	87.5
		91.7
	97.6	89.8
	97.9	97.5
	94.2	96.6
	94.8	98.4
	98.1	94.5
	97.6	92.6
	96.7	99.4
		97.9
MEAN	97.3	94.6
S.D.	1.8	3.8

**TABLE 8. Yield Data for Cast Versus Pellet (Grouped by calcium excess)**

	10% Excess Calcium		25% Excess Calcium		40% Excess Calcium	
	Cast	Pellet	Cast	Pellet	Cast	Pellet
	(%)					
	94.8	94.2	98.7	94.5	94.6	97.1
	96.7	98.4	94.2	96.6	95.6	96.2
	98.1	89.8		87.5	99.1	94.7
	97.9	92.6	99.7	99.4	96.9	98.2
		91.7	97.6	97.5		
			97.6	97.9		
MEAN	96.9	93.3	97.6	97.5	96.6	96.6
S.D.	1.5	3.2	2.1	4.3	1.9	1.5

**FIGURE 5. TGA Trace of Calcium Chloride Salt Pellets**

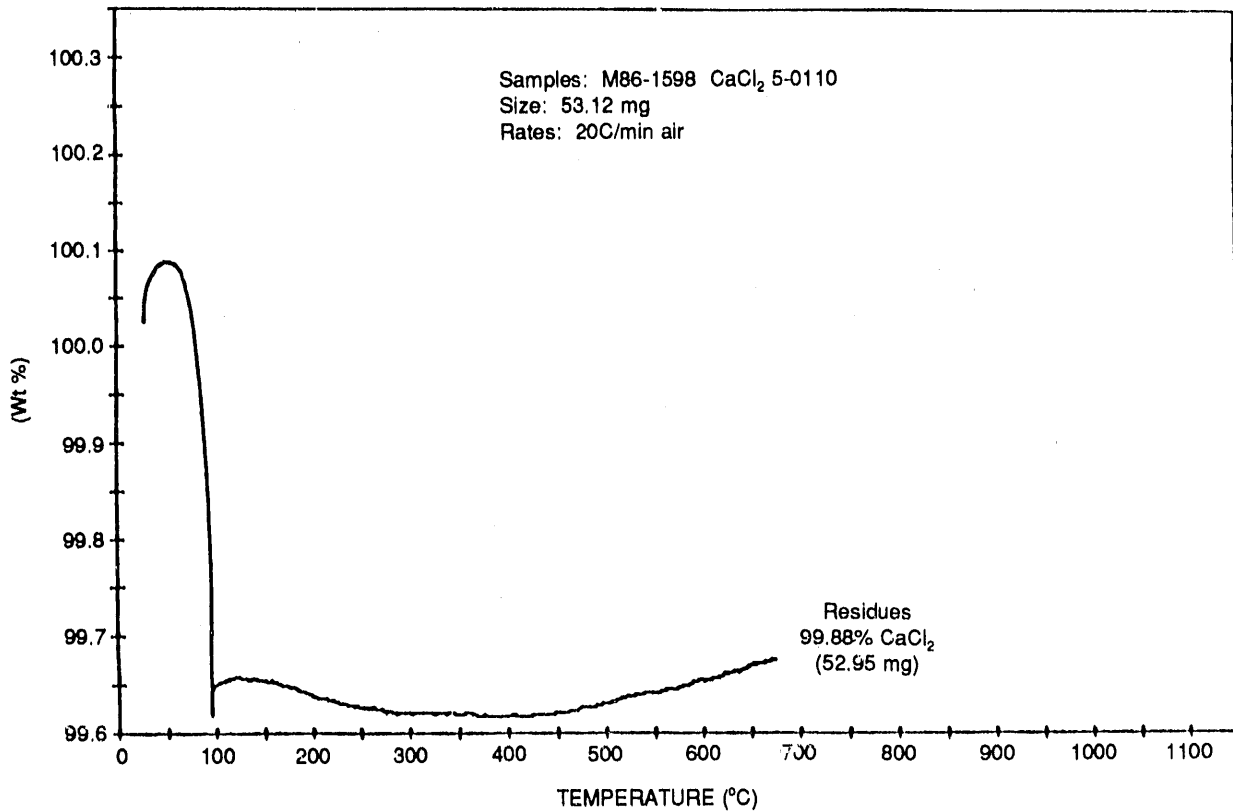




TABLE 9. Fine-Tuning Test Results Sorted by Excess Calcium

DOR Exp. Number	PSL Oxide	Excess Ca (%)	SLT to Oxide Ratio	Ca Pos.	Salt Entry	Wt. of Button (g)	Button Purity	Oxide Purity	*B Yield	Yield of Duplicate Exp.	Al (ppm)
47	C	10	5	B	Pell	61.07	0.993	0.882	91.70	92.58	47.00
62	A	10	4	B	Cast	64.11	0.998	0.882	96.67	97.92	68.50
48	C	10	4	M	Pell	59.68	0.995	0.882	89.79	98.20	42.50
*A 43	C	10	5	B	Pell	62.99	0.990	0.882	94.24	92.14	64.50
54	B	10	4	B	Cast	64.97	0.997	0.882	97.92	96.67	91.50
57	*B	10	5	M	Cast	63.15	0.994	0.882	94.84	98.07	96.00
64	C	10	4	M	Pell	65.21	0.998	0.882	98.35	89.79	85.50
59	A	10	5	M	Cast	65.00	0.998	0.882	98.07	94.84	55.50
66	B	10	5	B	Pell	61.55	0.995	0.882	92.58	91.70	71.00
52	B	25	4	B	Cast	64.87	0.995	0.882	97.57	*C	158.50
67	B	25	5	B	Pell	65.94	0.997	0.882	99.38	97.89	223.50
45	C	25	5	M	Pell	58.42	0.991	0.882	87.45	96.62	197.50
53	C	25	4	B	Pell	64.62	0.998	0.882	97.46	*C	46.50
69	B	25	5	B	Pell	64.82	0.999	0.882	97.89	99.38	201.00
55	B	25	4	M	Cast	63.06	0.989	0.882	94.23	*C	132.00
60	B	25	5	M	Pell	64.30	0.994	0.882	96.62	87.45	217.50
51	B	25	5	M	Cast	66.09	0.998	0.882	99.71	98.67	218.50
65	B	25	4	M	Pell	62.65	0.998	0.882	94.52	*C	127.50
49	B	25	5	M	Cast	65.70	0.994	0.882	98.67	99.71	218.50
61	A	25	5	B	Cast	65.47	0.986	0.882	97.59	*C	53.00
56	C	40	4	B	Pell	64.55	0.995	0.882	97.12	98.41	103.00
50	B	40	4	M	Cast	62.71	0.998	0.882	94.61	95.66	66.00
46	C	40	5	M	Pell	63.00	0.995	0.882	94.74	96.15	267.50
58	A	40	5	B	Cast	66.05	0.993	0.882	99.10	96.95	50.00
63	A	40	4	M	Cast	63.40	0.998	0.882	95.65	94.61	85.00
41	C	40	5	M	Pell	64.00	0.993	0.882	96.15	94.64	304.00
68	A	40	5	B	Cast	64.20	0.999	0.882	96.91	99.10	172.00
42	C	40	4	B	Pell	65.61	0.992	0.882	98.24	97.12	317.00
Avg.						63.83	0.995	0.882	95.99		132.19
Std. Dev.						1.86	0.0032	0.0001	2.86		82.34
Foundry Specs											*D
Avg. 10%						63.08	0.995	0.882	94.91		69.11
Std. Dev. 10%						1.85	0.003	0.000	2.91		17.95
Avg. 25%						64.18	0.994	0.882	96.46		163.09
Std. Dev. 25%						2.10	0.004	0.000	3.30		62.77
Avg. 40%						64.19	0.995	0.882	96.56		170.56
Std. Dev. 40%						1.11	0.003	0.000	1.49		103.68

\*A Different stirring program used

\*B Button weight/(75 g) (Oxide Purity)

\*C No Duplicate Experiment

\*D Al, Ga, Si: 1300&gt; [4 (ppm Ga) + 10 (ppm Al) + 10 (ppm Si)]

