RFP-3858
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U. S. DEPARTMENT OF ENERGY
CONTRACT DE-AC04-76DPO3533

Printed in the United States of America
Available from the
National Technical Information Service
U.S. Department of Commerce
Springfield, Virginia 22161
Price Code: 001-050 pages, Code A02
Price Code: 026-050 pages, Code A03
Price Code: 051-075 pages, Code A04
Price Code: 076-100 pages, Code A05
Price Code: 101-125 pages, Code A06

Printed
April 21, 1986

RFP-3858
UC-10 CHEMICAL SEPARATIONS
PROCESSES FOR
PLUTONIUM AND URANIUM
DOE/TIC-4500 (Rev. 73)

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RFP--3858

DE86 011673

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Prepared under Contract DE-AC04-76DP03533
for the
Albuquerque Operations Office
U.S. Department of Energy

SUBJECT DESCRIPTORS

Calcination
Calcium
Calcium Chloride
Ceramics
Direct Oxide Reduction
Electrorefining
Furnaces
Magnesium Chloride
Molten Salt
Oxides
Plutonium
Plutonium Dioxide
Plutonium Metal
Plutonium Oxide
Plutonium Processing
Plutonium Reduction
Purification
Pyrochemical Processes
Pyrometallurgy
Reduction
Salt Fluxing
Tilt-Pour Furnace

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ACKNOWLEDGMENTS

The authors gratefully acknowledge the outstanding support provided by all members of the DOR/ER Interface Task Team in performing the reported test work, compiling and analyzing the results, and preparing this report. A very special acknowledgment is due those Rocky Flats groups and personnel outside the Chemistry Research and Developmental Section who, by their assistance in key activities, made this effort possible. Particular thanks are expressed to: Vivian Giesland (559 Analytical Laboratories) for coordination of the analytical services provided; Greg Bird and Kay Kunert (Technical Operations Support) for providing production data, calcining oxides, and critical discussions on the production performance of DOR metal in ER; and Jim Selle (Plutonium Metallurgy Labs) and John Fraser (Technical Operations Support Lab) for their very thorough metallographical/SEM/XRD analytical work. The authors are also specifically indebted to the following people for their efforts and assistance throughout the test program: R. C. Baker, M. J. Cusick, R. F. Fitzpatrick, J. F. Guadagnoli, R. T. Ishmael, J. C. Keene, L. L. Martella, C. A. Nannie, F. L. Oetting, M. T. Saba, T. D. Santa Cruz, R. A. Silva, and C. M. Smith.

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ABSTRACT

Research test work and production data evaluation were performed by the Direct Oxide Reduction (DOR)/Electrorefining (ER) Interface Task Team to determine the cause for poor efficiency and yields during ER of DOR metal product. Production data and preliminary test results provided a working hypothesis. Extremely high loadings of impurities (whatever their exact source and identity) in the DOR product metal may lead to failure of the metal to become a molten anode at ER operating temperatures. Moderate impurity levels permit attainment of a molten anode, but lead to low yields because of premature anode solidification.

The test results did not conclusively prove the hypothesis or identify specific mechanisms, but were qualitatively supportive.

By stirring the molten anode metal pool, as well as the molten salt phase, generally good ER runs were obtained with both DOR and non-DOR feeds. These limited preliminary results suggest that anode stirring decreases the sensitivity of the ER process to DOR-related impurities.

Suggested corrective measures included (1) minimizing impurities in DOR feed to ER and (2) continued evaluation of anode stirring along with run termination by back-EMF measurements.

INTRODUCTION

During June 1983, Rocky Flats production ER began processing metallic feed produced by DOR of calcined plutonium oxide. Electrorefining of DOR metal peaked during July 1983 and continued through mid-October. During the July-September period, significant problems were experienced as a result of poor process yields from ER of DOR metal, and data were collected to confirm the magnitude of the problem. As a result of the initial evaluation, the DOE/ER Interface Task Team was established in October 1983 to determine the cause for poor DOE metal performance during ER and to recommend corrective measures based on combined technical and economic considerations.

The scope of work outlined for activity by the DOR/ER Interface Task Team included:

1. Participation of a working group from the Task Team in a Technology Exchange Program on DOR and ER with Los Alamos National Laboratory.

2. Ongoing dialogue with Pyrochemical Operations to provide interim recommendations for DOR/ER planning.

3. Comparative economic evaluation of alternate process paths to determine acceptable performance limits for the DOR/ER process.

4. Evaluation of production ER data to characterize the DOR/ER problem and provide guidance for planned test work.

5. Research test work to determine the cause for poor DOR metal performance in ER.

The objective of this report is to document the results for Items 4 and 5 and to offer recommendations based on these results.

CHARACTERIZATION OF THE DOR/ER PROBLEM

The following information was compiled and evaluated to characterize the DOR/ER problem

and to provide guidelines for interpreting DOR/ER test results. A description of the process equipment has been published.[1]

DOR Versus Non-DOR Performance During Production ER

Table 1 shows a comparison of the performance of DOR metal and non-DOR metal during ER in Building 371 production tilt/pour furnaces. DOR metal was processed initially by ER in June 1983, and 27 runs were initiated successfully through mid-October 1983. Through approximately the same time period (May 2, 1983 to October 3, 1983), 141 ER runs were initiated using non-DOR feed metal. As shown in Table 1, 60 to 70% of the initiated ER runs for both types of feeds were "good" runs, i.e., carried to successful termination using projected ampere-hour limits. The balance of runs were terminated due to cracked anode cups, loss of electrical current flow (noted as "amps lost" on producution run sheets), or other causes.

A notably higher percentage of the run terminations was attributable to "amps lost" for DOR metal feed than for non-DOR feed: 26% vs 15%. Although run sheets are not kept on "false starts" in which ER is not successfully initiated, operations personnel estimate eight to ten of these runs were experienced using DOR feed. Failure to initiate a run is rare for non-DOR feed. In these cases (20 to 25% of total attempted ER runs on DOR feed), the DOR metal appeared not to have become completely molten during heatup, despite normal operating temperatures being achieved; some softening was apparent.

Table 1 also shows anode depletion, product yield, and grams of holdup/run for DOR and

TABLE 1. Comparison of Performance for DOR and Non-DOR Feed to ER

Variable	Approximate Calendar Period	DOR Feed to ER		Non-DOR Feed to ER		Significance Level at Which Means Differ (%)
		No. Data Points	Value or Mean	No. Data Points	Value or Mean	
Electrorefining Runs:	DOR 6/14-10/13/83	27		–		
Percent of started runs that yielded:	Non-DOR 5/2-10/3/83	–		141		
"Good" runs to ampere-hour limit			66.7%		62.4%	
"Amps Lost"			25.9%		14.9%	
"Broken Cup" or "Other"			7.4%		22.7%	
Percent of attempted runs not started (estimated)			20-25%		Negligible	
Anode depletion (non-Pu):	DOR 6/14-10/13/83 Non-DOR 5/2-10/3/83					
For "Good" runs		16	73.2%	88	80.8%	91
For "Good" and "Amps Lost"		24	67.3%	109	79.3%	98
Product Yield (non-Pu):	DOR 6/14-10/13/83 Non-DOR 5/2-11/19/83					
For "Good" runs		17	37.9%	171	56.6%	99
For "Good" and "Amps Lost"		25	37.0%	190	57.9%	99
Holdup/Run (non-Pu): (grams)	DOR 6/14-10/13/83 Non-DOR 5/2-11/19/83					
For "Good" runs		17	624	156	645	<60
For "Good" and "Amps Lost"		25	643	178	621	<60

non-DOR runs. All three parameters are calculated on a non-plutonium basis as follows:

$$\text{Anode depletion (\%)} = 100 \times \frac{\text{Wt Feed} - \text{Wt Anode Heel}}{\text{Wt Feed}}$$

$$\text{Product Yield (\%)} = 100 \times \frac{\text{Wt Product Button}}{\text{Wt Feed}}$$

Holdup/run = New holdup weight before scrapeout, as calculated by difference on ER run sheets. (Scrapeouts are not performed after every ER run.)

Plutonium-basis values may also be calculated for these parameters by using the weight of plutonium in feeds, products, and anode heels in the above equations. Plutonium-basis values are also used later in this report.

The data clearly show that mean product yields for DOR feed are different from non-DOR feed. For "good" runs and also for "good plus amps lost" runs, the average ER product yield for DOR feeds is 19 to 21% (absolute yield) lower than for non-DOR feed. The actual yield, if all attempted ER runs on DOR feed were considered, would be significantly lower with an absolute difference from non-DOR feed of 30% yield. This significant shortfall in expected performance stimulated the DOR/ER test program discussed herein.