A PSL 44303

B PSL 44304

C PSL 44035

5:1 salt-to-oxide ratio shows (with 95% confidence) that cast salt produces significantly higher yields than pelletized salt.

No difference in average yield could be found by dividing the two salt-to-oxide ratio populations into the three levels of percent excess calcium.

Results of the physical characterization work showed there was no significant difference between the oxide from Line 16 and that from the Process Simulation Laboratory, either before or after recalcination. The only characteristic of noticeable difference was crystallite size after recalcination. The crystallite size of the recalcined Line 16 oxide was slightly greater than that of the recalcined Process Simulation Laboratory oxide. This difference caused no variation in behavior using these two oxides in this phase of DOR experiments. Detailed results of this physical characterization work will be discussed in another report.

### Impurities

Prior to the fine-tuning experiments, the means for measuring salt melt temperature was modified. During previous work, a closed-end tantalum tube containing a thermocouple was lowered into the melt. Near the end of the screening experiments phase, a commercially available thermocouple with a tantalum outer sheath over an inner Inconel sheath was used with no apparent problems. Subsequently, during the fine-tuning work, sheath corrosion occurred frequently and the thermocouples were replaced as attack appeared. Intermittent contamination of the DOR product metal with tantalum and nickel probably occurred. Therefore, the concentrations of these elements reported for this particular phase are probably inflated. To a lesser extent, the same may be said of chromium and iron since these are also present in Inconel.

Significant effort was expended in obtaining meaningful analytical data. The variability of calcium and magnesium values is shown in Table 10. As suggested in this report, calcium and magnesium are concentrated on the surface of

TABLE 10. Calcium and Magnesium in DOR Product by Atomic Absorption

Exp. No.	Calcium (ppm)	Magnesium (ppm)
41	8937,18665,265,578, 908,759,1522,386	82685,352310,3516, 12861
42	321,590,245,600	4157,6282,3792,7877
43	1177,220,1976,303	5356,2557,6320,2647
44	609,129,69,74,1046, 622,83,42	319,635,491,514
45	310,129	9092,2740,223,224
46	399	2263,204,164,165
47	665,265	3744,3756
48	137,561	446
49	74,74	2921,5157,782,765, 4712,2347,842,702
50	105,<51	194,663
51	82,141	3100,2287,485,481,875
52	119,67,56,298,98,92	11,438
53	360	2071,2975,678,560, <237,2609,641,204
54	<44,151	70,231
55	635,146	300,380
56	478,1091,682,34	1646,110,205,209,<230, 1589,34,461
57	167,<43,46,331, 50,>1980	191,297
58	<44	2705,207
59	378,40	2796,1873
60	97,203	73,140
61	15,510	3341,5100
62	<44,<49	610,963
63	61,68	384,210
64	177,136	90,82
65	326,454	2040,138
66	101,123	321,130
67	109,203	531,67
68	100,<45	632,520
69	111,89	127,77

DOR product from small-scale work, and there is no reason to expect a uniform layer. Because of the small metal product size, sampling normally included the untreated surface, and the scatter of data was expected. Distribution of calcium and

TABLE 11. PuO<sub>2</sub> Analyses Comparison

Iron (ppm)		Aluminum (ppm)	
Emission Spectroscopy	Atomic Absorption	Emission Spectroscopy	Atomic Absorption
25	157	50	238
25	135	10	81
25	164	10	108
250	52	25	159
250	80	50	122
10	71	25	85
10	52	50	163
25	134	10	233
25	128	25	316
<5	73	<5	186
25	141	10	336
25	60	25	126
250	135	50	99
		25	113
		50	110
		25	296
		25	132
		<5	161

magnesium between the interior and the surface needs further clarification.

The inability to obtain even a rough correlation for certain impurities between PuO<sub>2</sub> and metal product lead to a comparison of emission spectroscopy data and atomic absorption spectroscopy data. Atomic absorption results are generally more precise than those from emission spectroscopy. Comparison of aluminum and iron in plutonium oxide is depicted in Table 11. The iron values may be due more to non-homogeneity than bias, but 10 of 13 results are higher by atomic absorption than by emission spectroscopy. For aluminum in product metal, atomic absorption results compared reasonably well with the results by emission spectroscopy (Table 12). There is no reason to expect the atomic absorption results to be biased, so future analyses will utilize this technique.

The product metal impurity averages in Table 6 are discussed individually in relation to foundry specifications in a weighted combination of aluminum, silicon, and gallium, and for iron and nickel.

Al - The average concentration alone is sufficient to cause the combined foundry specification for 10 Al + 10 Si + 4 Ga <1300 ppm to be exceeded. The large standard deviation results, naturally, from the wide range of values in the table. Because most of the aluminum in the oxide reports to the product metal, the positive aspect is that approximately one-third of the aluminum values in the table would allow the combined foundry specification to be met. This suggests feasibility of controlling the process to provide acceptable aluminum concentrations in the oxide. Efforts to accomplish this are in progress.

TABLE 12. Aluminum Analysis of Product Metal Emission Spectroscopy Versus Atomic Absorption

	Emission Spectroscopy	Atomic Absorption
	(ppm)	
	103.0	20.0
	157.0	242.0
	99.0	211.0
	83.0	180.0
	81.0	19.0
	86.0	20.0
	135.0	215.0
	131.0	220.0
	280.0	123.0
	176.0	96.0
	157.0	55.0
	111.0	55.0
	114.0	51.0
	138.0	55.0
	127.0	66.0
	137.0	70.0
	280.0	66.0
	243.0	34.0
	289.0	33.0
	262.0	78.0
	243.0	326.0
	124.0	20.0
Average	161.6	102.5
Standard Deviation	68.7	86.5

When the data in Table 6 are sorted by calcium excess (Table 9), the average aluminum concentration in the buttons for 10% excess calcium is much less than either the 25 or the

40% excess calcium levels. The button calcium concentration is a function of how much calcium is added in a reduction (as discussed earlier) and aluminum concentration is less for the smaller percent excess calcium addition; therefore, one can conclude that aluminum is somehow associated with calcium.

Another way of controlling the Al-Si-Ga specification is by electrorefining the DOR product. Using the averages in Table 6, the percentage of DOR product for electrorefining and subsequent blending with the balance of the DOR product can be calculated with the following assumptions:

1. Oxide containing 1000 grams of plutonium yields 955 grams of DOR product.
2. Ten percent of the impurities will be in the electrorefining product.
3. Eighty percent of the DOR product accumulated as electrorefining product (80% product yield from ER).
4. Plutonium in the electrorefining residues will be ultimately converted to a usable form.

Calculations are shown in Appendix F with estimation that 40% of the DOR product requires electrorefining.

A more productive way of utilizing electrorefining would be to select six products from 28 with the greatest \*D values [ $*D = 10(\text{ppm Al}) + 10(\text{ppm Si}) + 4(\text{ppm Ga})$ ] and apply the same calculation procedure used in Appendix F. In this case, only 21% of the DOR product needs electrorefining to lower the \*D value of the entire population average to <1300 ppm.

Am - Not of concern in DOR metal from oxide produced by the existing aqueous process.

B - Well below any level of concern with respect to specifications.

C - The population average meets the foundry specification, but is near the limit. The only source of carbon identified is  $\text{PuO}_2$ . If improvement is needed, calcining efficiency is an obvious candidate. Other possibilities are being considered.

Ca - Calcium is a reactant in the DOR process and not homogeneously distributed (Table 10). Planned large-scale experiments will provide more insight. The same comments apply to magnesium. Some additional investigations on calcium and magnesium distribution were performed.

Samples from two buttons (DOR 41 and DOR 42) were sent to Materials Technology Physical Metallurgy to identify impurities and their locations. The remainder of the buttons were sent to the Aqueous Recycle Technology group for leaching in distilled water in an attempt to remove surface impurities.

#### Physical Metallurgy Analysis

The sample from DOR 41 showed calcium agglomerated at the surface and magnesium intermixed throughout the entire button. Phosphorous and chlorine were found in trace amounts only. Oxygen was not present with the calcium or magnesium.<sup>4</sup>

The DOR 42 specimen was free from inclusions except a light concentration of impurities at one end. These impurities were identified as magnesium with chlorine present in a few cases. An edge of the specimen near the impurity concentration contained elemental magnesium and a band of magnesium oxide.