The two largest nonproduct-output plutonium streams from ER are the anode heel and the furnace holdup. The data in Table 1 show that average anode depletions (for successfully initiated runs) are significantly different for DOR feeds from that of non-DOR feeds. The statistical significance of the difference of means is not as high as for product yield, but does indicate a real difference. DOR anode depletions are about 8 to 12% (absolute) lower than for non-DOR feed and appear to account for about half the yield shortfall.

It is worthwhile to compare the anode depletions achieved in production for only those runs in which an "amps lost" condition was noted on the production run sheet. For DOR and non-DOR feeds, the average anode depletions achieved were 55 and 73% (non-plutonium basis), respectively. If the "amps lost" condition is interpreted as maximum depletion achievable due to anode solidification, then the comparison of depletions demonstrates the earlier onset of solidification for DOR feed compared to non-DOR feed. The standard deviations for these two sample sets are 28 (DOR) and 24 (non-DOR), and the number of data points is rather small: DOR = 8, non-DOR = 19.

DOR Versus Non-DOR Feed Metal to ER

Initial evaluation of yield shortfall for DOR has focused attention on the cause for lower anode depletions. The earlier onset of the "amps lost" condition has, in turn, suggested the role of increased impurity level in DOR metal feed as a part of the overall problem. Over most of 1983, the composition of specific feed metal to an ER run was not obtainable from historical operating records, thus preventing a run-by-run comparison of feed composition with ER performance. However, an overall comparison of all DOR and non-DOR metal shipped to Building 371 for potential ER was possible. The effects of impurities are summarized in Table 2.

The data show that average carbon and aluminum levels in DOR metal are two to three times higher than for non-DOR metal. Iron levels are 2 to 10 times higher than for non-DOR, and average tantalum content is 60 to 160 times higher in DOR than non-DOR. The difference in average aluminum levels is significant at the 91% level, while all other means differ at >99% level. The data substantiate the expectation that typical DOR feed contains higher levels of impurities than MSE-α and MSE-Δ metal representing non-DOR feed to ER, and support the contention that earlier anode solidification might be caused by higher feed impurities.

ER Salts

Table 3 shows a comparison of starting salt variables for production ER runs. For ER of DOR

TABLE 2. Comparison of Impurity Levels in DOR and non-DOR Metal During 1983

Metal Source	Mean Impurity Level			
	Carbon (ppm)	Aluminum (ppm)	Tantalum (ppm)	Iron (ppm)
MSE-α	257	27	3.9	201
MSE-Δ	303	27	11	800
DOR	678	53	633	2105

TABLE 3. Initial ER Salt Variables—Production

	Wt % $MgCl_2$ in Salt		Wt Ratio $MgCl_2$ to Feed Metal	
	Range	Mean	Range	Mean
DOR:				
"Good" runs	4.28-10.08	5.88	0.0382-0.168	0.0729
All runs	4.28- 9.80	5.82	0.0431-0.168	0.0747
Non-DOR:				
"Good" runs	3.96- 9.8	4.34	0.034 -0.244	0.0455
All runs	3.96-4.41	4.29	0.034 -0.0668	0.0449

metal, the initial $MgCl_2$ level in the salt and the ratio of initial $MgCl_2$ to metal feed are both higher than for non-DOR metal. This reflects two characteristics of ER operation:

1. The amount of salt used and $MgCl_2$ added per run are relatively constant, regardless of feed metal quantity. Since ER runs with DOR feed metal typically used about 400 grams (g) less feed, the $MgCl_2$/feed ratio is higher for DOR feeds. Note that this also leads to a higher mean salt/metal ratio for DOR feed.

2. The target level of $MgCl_2$ in salt for both DOR metal and non-DOR metal treatment is approximately 4.3 wt %. However, during August-September 1983, DOR treatment was modified to use higher (up to ~10 wt %) $MgCl_2$ to investigate the process effect.

These runs (eight runs over 4.3 wt %) raise the mean to a significantly different level. The differences between DOR and non-DOR means shown in Table 3 are significant at the 99% level.

Although the impact of differences in initial salt variables was examined, the limited data at values different from the typical levels do not support any firm conclusions. There is very little difference in the salt variables within non-DOR feed runs. Within the "good" DOR feed runs, higher concentrations of $MgCl_2$ in the salt and higher $MgCl_2$/feed ratios appear to yield less than average holdup and higher average yields: 276 g/run vs 769 g/run holdup and 54.5% vs 31.0% yield (non-plutonium basis), respectively. If the anode is depleted to an "amps lost" condition, the differences in holdup and yield for high- and low-$MgCl_2$ salt runs are negligible. Average anode depletions for the "good" DOR runs are similar between high-$MgCl_2$ and low-$MgCl_2$ salt runs.

The plutonium content of various spent ER salts is shown in Table 4. The data indicate that there was no significant difference in the average plutonium lost to the salt per run for DOR from that of non-DOR feeds during ER. No further evaluation of the spent-salt plutonium content was performed.

Holdup During Production ER

The data in Table 1 show that the amount of new furnace holdup per run is not significantly different for DOR feed from that of non-DOR feed to ER. The mean amount of new holdup per

TABLE 4. Spent Production ER Salt Plutonium Content

	Plutonium Content of Product Salts (grams/salt batch)	
	Range	Mean
DOR:		
"Good" Runs	55-198	100.3
"Good and Amps Lost" Runs	47-198	100.5
Non-DOR:		
"Good" Runs	25-657	100.3
"Good and Amps Lost" Runs	25-657	100.1

run is approximately 620 to 650 g depending on the type of feed and whether only "good" runs or "good" plus "amps lost" runs are included in the analysis. No significant difference exists between DOR and non-DOR feeds if the "average percent of feed reporting to new holdup" is considered.

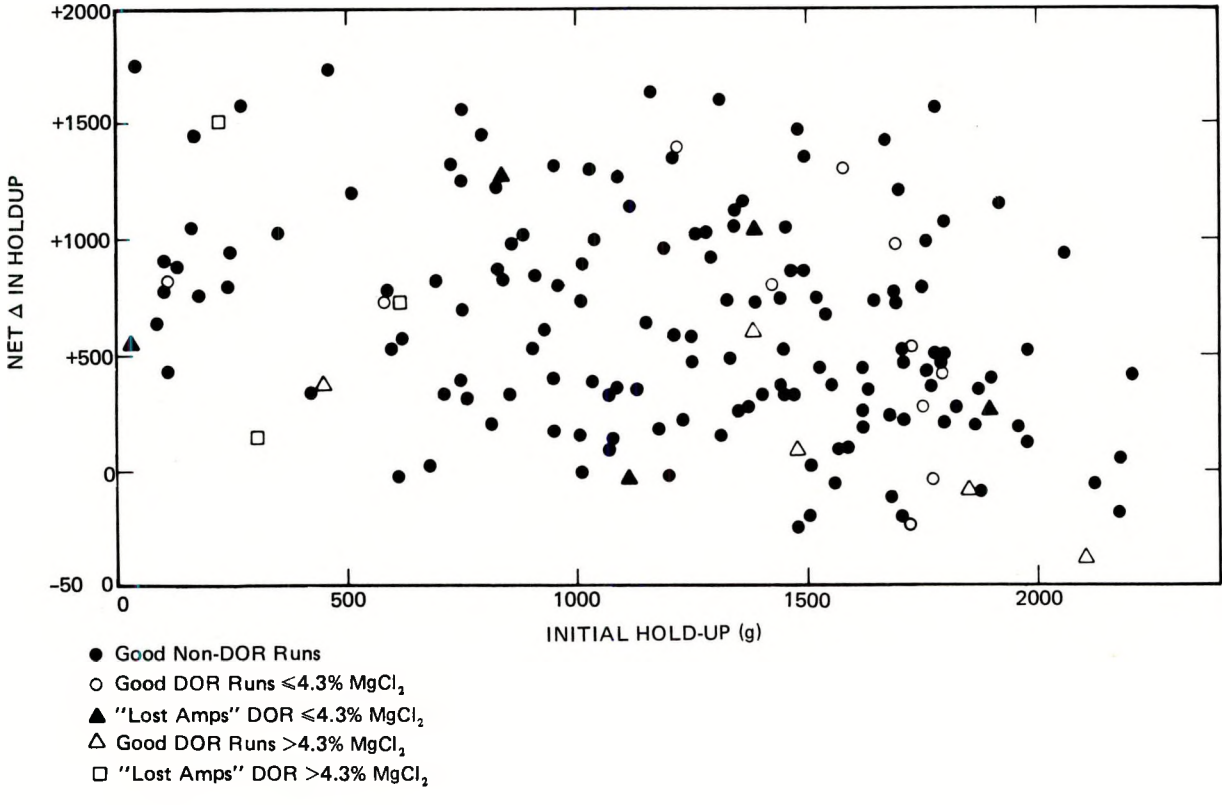
Holdup during ER has historically appeared to be a significant function of the amount of holdup already present in the furnace before a run starts. This effect is shown in Figure 1, where initial holdup is plotted against the amount of new holdup during a run (net change in holdup). The plot shows large scatter in the new holdup. At very low initial holdup ($\leqslant$500 g), the new holdup can exceed 1700 g and does not go negative. At very high initial holdup ($\geqslant$1500 g), new holdup remains below about 1700 g and is often negative. However, between about 500 and 1500 g of initial holdup (over one-half of all ER runs), the new holdup per run shows no significant trend. The 500-1500 g initial holdup plateau has a spread of approximately 0 to 1500 g of new holdup, essentially independent of initial holdup and apparently a function of other process variables (e.g., feed composition and atmosphere composition). It is noteworthy that all runs with DOR feed made with greater than the standard 4.3 wt % $MgCl_2$ in salt (and higher $MgCl_2$/feed ratios) fall in the lower holdup portion of the population.

Plutonium Transfer During Electrolysis

In production ER, "good" runs are terminated when projected ampere-hour limits are reached. Therefore, anode depletions achieved for "good" runs do not directly reflect depletion limits, but rather the efficiency of plutonium transfer during the run: grams of plutonium transferred per ampere-hour (g/A·hr). The transfer rate was calculated for DOR and non-DOR feeds from production ER data as:

$$\frac{\text{Initial feed metal weight (g)} - \text{anode heel weight (g)}}{\text{Ampere-hours of forward electrolysis}} = \text{transfer rate}$$

FIGURE 1. Effect of Initial Holdup and Percent $MgCl_2$ in Salt on ER Furnace Holdup



This transfer rate neglects the plutonium content of final salts and holdup. A "corrected" transfer rate in which salt plutonium content is accounted for is also used during analysis of DOR/ER test work. However, it should be noted that neither calculated transfer rate accounts for plutonium transferred from the anode to the salt via chemical reaction with $MgCl_2$. Mean values of the transfer rate were compared for DOR feeds and non-DOR feeds to ER, with results shown in Table 5.

The mean values for DOR vs non-DOR are not different at the 90% significance level, although the averages do vary in the direction supportive of more impurity transfer or other non-plutonium electron diversion during ER of DOR metal.

As expected, percent anode depletion (non-plutonium basis) for production ER runs with DOR feed correlates extremely well with grams/ampere-hour as calculated for this analysis. No such significant correlation exists between grams/ampere-hour and percent yield for DOR runs.

Discussion of DOR Versus Non-DOR Performance

Based on the preceding information, ER of DOR feeds appears to be characterized by three major performance phenomena as follows:

Phenomenon 1: Approximately 25% of the ER runs using DOR feed do not initiate and, therefore, achieve zero anode depletion and yield.

Phenomenon 2: About 20% of the ER runs on DOR feed are prematurely terminated due to loss of electrical current flow before the ampere-hour target is reached. Anode depletion (non-plutonium basis) averages 55.3%, and yield (non-plutonium basis) averages 35.1% for these runs.

Phenomenon 3: Approximately 50% of the ER runs on DOR feed go to normal termination: "good" runs. Anode depletion (non-plutonium basis) averages 73.2%, and yield (non-plutonium basis) averages 37.9%. The remaining 5% of runs are not clearly characterized. A comparison of the three performance phenomena described above with parallel groups for non-DOR feed is shown in Table 6.

TABLE 5. Transfer Rate for Production ER

	Number of Runs	g/A·hr
DOR Feed:		
"Good" Runs	17	2.39
"Good and Amps Lost" Runs	25	2.36
Non-DOR Feed:		
"Good" Runs	158	2.46
"Good and Amps Lost" Runs	175	2.55

Yield Versus Anode Depletion

The data in Table 6 show that when runs are prematurely terminated, DOR anode depletion and product yield lag non-DOR performance by 18 and 34% (absolute), respectively. (Definition of "Non-plutonium Basis" is repeated in Table 6.) Similarly, when normal, "good" runs are terminated, anode depletion and product yield for DOR feeds are lower than for non-DOR feeds by 7 and 19% (absolute), respectively. In both cases, the results indicate that more plutonium is exiting the process in salt or holdup (not as product) for DOR feed than for non-DOR feed. However, this conclusion is inconsistent with previous comparisons of holdup and plutonium loss in salt for DOR and non-DOR feeds. A number of mass balances were calculated to try to rationalize the data. One such calculated condensed phase mass balance (neglecting all gaseous species entering or leaving the system or transferring to cold equipment surfaces) for "good" ER runs on DOR metal and non-DOR metal feeds is shown in Figure 2, using actual average production values and calculating "salt out" by difference.

Mass balances such as shown in Figure 2 highlight the importance of differences in feed batch sizes between DOR and non-DOR ER runs. Salt-to-feed ratios average 1.28 ±0.21 for DOR feeds and 1.05 ±0.16 for non-DOR feeds. Even with constant plutonium losses in salt and holdup, the impact of these losses on calculated percent yield –

TABLE 6. ER Performance Phenomena for DOR and Non-DOR Feeds

Phenomenon	Identity for DOR Performance	Performance Characteristic	Total Attempted Runs (%)		Anode* Depletion (%)		Yield* (%)	
			DOR	Non-DOR	DOR	Non-DOR	DOR	Non-DOR
1	Low fluidity	ER run is not initiated due to incomplete melting and low anode fluidity	25	0	–	–	–	–
2	Amperes lost	Runs terminated before ampere-hour target reached due to "amps lost"	20	15	55.3	73.0	35.1	69.6
3	Low transfer rate	Normal termination, "good" run, but lower anode depletions for DOR feed	50	62	73.2	80.8	37.9	56.6
–	Other	Termination for mechanical or electrical reasons, e.g., broken anode cup	5	23	–	–	21	~8

*Non-plutonium basis definition:

$$\text{Anode depletion (\%)} = 100 \times \frac{\text{Wt Feed} - \text{Wt Anode Heel}}{\text{Wt Feed}}$$

$$\text{Product Yield (\%)} = 100 \times \frac{\text{Wt Product Button}}{\text{Wt Feed}}$$

would be greater for DOR feed. If the percent plutonium in salt is constant, the effect of the difference in the salt-to-feed metal ratio is even greater. Note that Figure 2 shows more salt "out" than "in" for DOR feed (possibly due to inclusions in feed buttons or chemical reactions increasing salt mass). Mass balance calculations indicate that about 3 to 4% (absolute) higher yields could be achieved for DOR feed simply by using larger metal charges (similar to those for non-DOR feed) if all other losses remain constant.

It should be recognized that the magnitude of yield shortfall for DOR feed is not as large if plutonium-basis parameters are used, since DOR feed plutonium content may be several percent lower than molten salt extraction (MSE) feed.