#### Aqueous Recycle Technology Analysis

When leached, DOR 41 and DOR 42 lost 13% and 4% of their weight, respectively. This supports the Physical Metallurgy results that showed DOR 41

had large agglomerations of calcium at the surface and magnesium dispersion throughout the button while DOR 42 showed only small quantities of magnesium and magnesium oxide localized in one area. The leach solution along with a small amount of precipitate contained within the solution were analyzed for plutonium. Less than one-half gram of plutonium was found in the precipitate (compared with the 6.5-gram weight loss from the two buttons), and no plutonium was found in the leach solution. The weight loss from the buttons resulted from elements or compounds reacting with water. The major impurities in the buttons are calcium and magnesium; and because they readily react with water, they are assumed to be the major constituents removed by leaching.

Cr - The oxide analyses for chromium (Table 13) do not account for the levels in the metal products. The fact that previous small-scale experiments (Salt Comparison) did not show a problem with chromium levels, along with the possibility for contamination from corrosion of the thermocouples, suggests that chromium will not present a problem in future work.

Fe - Iron is not expected to present a problem for the same reason explained for chromium.

Ni - Nickel is not expected to be a concern for the same reason as given for chromium.

Although the need to electrorefine because of the iron and nickel content in the product metal is unlikely, calculations can be made similar to those made for the aluminum plus gallium plus silicon Foundry specification. They show that if the six products used for the previous calculation, plus the three highest for iron plus nickel, plus one third of the total product were electrorefined and blended, the iron plus nickel Foundry specification would be met. The calculations are shown in Appendix G.

Averages for the remaining elements (except tantalum) in Table 6 meet their specifications. As previously stated, tantalum was introduced by corrosion of the thermocouple sheaths.

TABLE 13. Impurities in Plutonium Oxide

Run	Pu Chemistry		Photographic Emission Spectroscopy											IR Spec		Atomic Absorption			
	C	U	Ta	W	Al	B	Ca	Cr	Fe	Ga	Mg	Ni	Si	NO <sub>3</sub>	SO <sub>4</sub>	Al	Cr	Fe	Ni
41A-Box	71	<205	<10	<10	35	<1	<15	<7	<8	<5	<7	<5	<5	<0.02	1.27				
41B-Box	57	<205	<10	<10	18	<1	<5	<5	<5	<7	<5	<5	<8	<0.02	1.28				
41C-Box	72	223	<10	<10	18	<2	<5	15	<8	<7	<5	<5	<8	<0.02	1.52				
41D-Box	60	<205	10	<10	18	<1	<5	<5	<5	<7	<5	<5	<8	<0.02	1.19				
41A-Ox	64	<205	<10	<10	<15	<1	<5	<8	8	<7	<5	<5	<5	<0.02	<0.25				
41B-Ox	83	<205	<10	<10	<5	<1	<5	33	18	<7	<5	<5	<5	<0.02	<0.25				
41C-Ox	91	<205	<10	<10	<8	<1	<5	33	10	<7	<5	<5	<5	<0.02	<0.25				
41D-Ox	58	<205	<10	<10	<8	<2	<5	10	15	<7	<5	<5	<5	<0.02	<0.25				
42A-Box	251	252	<10	<10		<1	<5			50	5	10	10			111	35	50	<28
42B-Box	113	264	<10	<10		<1	<5			10	<5	10	10			113	31	141	<32
42C-Box	182	339	<10	<10		<1	<5			50	<5	10	10			99	<28	50	<30
42D-Box	108	300	<10	<10		<1	<5			10	<5	25	25			127	<29	40	<29
42A-Ox	134	249	<10	<10		<1	<5			10	<5	10	10			297	59	<30	<27
42B-Ox	277	284	<10	<10		<1	50			10	<5	10	10			132	<28	42	<31
42C-Ox	213	<200	<10	<10		<1	<5			10	<5	10	10			161	<29	135	<28
42D-Ox	226	282	<10	<10		<1	<5			10	<5	10	10			197	<26	60	<31
43A-Box	138	227	10	<10		<1	5			100	5	5	5			48	<28	135	<28
43B-Box	131	298	10	<10		<1	5			50	5	5	5			159	<29	164	<31
43C-Box	92	273	25	<10		<1	<5			25	<5	100	100			33	<31	40	<26
43D-Box	97	366	10	<10		<1	5			100	5	10	10			37	<30	39	<29
43A-Ox	126	344	10	<10		<1	5			50	5	5	5			81	<29	157	<29
43B-Ox	70	306	10	<10		<1	5			50	5	5	5			108	<28	64	<31
43C-Ox	141	358	10	<10		<1	5			25	5	<5	<5			57	<29	<30	<30
43D-Ox	110	348	10	<10		<1	5			50	5	5	5			293	<27	36	<32

Ox - After high temperature calcination

Box - Before high temperature calcination

Metal impurity data in Table 6 were sorted according to salt entry, and the population averages and standard deviations shown in Table 14 resulted. The difference appeared significant until it was noted that none of the experiments with cast salt included plutonium oxide from Batch C. As shown in Table 14, many impurities in the metal product from Batch C show higher averages than those from Batches A or B.

Evaluation of the analytical data available (Table 13) for oxide did not help make meaningful comparisons between impurities in the oxide and the product metal because different analytical methods had been used for the elements of interest. This, combined with possible contamination from corrosion of the thermocouples, made resolution of the issue impossible.

It is worth noting that the impurity in the product from each of three experiments (Nos. 61, 62, and 63, Table 6) meet foundry specifications except tantalum. This is not surprising, considering the thermocouple corrosion. Tantalum content has not been a problem in previous DOR product; therefore, it is reasonable to assume it will not be of future concern.

## CONCLUSION

Commercially available calcium chloride containing no boron or other unwanted impurities has been obtained. Both anhydrous and hydrated species have been used in the form of dried pellets and solid castings to obtain high yields in the DOR experiments. Neutron activation analysis proved that even when calcium chloride dihydrate is air dried at 230 °C, no significant amount of oxygenated species is present in the dried salt.

Parametric limits achieving 95% product metal yields have been established by experiments utilizing 100 grams or less of plutonium dioxide per experiment. The small-scale equipment offered several advantages over the large-scale equipment. These included less time expended, reduced quantities of fissile materials, and less waste requiring recovery.

It was shown that a salt-to-oxide ratio of 4 to 1 provided high yields with both cast and pelletized salt.

Calcium metal excesses of 10, 25, and 40% were used successfully. However, significant calcium levels were found in the product metal from the 40% calcium experiments, as evidenced by the high weight losses on leaching. Product yields did not differ significantly with calcium metal position. Evaluation of the yield data for cast versus pelletized salt with 10 and 25% excess calcium showed a 2.7% higher yield for cast salt at the 94% confidence level.

Although not proven conclusively, the hypothesis that moisture was picked up by calcium chloride or plutonium oxide from the glovebox atmosphere is consistent with observations and results. High yields were obtained consistently when precautions were taken to minimize moisture pickup with respect to plutonium oxide and calcium chloride. It is reasonable to assume that moisture effects on yield would be more pronounced as scale is reduced. Thus, small-scale yields should be "worst case" in comparison to full-scale yields with equivalent moisture contact. No evidence of foaming was observed during any small-scale experiments. The implications are that careful handling or improved operating procedures are required to obtain maximum yields when working in a relatively moist glovebox atmosphere.

Each of the two stirrer designs produced product metal yields in the 90+% range. Thus, adequacy, but not optimization, was established.

Of the impurities in DOR product, those of greatest concern are aluminum, chromium, iron, nickel, and tantalum because average concentrations of these elements presented the largest deviations from foundry specifications. Aluminum was present in the feed oxide, as shown by the atomic absorption spectroscopy analyses in much higher concentration than indicated by the emission spectroscopy analyses used heretofore. The high concentrations of other elements probably resulted to a significant extent from thermocouple corrosion. Aluminum presents the greatest concern regarding corrective

TABLE 14. Fine-Tuning Test Results Sorted by Salt Entry

DOR Exp. Number	PSL. Oxide	Excess Ca (%)	SLT to Oxide Ratio	Ca Pos.	Salt Entry	Wt. of Button (g)	Button Purity	Oxide Purity	*B Yield	Yield of Duplicate Exp.
55	B	25	4	M	Cast	63.06	0.989	0.882	94.23	*C
59	A	10	5	M	Cast	65.00	0.998	0.882	98.07	94.84
50	B	40	4	M	Cast	62.71	0.998	0.882	94.61	95.66
68	A	40	5	B	Cast	64.20	0.999	0.882	96.91	99.10
52	B	25	4	B	Cast	64.87	0.995	0.882	97.57	*C
54	B	10	4	B	Cast	64.97	0.997	0.882	97.92	96.67
61	A	25	5	B	Cast	65.47	0.986	0.882	97.59	*C
58	A	40	5	B	Cast	66.05	0.993	0.882	99.10	96.95
49	B	25	5	M	Cast	65.70	0.994	0.882	98.67	99.71
63	A	40	4	M	Cast	63.40	0.998	0.882	95.65	94.61
62	A	10	4	B	Cast	64.11	0.998	0.882	96.67	97.92
57	B	10	5	M	Cast	63.15	0.994	0.882	94.84	98.07
51	B	25	5	M	Cast	66.09	0.998	0.882	99.71	98.67
47	C	10	5	B	Pell	61.07	0.993	0.882	91.70	92.58
66	B	10	5	B	Pell	61.55	0.995	0.882	92.58	91.70
69	B	25	5	B	Pell	64.82	0.999	0.882	97.89	99.38
46	C	40	5	M	Pell	63.00	0.995	0.882	94.74	96.15
53	C	25	4	B	Pell	64.62	0.998	0.882	97.46	*C
64	C	10	4	M	Pell	65.21	0.998	0.882	98.35	89.79
45	C	25	5	M	Pell	58.42	0.991	0.882	87.45	96.62
*A 43	C	10	5	B	Pell	62.99	0.990	0.882	94.24	92.14
56	C	40	4	B	Pell	64.55	0.995	0.882	97.12	98.41
41	C	40	5	M	Pell	64.00	0.993	0.882	96.15	94.64
65	B	25	4	M	Pell	62.65	0.998	0.882	94.52	*C
60	B	25	5	M	Pell	64.30	0.994	0.882	96.62	87.45
67	B	25	5	B	Pell	65.94	0.997	0.882	99.38	97.89
48	C	10	4	M	Pell	59.68	0.995	0.882	89.79	98.20
42	C	40	4	B	Pell	65.61	0.992	0.882	98.24	97.12
Avg.						63.83	0.995	0.882	95.99	
Std. Dev.						1.86	0.0032	0.0001	2.86	
Foundry Specs										
Avg. Cast						64.52	0.995	0.88	97.04	
Std. Dev. Cast						1.13	0.004	0.00	1.69	
Avg. Pell						63.23	0.995	0.88	95.08	
Std. Dev. Pell						2.14	0.003	0.00	3.32	