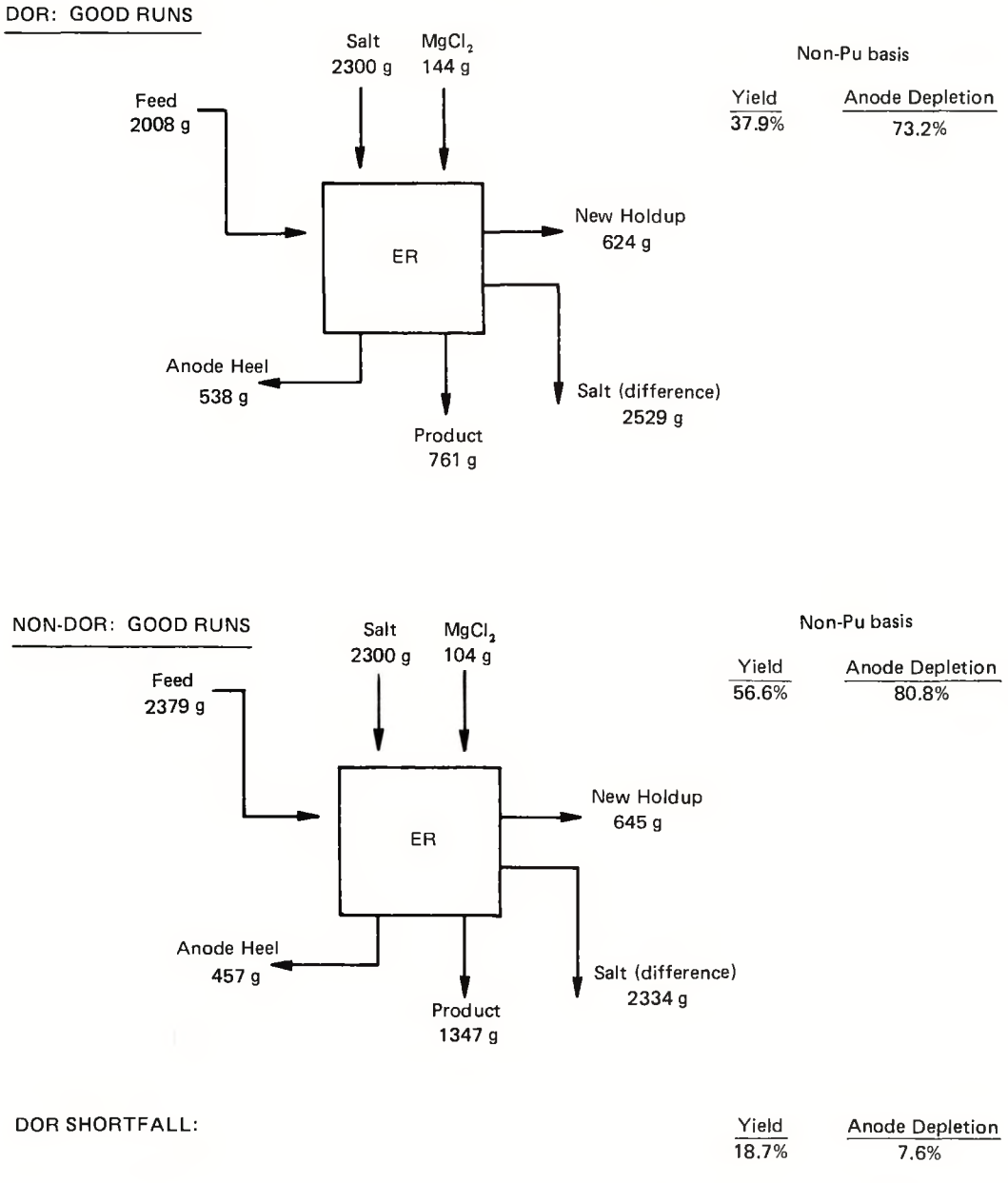
Possible Physicochemical Causes

In Phenomenon 1, the influence of feed metal quality is paramount. Most impurities reporting to the feed button from oxide are soluble in plutonium at normal operating temperature prior to anode depletion. Therefore, impurities from the DOR process itself, or particular DOR process variables, may contribute primarily to failure to initiate an ER run. The specific causes of incomplete melting or lack of fluidity are not known.

In Phenomenon 2, both the increased frequency of "amps lost" termination and the significantly lower anode depletions experienced point to the role of impurities in causing premature termination. Whether these impurities are initially soluble and precipitate as high-melting compounds or elements as plutonium is depleted, or whether they are mechanically carried over from DOR and trapped at the salt-metal interface, is unknown.

Since lower transfer rates are indicated by Phenomenon 3, a close examination of ER process chemistry during ER of DOR metal is suggested.

FIGURE 2. Condensed Phase Mass Balances for "Good" ER Runs on DOR and Non-DOR Feed



Runs proceed to normal termination at ampere-hour targets but show anode depletions lower than for comparable non-DOR feeds to ER. Other electrochemical reactions or undefined sources of electronic conduction could result in lower current efficiencies for plutonium transfer.

DOR/ER TEST PROGRAM

A test program was initiated during October 1983 to investigate potential causes for performance shortfalls for DOR metal when electrorefined in production tilt/pour facilities. Test work was conducted using production-scale DOR equipment and tilt/pour ER facilities, as well as stationary furnaces for vacuum melting and drip casting tests. Various other equipment was also used for intermediate DOR metal treatment as required. Test work was specifically aimed at determining and demonstrating the cause of low anode depletions during ER of DOR metal. A description of the test program, with results, observations, and

appropriate preliminary conclusions, is presented in this section.

Test Plan

A test plan was initially laid out with flexibility for downstream changes as guided by interim results. The initial test plan called for a four-part ER sequence using:

1. Non-DOR metal
2. Pure alpha DOR metal
3. Pure delta DOR metal
4. Impure delta DOR metal

DOR metal, treated by vacuum melting, vacuum casting, drip casting, aqueous leaching, and consolidation under a salt cover, was electrorefined to evaluate the effect of each of these treatment methods.

The initial four-part sequence was structured to demonstrate the role of DOR-related impurities, such as calcium and magnesium, interacting with plutonium oxide containing delta levels of gallium and oxide from aqueous processing containing minimal gallium levels. The oxide reduction process was rate-limiting and left ample ER furnace time for ER tests on a variety of DOR feeds to evaluate the effect of intermediate treatment. Extensive feed and product sampling was planned to characterize the role of impurities.

Stationary equipment was used for intermediate DOR button treatment by vacuum melting and drip casting.[1] Feed and product sampling during the actual test program was not as comprehensive as planned. As the test program progressed, anode-stirring evaluation was introduced and continued through the close of the test sequence.

Procedures

Calcination

Calcination of oxides was performed in front-loading muffle furnaces by holding 2 to 2.5 kilograms of oxide at 850 °C for six to eight hours in air. Run conditions and batch sizes are summarized in Table 7. Alpha oxide and impure delta oxides were calcined in one six-hour treatment at 850 °C. Pure delta oxide was produced by burning pure delta metal to oxide, followed by two-stage calcination for four hours at 850 °C in each stage. Feed oxides and calcines were sampled, but no samples were taken between calcining stages for pure delta oxide. "Green cake" and pure delta oxides were calcined in two lots; three lots of impure delta oxide were calcined.

Direct Oxide Reduction

Direct oxide reductions of pure and impure delta oxides and pure alpha oxide were conducted using

TABLE 7. Summary of Calcination Run Conditions

Run No.	Feed Type	Treatment Conditions		Feed Weight (g)	Product Weight (g)
		Time (hr)	Temperature (°C)		
95	Alpha oxide	6	850	2090	1984
109	Alpha oxide	6	850	2075	1992
767733	Pure delta oxide	4	850	2219	–
	Pure delta oxide	4	850	–	2219
767736	Pure delta oxide	4	850	2247	–
	Pure delta oxide	4	850	–	2253
110	Impure delta oxide	6	850	2264	2252
112	Impure delta oxide	6	850	2216	2204
112	Impure delta oxide	6	850	1991	1992

TABLE 8. Summary of Direct Oxide Reduction Run Conditions and Results

		Feed Mix (g)			Products/Results								
(DOR/ER Run No.)	Feed Type	Oxide	Ca	Salt	Metal Button Weight (g)	Subsequent T/P ER Run No.	Button Characteristics	White Salt (g)	Black Salt (g)	Ca Button (g)	Stoichiometric Calcium Addition* (%)	Pu in Product Button (%) Individual 100% Assays**	Pu in Product Button (%) Calorimetric (grouped buttons)
1	Alpha Oxide	550	225	2500	469	021		2736	0	36	38.4	96.8	
2	Alpha Oxide	550	225	2500	489	021		2691	0	38	38.4	99.5	
3	Alpha Oxide	550	225	2500	453	021		2719	0	41	38.4	93.3	96.1
4	Alpha oxide	550	225	2500	476	021	Rough lower surface	2705	0	38	38.2	97.6	
5	Alpha oxide	550	225	2500	477	–	Top surface slushy	2941	0	37	38.2	98.3	
6	Alpha oxide	550	225	2500	0	–	No button produced	2299	917	0	38.2	–	
7	Alpha oxide	637	240	2700	515	–	Rough top sfc – three layers	2675	275	38	27.3	91.6	
8	Pure delta oxide	550	225	2500	430	–	Poorly consolidated – to be rerun	2406	165	42	39.0	88.3	
9	Pure delta oxide	550	225	2500	425	025	Rough lower surface	2599	182	33	39.0	87.2	
10	Pure delta oxide	545	225	2500	403	025	Poorly formed button	2773	0	22	37.7	82.1	85.1
11	Pure delta oxide	550	225	2500	435	025	Rough button	2198	359	37	37.0	89.4	
12	No. 8 button rerun	410	100	2500	521	025	Lumpy button	3229	0	12	–	–	
13	Pure delta oxide	550	225	2500	471	–	Slightly rough upper surface	2497	235	54	42.5	98.7	
14	Pure delta oxide	400	160	1993	307	033	Poorly formed button	1806	285	–	39.3	87.5	
15	Pure delta oxide	304	210	2500	257	033		–	–	–	140.7	–	
16	Pure delta oxide	500	205	2500	385	–	Poorly formed button	2872	0	–	42.8	87.8	
17	Impure delta oxide	473	205	2298	379	033		2716	0	–	49.2	–	
18	Impure delta oxide	500	205	2300	323	–		2433	184	–	41.1	–	78.3
19	Impure delta oxide	500	205	2300	0	–	No button produced	0	2740	72	41.1	–	
20	Impure delta oxide	500	205	2225	288	033		2033	271	6	41.1	–	
21	Impure delta oxide	500	205	2225	340	033		2449	0	40	41.1	–	
22	Impure delta oxide	500	205	2300	0	–	No button produced	2550	420	–	41.7	–	

*Based on 99.5% Ca in Ca pellets, Pu assay reports on DOR Run Sheets, all Pu as PuO_2, and all other reducible oxides neglected.