\*A Different stirring program used  
 \*B Button weight/(75 g) (Oxide Purity)  
 \*C No Duplicate Experiment

A PSL 44303  
 B PSL 44304  
 C PSL 44035



TABLE 14. Fine-Tuning Results Sorted by Salt Entry (Concluded)

RFP-4128

DOR Exp. Number	Al	Am	B	C	Cr	Fe	Ga	Ni	Si	Ta	U	W	*D	*E
	(ppm)													
55	132	41	5	161	178	175	19	52	28	75	32	<10	1676	228
59	55	56	9	75	46	150	30	33	19	75	33	<10	870	184
50	66	55	3	123	165	204	18	54	44	1000	28	<10	1177	259
68	172	47	17	66	74	258	17	32	52	375	29	<10	2308	290
52	158	48	10	174	130	188	19	58	50	512	34	<10	2166	247
54	91	52	11	84	34	138	26	32	109	1550	35	<10	2116	171
61	53	82	8	88	37	144	30	35	5	150	33	<10	700	180
58	50	40	20	120	82	270	36	2226	68	375	24	<10	1329	2497
49	218	36	6	118	178	208	18	37	41	10	21	<10	2667	246
63	85	59	15	115	80	115	19	41	16	100	27	<10	1091	157
62	68	52	10	99	52	164	33	28	38	262	33	<10	1199	193
57	96	45	11	126	440	506	19	96	80	1750	30	<10	1836	603
51	218	42	3	134	203	233	18	45	28	750	34	<10	2542	279
47	47	47	9	220	480	840	21	768	47	10	31	<10	1026	1609
66	71	50	6	193	401	511	19	2708	58	130	41	<10	1368	3219
69	201	48	5	315	93	251	19	51	61	150	35	<10	2696	303
46	267	122	8	214	352	917	25	159	35	10	30	<10	3125	1077
53	46	52	7	190	295	719	19	129	45	25	29	<10	996	849
64	85	50	8	261	321	701	19	102	57	10	33	<10	1501	803
45	197	42	10	209	572	947	19	892	41	10	34	<10	2468	1839
*A 43	64	44	7	394	225	1207	20	160	68	137	46	<10	1410	1368
56	103	54	8	300	298	722	19	132	73	17	33	<10	1341	854
41	304	86	7	386	344	873	20	123	30	30	39	<10	3420	996
65	127	55	4	201	98	264	19	33	25	10	35	<10	1601	297
60	217	43	6	371	98	280	18	40	11	17	33	<10	2359	320
67	223	38	17	201	93	227	20	589	66	17	34	<10	2980	817
48	42	50	6	249	309	749	20	139	32	17	37	<10	832	888
42	317	28	10	276	409	901	20	143	47	10	18	<10	3720	1044
Avg.	132	52	9	194	225	470	21	329	46	263	32	<10	1893	779
Std. Dev.	82	17	4	91	154	320	4	628	22	444	5	0	819	743
Foundry Specs	*D	200	50	200	100	*E	*D	*E	*D	100	100	200	<1300	<400
Avg. Cast	112.6	50.6	10.1	114.3	130.9	212.0	23.3	213.2	44.73	537.3	30.5	0.0	1667.4	425.3
Std. Dev. Cast	58.6	11.1	4.9	30.6	105.9	96.0	6.5	581.2	27.3	549.9	4.0	0.0	628.2	607.7
Avg. Pell	154.3	54.2	8.1	265.5	292.7	674.1	19.9	411.3	46.6	40.1	34.0	0.0	2089.5	1085.4
Std. Dev. Pell	94.2	21.8	2.9	69.9	142.7	291.6	1.5	667.5	17.1	49.9	5.9	0.0	909.7	712.0

\*D Al, Ga, Si: 1300 &gt; [4 (ppm Ga) + 10 (ppm Al) + 10 (ppm Si)]

\*E Fe, Ni: 400 &gt; [(ppm Fe) + (ppm Ni)]

action. Selective electrorefining of 21% of the DOR product and subsequent blending with the original material would allow the specification for aluminum, silicon, and gallium to be met. A better approach would be reducing aluminum content of the plutonium oxide going to the DOR process.

Calcium and magnesium were surface contaminants on the unstirred small-scale DOR products. The product metal was stirred during one experiment, and magnesium was observed in the interior of the button by elemental mapping. Calcium was not detected inside the button.

The concentration of iron and nickel in the DOR product was compromised by corrosion of the tantalum sheath covering the Inconel thermocouple assembly in units procured off-site. Contamination of the DOR product metal with tantalum, nickel, iron, and chromium must have occurred. It was impossible to isolate the magnitude of product contamination by thermocouple corrosion. Therefore, calculation was made of the fraction of DOR product metal needing electrorefining so that blending the electrorefined product with the remaining untreated DOR product metal would yield a foundry acceptable material. The calculation shows that if six DOR product metals are electrorefined because of aluminum, then electrorefining an additional three and one-third product metals (representing one-third of the total DOR product) and blending with the remaining DOR product metals will allow the foundry specification to be met. This should be regarded as a "worst case" with respect to iron and nickel. It should be noted that chromium essentially meets the specification with the one-third electrorefining scenario.

The high tantalum in the DOR product is not consistent with the levels found during previous small-scale work. This, along with the known corrosion problem, leads to the conclusion that tantalum impurity levels can be controlled.

## RECOMMENDATIONS

The use of cast calcium chloride is recommended based on the increased yields obtained in this study and the reduced potential for moisture pickup. Special effort may be needed to adapt the exclusive use of cast salt in Production Operations. Efforts are under way to permit operating with cast salt in the production parameter verification (Phase IIC).

A 4-to-1 salt-to-oxide ratio would reduce salt waste generation 20% without sacrificing yield; therefore, it was recommended for inclusion in Phase IIC and the production yield demonstration (Phase IIF). The recommendations were accepted.

A calcium excess of approximately 25% is recommended. A 10% excess was used successfully in the small-scale work but under highly controlled conditions. Excesses of 10 and 20% were recommended and will be compared in Phase IIC while 25% excess was recommended and will be used in Phase IIF.

Calcium metal positioning made no difference in yield. The scatter of sample results precludes a comparison of magnesium metal generation from reaction with the crucible. Common practice is to position the calcium near the middle of the salt charge, and that is recommended.

Stirring is scale-dependent and is included for more detailed investigation in Phase IIC. The results should provide the basis for a recommendation to Production Operations.

The question of hold time after stirring may be scale-dependent, and the results of Phase IIC should again be the basis for recommendations.

Some evidence of increasing magnesium inclusions, when the metal product was stirred, was obtained from the small-scale experiments. However, no successful large-scale DOR runs have been made without stirring the metal phase. The recommendation was made and accepted to compare stirred versus non-stirred in Phase IIC.

**REFERENCES**

1. A. Glassner, *The Thermochemical Properties of Oxides, Fluorides, and Chlorides to 2500 °K*, ANL-5107, Argonne National Laboratory, 1957.
2. D. H. Riefenberg, *Plutonium Inclusions Analysis*, RFP-4412, Rockwell International, Rocky Flats Plant, Golden, CO, November 1, 1986.
3. L. J. Mullins and C. L. Foxx, *Direct Reduction of  $^{238}\text{PuO}_2$  and  $^{239}\text{PuO}_2$  to Metal*, LA-9073, Los Alamos National Laboratory, 1982.
4. D. H. Riefenberg, "Plutonium Inclusions Analysis (2)," RFP-4411, Rockwell International, Rocky Flats Plant, Golden, CO, February 17, 1987.

**APPENDIX A****Neutron Activation Results on Calcium Chloride**

Samples of Fisher anhydrous calcium chloride powder, Baker  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  crystals, and pellets made from the Fisher powder were dried in an air oven at approximately 230 °C. The samples were transferred to an inert atmosphere glovebox where they were re-dried to remove any moisture picked up during transfer and then individually sealed in polyethylene capsules. The capsules were sent to IRT Corporation for analysis. The neutron activation results are as follows:

Sample Type	Sample Weight	O (%)	Calculated as CaO (%)
Fisher Powder (Anhydrous)	8.58	0.09	0.23
Baker $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	7.56	0.10	0.25
Fisher Pelletized (Anhydrous)	8.54	0.07	0.18

## APPENDIX B

Foundry Specifications for Plutonium Metal  
(All Values in ppm)

Element	Upper Limit	Element	Upper Limit
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

\*For Ga, Al, and Si: Each button shall conform to the following limits:

$4 \text{ (ppm Ga)} + 10 \text{ (ppm Al)} + 10 \text{ (ppm Si)} < 1300$

\*\*The Fe plus Ni shall be  $< 400$  ppm

## APPENDIX C

"t" test calculation for data in Table 8

<u>Cast</u>	<u>Pelletized</u>
$\bar{X}_9 = 97.3$	$\bar{X}_{11} = 94.6$
S.D. = 1.8	S.D. = 3.8
S.D. = S	
$S_c^2 = 1.8^2 = 3.24$	$S_p^2 = 3.8^2 = 14.44$
$V_c = \frac{3.24}{9} = 0.36$	$V_p = \frac{14.44}{11} = 1.31$

$$f = \frac{(0.36 + 1.31)^2}{\frac{0.13^2}{10} + \frac{1.72^2}{12}} - 2 = 16$$

from the t vs. f table,  $t = 2.07$  for the 94% confidence level.

$$u = (t) \times (V_c + V_p)^{1/2}$$

$$(V_c + V_p)^{1/2} = 1.29$$

$$u = (1.29) \times (2.07) = 2.67$$

$$|\bar{X}_c - \bar{X}_p| = 2.7$$

Since  $|\bar{X}_c - \bar{X}_p| > u$ , cast and pelletized differ with regard to their average performance at the 94% confidence level.

## APPENDIX D

"t" test calculation for data in Table 10 sorted by position

Ca on Bottom

$$\bar{X}_b = 96.74$$

$$S.D. = 2.21$$

$$S_b^2 = 4.88$$

$$V_b = \frac{4.88}{14} = 0.35$$

PuO<sub>2</sub> on Bottom

$$\bar{X}_m = 95.95$$

$$S.D. = 2.91$$

$$S_m^2 = 8.47$$

$$V_m = \frac{8.47}{14} = 0.60$$

$$f = \frac{(0.35 + 0.60)^2}{\frac{0.35 + 0.60}{15}} - 2 = 14.3$$

$$t_{.95} = 1.761$$

$$(V_b + V_m)^{1/2} = 0.975$$

$$u = (t_{1/2}) \times (V_b + V_m)^{1/2} = (1.761)(0.975) = 1.72$$

$$|\bar{X}_b - \bar{X}_m| = 0.79$$

Since  $|\bar{X}_b - \bar{X}_m|$  is not greater than  $u$ , the means of the sample populations do not differ at the 90% confidence level.