**100% minus total impurities.

conventional DOR production practice. Twenty-two DOR runs were made to produce 19 buttons, one of which (DOR/ER 8) was rerun. Feed mixes are given in Table 8.

Runs DOR/ER 1 through 13 (alpha oxide and pure delta oxide) were made in production DOR equipment.[1] Thirteen product buttons were routed to tilt/pour ER runs as shown in Table 8. Composite oxide samples were taken of pure delta oxide feed, and product buttons were sampled for both chemical analyses and metallographic/SEM examination. Additional oxide samples were also taken to characterize feed to DOR runs.

As shown in Table 8, the third lot of buttons for ER (to ER 033) was actually produced from a mixture of pure delta and impure delta oxide.

Electrorefining

ER tests were performed using a tilt/pour ER furnace.[1] A summary of ER runs and test conditions is given in Table 9. Twenty-four ER runs were performed using feed metal charges of 712 to 2500 g. Three of the runs were reruns or continuations of previous tests; the remaining 21 tests used fresh feed ranging in weight from 981 to 2500 g.

Salt additions were maintained at 2300 to 3123 g of NaCl-KCl in equimolar proportions and 99 to 130 g $MgCl_2$ for runs on fresh feed. Inside cell temperatures were maintained at 745 to 770 °C during ER, and stirring was held at 165 revolutions per minute (rpm).

Fifteen of the 24 runs were performed with only the salt-phase stirred, as practiced in production at Rocky Flats. Four runs used a tantalum stirrer to stir the metal anode and the salt phase during ER. During these four runs, ER was performed at 15 to 19 amperes (A) and 2.5 to 2.6 volts (V), rather than the normal range of 5.8 to 6.0 V and 46 to 60 A used for all other runs. During the last five runs, the metal and salt phases were stirred with ceramic and tantalum blades, respectively. The electrolytic cell was pretreated by reverse electrolysis at 5 to 20 A for 5 to 20 minutes on all but the last five runs.

Conventional production practice at Rocky Flats for startup, run sequencing, and pouring were followed for tilt/pour ER runs. Electrolysis was continued until significant changes in back-electromotive force (EMF) or large cell resistance shifts indicated the onset of significant anode polarization or until electrical contact was broken. Increased cell resistance was evidenced by the need to increase the applied potential to maintain a given amperage value. Back EMF was measured by turning off the applied potential and observing the resultant cell potential.

Feed buttons were calorimetered for plutonium determination and independently sampled for chemistry if no previous analytical data were available. Anode heels and product buttons were also sampled for chemical analysis and selected anode heels and other materials were evaluated by metallography/SEM/XRD (scanning electron microscopy, x-ray diffraction).

Vacuum Melting/Drip Casting

Vacuum melting and drip casting were performed in stationary furnaces as an intermediate treatment of DOR buttons prior to ER. Vacuum melting (VM) and anode drip casting (AC) runs and conditions are summarized in Table 10.

Three vacuum-melting runs were made, with the first run constituting a shakedown test on one DOR button. The following two runs (VM-2 and VM-3) provided treated feed to drip castings AC-1 and AC-2. Vacuum melting run conditions for VM-2 and VM-3 varied as shown in Table 10: 10-1/4 to 13-1/2 hours at 650 to 1000 °C with vacuum of 0.045 to 127 torr. In all cases, vacuum treatment was made in two sequential steps.

Drip casting was accomplished by bringing the vacuum-melted product to melting temperature and allowing metal to drip from the funnel container into an anode mold. Casting was completed in a single step and provided feed to Runs ER-019 (AC-1) and ER-022 (AC-2).

DOR Button Leaching

The effect of using leached DOR buttons for ER feed was also evaluated during the test sequence.

TABLE 9. Summary of Tilt/Pour ER Run Conditions

Run No.	Metal Feed Type	Feed Weights (g) Metal Net	Pu	$MgCl_2$	NaCl KCl	Total A·hr	Stirring (rpm)	Reverse Electr. (A) (min)	Cell Temperatures (°C) Outside	Inside	Cell Resistance (Ω) Begin	End	Back EMF (V) Begin	End	Comments
018	Foundry reject metal	2500	2486	189	3123	810.7	Salt (160)	5 (20)	–	750	0.094	0.13	0.227	0.471	Non-DOR base case
019	DOR & vac. melt & drip cast	981	967	130	2900	286.3	Salt (160)	20 (20)	–	750	0.108	0.121	0.032	0.401	Cracked cup
020	DOR & MS consolidation (321)	1633.5	1585	126	2800	296	Salt (160)	20 (20)	–	760	0.090	0.103	0.016	0.554	
021	DOR/ER 1-4 (pure alpha)	1789	1761	121	2700	606.4	Salt (160)	20 (20)	–	750	0.085-0.089	0.113	0.037	0.506	
022	DOR & vac. melt and drip cast	1322	1308	112	2500	316.8	Salt (160)	20 (20)	–	765	0.088	0.108	0.044	0.302	
023	Leached DOR buttons	1670	1599	108	2383	419.1	Salt (160)	20 (20)	–	770	0.097	0.133	0.047	0.730	Dirty/rough buttons
024	T/P DOR buttons	1744	1723	103	2300	214	Salt (160)	20 (20)	–	775	0.105	0.115	0.089	0.349	Broken cup
024A	ER–024 rerun & T/P DOR	1963	1939	130	2900	541.2	Salt (170)	10 (5)	945	770	0.098	0.108	0.664	0.506	
025	DOR ER 9-12 (pure delta)	1664	1614	116	2600	484.8	Salt (170)	10 (5)	945	775	0.097	0.109	0.073	0.489	
026	T/P DOR buttons	2228	2142	116	2600	576.3	Salt (170)[1]	10 (5)	940	770	0.094	0.141	0.395	0.932	
027	DOR & vac. casting in 771	1677	1658	103	2300	513.7	Salt (165)	10 (5)	930	765	0.103	0.122	0.217	0.526	
028	DOR buttons	2173	2149	103	2300	504.3	Salt (165)	10 (5)	930	770	0.095	0.116	0.219	0.669	

[1] Salt prestirred 5-10 minutes before reverse and forward electrolysis.

TABLE 9. Continued

Run No.	Metal Feed Type	Feed Weights (g) Metal Net	Pu	$MgCl_2$	NaCl KCl	Total A·hr	Stirring (rpm)	Reverse Electr. (A) (min)	Cell Temperatures (°C) Outside	Inside	Cell Resistance (Ω) Begin	End	Back EMF (V) Begin	End	Comments
029	DOR buttons – split w/030	2078	2053	103	2300	467.0	Anode (165)/metal[2]	10 (5)	930	770	0.161	0.213	0.020	0.025	Power loss – terminated
029A	ER-029 anode heel–continuation	712	687	029–Salt		133.2	Anode (165)/metal[2]	10 (5)	930	745	0.225	0.635	0.039	0.065	
030	DOR buttons – split w/029	1957	1933	103	2300	423.5	Salt (165)	10[5] (5)	925	765	0.096	0.115	0.174	0.589	
030H	ER-030 anode heel – continuation	766	743	030–Salt		1.3	Anode (165)/metal	10[5] (5)	930	–[4]	0.287	–	–	–	Feed would not melt
031	DOR buttons – split w/032	1521	1498	103	2300	361.2	Salt (165)	10[5] (5)	930	770	0.099	0.115	0.105	0.487	
032	Leached DOR buttons – split w/031	1803	1746	103	2300	535.2	Salt (165)	10[5] (5)	930	–[4]	–	–	0.113	0.851	
033	DOR/ER 14-21 (pure/impure delta mix)	1506	1406	103	2300	324.6	Anode (165)/metal[3]	10[5] (5)	925	–[4]	0.133	0.168	0.057	0.091	
034	MSE delta metal	1593	1569	99[5]	2300	552.7	Salt/anode (170)[6]	None	930	–[4]	0.097	0.120	0.055	0.56	ER continued beyond indicated cutoff point
035	DOR buttons	1655	1633	99[5]	2300	569.3	Salt/anode (170)[6]	None	930	–[4]	0.103	0.115	0.033	0.495	
036	Mix – DOR/MSE metal	1604	1582	99[5]	2300	491.4	Salt/anode (170)[6]	None	930	–[4]	0.104-0.109	0.126	0.065	0.240	
037	MSE delta metal	2138	2106	100[5]	2400	–	Salt/anode (170)[1,6]	None	930-945	–[4]	0.120	–	0.087	–	Amperes lost early in run
038	DOR buttons	1231	1187	100[5]	2300	285.4	Salt/anode (170)[1,6]	None	925	765	0.117	0.134	0.164	0.311	

[1] Salt prestirred 5-10 minutes before reverse and forward electrolysis.
[2] Metal stirrer used for anode and salt at 2.4 V, 15 A maximum.
[3] Metal stirrer used for anode and salt at 2.6 V, 15-19 A.
[4] Thermocouple broken.
[5] High-purity Anderson-Physics salt.
[6] Salt stirred with Ta metal blades, anode with ceramic blade–operations at normal cell voltage/amperage.

TABLE 10. Summary of Stationary Furnace Vacuum Melt and Drip (Anode) Cast Tests

Test No.	Feed Type	Feed Weight (g)	Performance Parameters		Run Conditions: Total Time at Temp. (hr)	Run Conditions: Temp. (°C)	Run Conditions: Vacuum (torr)	Product Disposition
Vacuum Melting								
VM-1 (A&B)*	Production DOR button	432	1 g condensate collected	A	3	750	0.06-2	–
				B	3	850	0.06	
VM-2 (A&B)*	Production DOR buttons (five buttons)	2184	7 g condensate collected	A	10-1/4	750-850	0.045-2	AC-1
				B	12	850	0.045	
VM-3 (A&B)*	Production DOR buttons (six buttons)	2484	34 g condensate collected with some splatter	A	13-1/2	650-850	0.045-127	AC-2
				B	12	680-1000	0.045-127	
Anode Casting								
AC-1	VM-2 product	2028	48.9% yield to product			Melt and cast		ER-019
AC-2	VM-3 product	2274	59% yield to product			Melt and cast		ER-022
AC-3	Production DOR buttons	1911	33% yield; feed incompletely molten			Melt and cast		–

*A and B represent consecutive treatments, with B treating the product from A.

Two groups of DOR buttons were leached in water or nitric acid solutions to remove soluble impurities (e.g., calcium) from the button surface. Whole buttons fed to ER-023 and button halves fed to ER-032 were leached by nonagitated submersion in open containers at ambient temperature. Leaching in water was sufficient for relatively clean surface buttons, while 0.5*M* HNO_3 solutions were used for rough-surfaced, dirty buttons. Several exposures to fresh leach solution were required to complete the cleaning process. Completion was identified visually by the cessation of gas evolution and required from one-quarter to seven hours, depending on button cleanliness. Leach solution samples were collected for analysis.

Results and Discussion

Calcination

Feed and product weights for oxides calcined as part of the test sequence are given in Table 7. Analytical data for feeds and products are given in the Appendix, Table A1.

Calcination of "green cake" (α-oxide) resulted in 4 to 5% oxide weight loss and a decrease from 132 to 100 parts per million (ppm) and 48 to 21 ppm in carbon content for Runs 95 and 109, respectively. Mass balance calculations indicate carbon losses for Runs 95 and 109 at 28% and 58%, respectively. Mass balances also suggest 70 to 75% iron loss for both runs; however, this is likely related to formation of stable complex iron species not digested for atomic absorption (A.A.) analysis. Product oxides for DOR showed 1000 ppm calcium by E-spec with tantalum and tungsten levels of <10 ppm. Gallium was only analyzed in product from Run 109 and showed 28 ppm, an apparent loss of over 80%. Again, this is likely due to analytical or sampling errors since no volatile gallium species are expected in feed oxides.

Two-stage calcination of pure delta oxide (produced from burning delta metal) resulted in negligible weight loss in Run 767733 and a weight gain in Run 767736. These results may be due to incomplete burning of the metal prior to calcination and prompt calcination before significant pickup of moisture or other reactants from the

atmosphere. Carbon level was decreased from 198 to 118 ppm for oxide in Run 767733 and from 197 to 104 ppm for Run 767736. Mass balance calculations indicate a carbon loss of 40 to 47% and 1 to 21% iron loss during calcination. However, iron loss is not supported by the combined oxide feed analysis taken prior to DOR. Both calcined oxide samples show relatively low calcium contents and <10 ppm tantalum and tungsten, although the E-spec magnesium level in one run product shows 1000 ppm. Again, gallium levels showed a decrease as a result of burning and calcining, but this is thought to be due to analytical or sampling errors; no volatile species are known.

There are notable differences between the combined oxide DOR feed sample and the two calcined oxides. The calcium level (by A.A.) shown for DOR oxide feed is 1730 ppm, significantly higher than the calcined oxide samples. Higher nickel and magnesium are also indicated in the combined oxide DOR feed sample than in the calcined oxides, 1000 and 3150 ppm, respectively. Likewise, tantalum and tungsten in the combined oxide DOR feed sample were 20 and 50 ppm, respectively.

Pure delta metal burned to produce oxide for calcination showed <10 ppm calcium, 235 to 375 ppm iron, and 195 to 225 ppm nickel, all significantly lower values than indicated in calcined and uncalcined oxide. Iron and nickel pickup may be associated with contamination from the vessel used during burning; however, the source of calcium is unknown.

Impure delta oxide showed 0 to 0.5% weight loss during calcination. Carbon levels decreased from 473 to 243 ppm for Run 110, from 380 to 270 ppm for Run 111, and remained unchanged for Run 112. The calculated carbon losses are 51 to 71% for the first two runs and 0% for Run 112. Again, some iron loss is suggested by the analytical data. Calcium and magnesium levels in calcined oxides are low, as are tantalum and tungsten levels.

The analytical data for calcined oxides support the use of calcined "green cake" as a pure alpha oxide feed for DOR/ER evaluation. With the exception of calcium, all impurities are at very low levels. The delta oxide analyses indicate that the pure delta oxide prepared for test work does not exhibit significantly lower impurity levels than the impure delta oxide. Indeed, iron, nickel, magnesium, and calcium levels are generally higher in the calcined pure delta oxide than in the calcined impure delta oxide. Both pure and impure delta oxides more accurately qualify as intermediate grade with respect to impurities. Neither show the consistently low impurity levels of the pure alpha oxide nor exceptionally high levels of suspect impurities (e.g., >1000 ppm carbon, aluminum, tantalum, and tungsten).

Direct Oxide Reduction

Results of DOR runs and test conditions are listed in Table 8 for the three types of oxide feed. Three of the twenty-one runs initiated on fresh oxide feeds failed to produce product buttons, and an additional eight runs produced appreciable quantities of black salt. Ten runs yielded product buttons with negligible black salt formation.

The overall product yield for DOR (plutonium in the feed oxide divided by the product metal weight–non-plutonium product basis) was 77.5%, including the "no-button" runs. Plutonium yields for individual runs were calculated based on "100% minus" assays, oxide plutonium assays by calorimetry (from DOR run sheets), and feed/product weights given in Table 8. Values ranged from 82.1 to 100.7% of contained feed plutonium reporting to the product button. Pure alpha oxide averaged 96.4% plutonium yield, while pure delta oxide averaged 88.7%. Insufficient assay information is available for a meaningful average on impure delta oxide runs.

Groups of DOR buttons were calorimetered in preparation for ER, and overall average yields based on the button calorimetric data are also shown in Table 8. Calculated plutonium yields for pure alpha, pure delta, and mixed delta oxide reductions were 96.1, 85.1, and 78.3%, respectively. Calorimetric plutonium assays for the three DOR product button types were (1) pure alpha - 0.9843 g/g, (2) pure delta - 0.9700 g/g, and (3) mixed delta - 0.9336 g/g.

The stoichiometric excess of calcium added varied from 27.3 to 140.7%. However, except for two runs, all calcium additions for the oxide reduction were in the range of 37.0 to 49.2% in excess of stoichiometric requirements. Assumptions used for this calculation are shown in Table 8.

Analytical data for product DOR buttons are given in the Appendix, Table A2. Mass balances based on these data were calculated for several cases and proved relatively meaningless for most components due to:

1. Material inhomogeneity and resulting sampling error.

2. Analytical error inherent in E-spec analyses or specific analytical procedures.

3. Contamination of the product by unquantifiable inputs such as magnesium from crucible reduction or tantalum from the stirrer.

4. Lack of analytical data for major process streams; e.g., salts and calcium.

Analytical results for pure alpha DOR runs suggest increases in gallium concentrations during reduction. If the effect is real, the source (e.g., contamination from previous runs and feed salts) is unknown. This result may simply reflect an effect of sampling. Analytical data also show apparent nickel, tantalum, carbon, chromium, aluminum, and iron pickup during treatment. Calcium and magnesium increases are indicated, as expected from process chemistry considerations. The very limited feed salt analytical data collected are given in the Appendix, Table A3 and indicate that a fraction of the iron and aluminum inputs from this source could account for indicated metal pickup. DOR/ER Buttons 1-4 (treated in ER-021) generally show low levels of impurities with the exception of one calcium (5000 ppm) and one nickel (1700 ppm) value. Chromium and magnesium also appear high (500 to 1000 ppm) but were determined by semiquantitative E-spec analysis.

Results for pure delta DOR runs also indicate modest gallium pickup during DOR. However, the apparent decrease in gallium level during calcining suggests that gallium may actually be present in calcined oxide at higher levels but unreported due to the analytical procedure used (stable forms undigested for analysis). Also, gallium may be quite nonhomogeneous in DOR product buttons because of the presence of free calcium.

Within E-spec analytical error, the product levels of chromium, aluminum, and tungsten, as expected, are relatively low. In spite of low tantalum in the feed oxide, up to 2000 ppm was observed in one product button. Iron level in the product is in agreement with feed oxide analysis, while some nickel increase and modest carbon loss are indicated. High levels of calcium gain are shown. The pure delta metal produced for ER does appear to be relatively pure, with the notable exception of one high tantalum value (2000 ppm) and one high magnesium value (2250 ppm), both by E-spec. The calcium level of 1.45% for DOR/ER 10 is also exceptionally high. It should be noted that accurate calcium determination levels in DOR buttons are nearly impossible to obtain due to button inhomogeneity and associated sampling error. In comparison to pure alpha feed, aluminum, tungsten, nickel, and iron levels are similar, chromium and carbon are slightly lower, and aluminum is slightly higher. Both tantalum and calcium are highly variable.

Insufficient product button analytical data are available to comment on impure delta oxide DOR runs. However, the final button lot for ER (DOR/ER 14 to 21), intended to represent a less pure delta feed, does appear to be higher in carbon, iron, nickel, and aluminum impurities. Calcium and magnesium also appear higher in this lot.

No unique feed properties appear to correlate with the failure to generate product buttons in Runs DOR/ER 6, 19, and 22. However, improper stirring (e.g., broken blade and incorrect placement) was associated with each of these runs. Crucible breakage also occurred during Run 6. No clear correlation exists for feed nor other data with the quantity of black salt in products. Initial DOR runs did tend to yield higher quality buttons and higher yields than later runs. The onset of rougher surface features and poorly formed buttons in later runs appear to correlate with lower grade (percent

plutonium) product buttons, poorer plutonium yields, and increased frequency of black salt generation in later runs. It was also noted that poorly consolidated buttons and foaming were much more frequent in runs made in research furnaces (DOR/ER 14 to 22) than in runs made in production equipment used for Runs DOR/ER 1 to 13.

Samples of DOR buttons from DOR/ER 1 and DOR/ER 3 to 17 were examined metallographically with SEM and XRD to characterize inclusions present within the buttons. Results of these analyses are summarized as follows:

1. Frequent occurrences of inclusions showing major calcium and chlorine together.

2. Frequent occurrences of inclusions with zero to trace chlorine and major calcium and magnesium.

3. Occasional appearance of:
   - Chromium inclusions
   - Holes from inclusions that were polished out and showed plutonium only
   - Tantalum (rare appearance)
   - Calcium only

There did not appear to be a clear correlation between the types of inclusions and the quality of buttons produced or subsequent ER performance. The identity of the inclusions cannot be unambiguously determined. However, the major calcium-chlorine associations are likely DOR salt remaining within the DOR button, perhaps with oxides precipitated on cooling. The calcium-magnesium associations (Item 2 above) with minor or no chlorine appear and behave distinctly, as if they were metallic rather than oxidic; however, no clear identification has been made.

Electrorefining

Results of tilt/pour ER runs are summarized in Table 11. Analytical results for metal feed and ER products are given in the Appendix, Table A4. The data in Table 11 show anode depletions for successful runs ranging from 49.6 to 97.8% on a plutonium basis and 48.1 to 96.3% on a net weight basis. Pouring yields of 20.3 to 92.4% (plutonium basis) or 19.5 to 91.2% (non-plutonium basis) were experienced. Transfer rates based on accounting for plutonium in the salt (i.e., corrected) range from 2.07 to 2.77 g Pu/A·hr. Feed composition data in Table A4 show the following ranges for the impurities listed:

Cr	- 54-765 ppm
Ga	- 0.075-1.055 wt %
Al	- <5-500 ppm
W	- <10-178 ppm
Ca	- 10-31,900 ppm
C	- 81-1,510 ppm
Ta	- <10-1,599 ppm
Fe	- 340-2,690 ppm
Ni	- 78-3,954 ppm
Mg	- <5-4,144 ppm

Note that these ranges represent the calculated weighted average composition for feed to ER, i.e., several DOR buttons, not the ranges represented by individual buttons to ER.

Initial Test Plan Runs

The initially planned four-test sequence is represented by ER Runs ER-018, ER-021, ER-025, and ER-026. A summary of performance for these runs is given in Table 12. The anode depletion experienced for ER-025 probably represents a lower value for this type of feed than the other two feeds. If delta DOR feed metal does yield lower anode depletion, several potential causes may contribute.

The hypothesis suggested by the test sequence results is that high gallium levels in combination with DOR-related chemical and physical impurities (e.g., calcium, magnesium, and other impurities such as salt inclusions, and unreduced plutonium

TABLE 11. Tilt/Pour ER Results

ER Run No.	Product Weight (g)				Transfer Rate (g/A·hr)[1]		Pouring Yield (%)		Anode Depletion (%)		Estimated Pu Content (%)[2]		Comments
	Product	Salt	Anode Heel	New Holdup	Corrected Basis	Uncorrected Basis	Pu Basis	Net Wt Basis	Pu Basis	Net Wt Basis	Salt	Anode	
018	1114	3211	305	+996	2.597	2.708	44.8	44.6	88.7	87.8	2.8	92.1	
019	877	3170	189	-149	2.55	2.766	90.7	89.4	81.9	80.7	1.9	92.6	Cracked cup
020	472	2950	847	+253	2.46	2.655	29.8	28.9	49.6	48.1	2.0	94.3	
021	1515	2821	163	-39	2.45	2.681	86.0	84.7	92.3	90.9	5.0	82.8	
022	827	2677	471	-62	2.420	2.686	63.2	62.6	65.1	64.4	3.1	97.0	
023	755	2551	573	+242	2.40	2.618	47.2	45.2	68.6	65.7	3.6	87.6	
024	1598	2483	228	-166	–[3]	–[3]	–	–	86.9	86.9	–[3]	–[3]	Broken anode cup
024A	623	3066	408	+889	2.61	2.867	32.1	31.7	80.2	79.2	4.6	94.1	
025	938	2796	325	+312	2.57	2.756	58.1	56.4	83.0	80.5	3.2	84.6	
026	434	2877	689	+883	2.29	2.665	20.3	19.5	71.8	69.1	7.6	87.5	
027	1452	2454	286	-114	2.56	2.708	87.6	86.6	83.9	82.9	2.9	93.4	
028	982	2512	848	+172	2.40	2.627	45.7	45.2	61.7	61.0	4.5	97.2	
029	1230	2455	714	+78	2.77	2.921	59.9	59.2	66.4	65.6	2.9	96.5	
029A	279	2262	335	+131	2.36	2.830	40.6	39.2	54.9	52.9	2.8	92.5	
029+A[4]	1509	2775	335	+209	2.74	–	73.5	72.6	84.9	83.9	3.3	92.5	
030	746	2515	799	+262	2.48	2.734	38.6	38.1	59.9	59.2	4.1	97.0	
030H	76	2438	754	-218	–	–	–	–	–	–	–	–	Anode heel would not remelt
031	976	2501	571	-33	2.41	2.630	65.2	65.0	63.4	62.5	3.1	96.0	
032	950	2700	431	+81	2.07	2.564	54.4	52.7	78.6	76.1	9.7	86.8	
033	948	2542	589	-181	2.49	2.825	67.4	62.9	65.2	60.9	4.2	83.0	
034	1402	2492	59	+23	2.57	2.775	89.4	88.0	97.8	96.3	4.4	59.3	
035	1509	2708	270	-498	2.132	2.433	92.4	91.2	87.8	83.7	6.0	91.9	
036	1227	2598	273	-110	2.39	2.709	77.6	76.5	84.1	82.8	5.7	91.9	
037	1931	2416	70	+200	–	–	–	–	–	–	–	–	Failed run–Low Amperes
038	446	2399	485	+294	2.53	2.614	37.6	36.2	62.8	60.6	3.5	90.9	

[1] Transfer rate (g/A·hr): Corr. basis = $\frac{\text{Feed} - \text{anode heel} - \text{Pu in salt}}{\text{A·hr}}$; uncorr. basis = $\frac{\text{Feed} - \text{anode heel}}{\text{A·hr}}$

[2] Salts were counted, anode heel Pu determined by feed impurity content, holdup Pu by difference.

[3] Broken anode cup.

[4] Calculated combined results for 029 and 029A.

TABLE 12. Feed Composition and Anode Depletion Data for the Three ER Runs Comprising the Initial Test Plan

ER Run No.	Feed Type and Conditions Represented	Anode Depletion (%)		Composition (ppm)								
		Pu Basis	Non-Pu Basis	Cr	Al	W	Ca	C	Ta	Fe	Ni	Mg
018	Non-DOR–high gallium	88.7	87.8	765	31	<10	10	175	<10	340	78	<5
021	DOR–low gallium	92.3	90.9	880	106	<10	1450	139	106	527	745	420
025	DOR–high gallium	83.0	80.5	75	180	10	318	83	1050	595	480	347
026	DOR–high gallium	71.8	69.1	307	147	169	1902	396	338	1722	3954	104

oxide) somehow limit anode depletion. These results suggest that in the absence of either gallium or DOR-related impurities, the effect is insignificant, assuming that both DOR feeds contained equal amounts of DOR-related impurities. Feed composition data show somewhat higher aluminum and significantly higher tantalum for ER-025 feed. However, most other impurities are comparable or lower than ER-018 or ER-021. Calorimetric plutonium values for feeds to ER-018, ER-021, ER-025, and ER-026 were 0.991, 0.984, 0.970, and 0.961 g/g, respectively.

The difference between results may well be due to significant amounts of included salt and other inhomogenously distributed DOR-related impurities (surface or inclusions). In this case, these types of impurities are more clearly shown by calorimetric plutonium data than the chemical analyses.

Data given in Table 9 do not reveal any key operating condition differences that might account for lower anode depletions in ER-025 and ER-026. There were no physical ER procedures that might have caused the difference in anode depletions prior to run termination. Transfer rates for plutonium (g/A·hr) are similar for ER-018 and ER-025.

An overall summary of ER run results with various feed compositions is given in Table 13. Runs ER-028, ER-030, and ER-031 were made using delta production DOR metal feeds under ER test conditions similar to those used for ER-025. The resulting anode depletions achieved were very consistent (59.9 to 63.4% plutonium basis, 59.2 to 62.5% non-plutonium basis) and much lower than for pure delta DOR metal in ER-025. These runs may be combined with ER-026 as the impure delta case. Two important feed differences may be related to the poorer ER performance:

1. Impurity levels are significantly higher than for the pure delta feed (ER-025). Iron, nickel, and chromium are higher, and calcium, carbon, and magnesium are much higher than ER-025 feed.

2. Feed buttons were drawn from stocks of past DOR buttons from production operations (as opposed to research tests), possibly during a period when buttons were being selectively stocked rather than electrorefined (based on poor or dirty appearance).

Either "high-grading" or routine production procedures could have yielded buttons containing much higher levels of DOR-related inclusions for feed in ER-028, ER-030, and ER-031. This is supported by the comparison of the calcium and magnesium feed concentrations shown in Table 13. Total calcium and magnesium for ER-025 is 665 ppm, while totals for the production DOR button feeds to ER-028, ER-030, and ER-031 range from 1567 to 3271 ppm. Although plutonium assay data for these ER feeds from production DOR ranged from 0.9849 to 0.9890 g/g plutonium, earlier calorimetric values on the same DOR button batches showed values of 0.955 to 0.968, suggesting the presence of large quantities of impurities.

The results for production DOR feeds, compared to ER-018, ER-021, and ER-025, indicate that

TABLE 13. Summary of Tilt/Pour ER Results and Feed Metal Compositions

Run No.	Metal Feed Type	Stirring	Holdup		Non-Pu Basis		Pu Basis	Feed Metal Composition									
			New (g)	Increase (%)	AD (%)	Yield (%)	AD (%)	Cr (ppm)	Al (ppm)	W (ppm)	Ca (ppm)	C (ppm)	Ta (ppm)	Fe (ppm)	Ni (ppm)	Mg (ppm)	Pu (g/g)
018	Foundry reject metal	Salt	996	–[1]	87.8	44.6	88.7	765	31	<10	10	175	<10	340	78	<5	0.995
019	DOR & vac. melt & drip cast	Salt	-149	-15.0	80.7	89.4	81.9	100	500	<10	400	–	500	1,300	408	25	0.986
020	DOR & MS consolidation (321)	Salt	+253	+30.0	48.1	28.9	49.6	54	32	<10	>1,000	776	20	1,200	420	>1,000	0.971
021	DOR/ER 1-4 (pure alpha)	Salt	-39	-3.5	90.9	84.7	92.3	880	106	<10	1,450	139	106	527	745	420	0.984
022	DOR & vac. melt & drip cast	Salt	-62	-5.7	64.4	62.6	65.1	284	163	–	<45	81	–	664	250	>45	0.989
023	Leached DOR buttons	Salt	+242	+23.4	65.7	45.2	68.6	148	26	32	347	1,510	880	2,690	734	215	0.957
024	T/P DOR buttons	Salt	-166	-10.9	86.9	–	86.9	136	27	180	229	708	454	1,139	1,896	100	0.988
024A	ER-024 rerun & T/P DOR	Salt	+889	–[1]	79.2	31.7	80.2	129	25	178	228	715	497	1,144	1,822	100	0.988
025	DOR/ER 9-12 (pure delta)	Salt	+312	+35.1	80.5	56.4	83.0	75	180	10	318	83	1,050	595	480	347	0.970
026	T/P DOR buttons	Salt	+883	–[1]	69.1	19.5	71.8	307	147	169	1,902	396	338	1,722	3,954	104	0.961
027	DOR & vac. cast in 771	Salt	-114	-12.4	82.9	86.6	83.9	66	66	8.4	499	492	28	700	467	307	0.989
028	DOR buttons	Salt	+172	+21.4	61.0	45.2	61.7	237	64	<10	1,591	645	201	1,031	784	1,680	0.989
029&A[2]	DOR buttons–split w/030	Metal stir–anode	+209	+21.5	83.9[2]	72.6[2]	84.9[2]	753	338	7.9	1,840	900	1,599	701	436	696	0.988
030	DOR buttons–split w/029	Salt	+262	+22.1	59.2	38.1	59.9	753	338	7.9	1,840	900	1,599	701	436	696	0.988
031	DOR buttons–split w/032	Salt	-33	-2.3	62.5	65.0	63.4	349	123	1.9	1,012	428	1,032	1,572	1,766	555	0.985
030H	ER 030 anode heel	Metal stir–anode	Initial anode did not melt														
032	Leached DOR buttons–split w/031	Salt	+81	+7.0	76.1	52.7	78.6	349	123	1.9	1,012	428	1,032	1,572	1,766	555	0.986
033	DOR/ER 14-21 (pure/impure delta mix)	Metal stir–anode	-181	-14.5	60.9	62.9	65.2	62	295	<10	30,430	194	674	735	793	3,507	0.934
034	MSE delta metal	Metal/ceramic–salt/anode	+23	+2.2	96.3	88.0	97.8	600	<5	<10	10	357	<10	1,300	240	1,000	0.985
035	DOR buttons	Metal/ceramic–salt/anode	-498	-45.0	83.7	91.2	87.8	148	48.5	<10	154	307	143	887	201	213	0.987
036	Mix–DOR/MSE metal	Metal/ceramic–salt/anode	-110	-18.1	82.8	76.5	84.1	520	170	4	971	578	875	1,032	616	632	0.986
037	MSE delta metal	Metal/ceramic–salt/anode	Run failed–Low