Note: As a point of reference, the degree of not differing increases with increasing confidence level.

## APPENDIX E

"t" test yield calculation for the salt-to-oxide ratio  
(4:1) calcium position interaction, data from Table 10

<u>Bottom</u>	<u>Middle</u>
$\bar{X}_6 = 97.5$	$\bar{X}_6 = 94.5$
S.D. = 0.6	S.D. = 2.8
S.D. = S	
$S_b^2 = 0.56^2 = 0.31$	$S_m^2 = 2.8^2 = 7.84$
$V_b = \frac{0.36}{6} = 0.052$	$V_m = \frac{7.84}{6} = 1.31$

$$f = \frac{(0.05 + 1.31)^2}{\frac{0.052}{7} + \frac{1.31^2}{7}} - 2 = 6$$

from the t vs. f table, t = 2.58 for the 96% confidence level.

$$u = (t) \times (V_b + V_m)^{1/2}$$

$$(V_b + V_m)^{1/2} = 1.15$$

$$u = (2.58) \times (1.15) = 2.97$$

$$|\bar{X}_b - \bar{X}_m| = 2.98$$

Since  $|\bar{X}_b - \bar{X}_m| > u$ , cast and pelletized differ with regard to their average performance at the 96% confidence level.



## APPENDIX E (Concluded)

"t" test calculation for cast vs. pellets at  
5:1 salt-to-oxide ratio from Table 12

<u>Cast</u>	<u>Pelletized</u>
$\bar{X}_7 = 97.8$	$\bar{X}_9 = 94.5$
S.D. = 1.6	S.D. = 3.6
S.D. = S	
$S_c^2 = 1.6^2 = 2.6$	$S_p^2 = 3.6^2 = 13.0$
$V_c = \frac{2.6}{7} = 0.36$	$V_p = \frac{13.0}{9} = 1.44$

$$f = \frac{(0.36 + 1.44)2}{\frac{0.36^2}{8} + \frac{1.44^2}{10}} - 2 = 13$$

from the table,  $t = 2.16$  for the 95% confidence level.

$$u = (t) \times (V_c + V_p)^{1/2}$$

$$(V_c + V_p)^{1/2} = 1.34$$

$$u = (2.16) \times (1.34) = 2.90$$

$$|\bar{X}_c - \bar{X}_p| = 3.3$$

Since  $|\bar{X}_c - \bar{X}_p| > u$ , cast and pelletized differ with regard to their average performance at the 95% confidence level.

## APPENDIX F

### Calculations for Electrorefining Requirements Based on Aluminum, Silicon, and Gallium Impurity Levels

Using X as the grams of DOR product to electrorefining,

$$\text{PPM Al in blend} = \frac{132(955 - X) + 13.2(0.8X)}{955 - X + 0.8X} = \frac{126060 - 132X + 10.56X}{955 - 0.2X} = \frac{126060 - 121.44X}{955 - 0.2X}$$

$$\text{PPM Si in blend} = \frac{47(955 - X) + 4.7(0.8X)}{955 - 0.2X} = \frac{44885 - 47X + 3.76X}{955 - 0.2X} = \frac{44885 - 43.24X}{955 - 0.2X}$$

$$\text{PPM Ga in blend} = \frac{21(955 - X) + 2.1(0.8X)}{955 - 0.2X} = \frac{20055 - 21X + 1.68X}{955 - 0.2X} = \frac{20055 - 19.32X}{955 - 0.2X}$$

$$\frac{10(126060 - 121.44X)}{955 - 0.2X} + \frac{10(44885 - 43.24X)}{955 - 0.2X} + \frac{4(20055 - 19.32X)}{955 - 0.2X} = 1300$$

$$1260600 - 1214.4X + 448850 - 432.4X + 80220 - 77.28X = 1241500 - 260X$$

$$1789670 - 1724.08X = 1241500 - 260X$$

$$548170 = 1464.08X$$

$$X = 374.4$$

$$\% \text{ DOR Product to ER} = \frac{374.4 * 100}{955} = 39.2$$

## APPENDIX G

Calculations for Electrorefining Requirements  
Based on Iron and Nickel Impurity Levels

Please note: The same assumptions made for Appendix F apply.

The average Iron and Nickel in Product Metal equals:

$$\frac{[322 + 82 + 184 + 30 + 25 + 108 + 250 + 100 + 104 + (0.333)*(161)]}{9.333} = 134.9 \text{ ppm}$$

The average Iron and Nickel in the remaining DOR Product Metal equals:

$$\frac{[(0.667)*(1609) + 193 + 888 + 1368 + 171 + 603 + 803 + 184 + 247]}{18.667} +$$

$$\frac{(849 + 228 + 320 + 229 + 297 + 180 + 854 + 259 + 157 + 290)}{18.667} = 495.3 \text{ ppm}$$

The Iron and Nickel after Blending equals:

$$\frac{(134.9)*(9.333)*(0.8) + (495.3)*(18.667) + (400)*(9.333)*(0.2)}{28} =$$

$$\frac{1006.9 + 9247.3 + 746.4}{28} = \frac{11000.6}{28} = 393 \text{ ppm}$$

**END**

---

**DATE  
FILMED**

4/10/92

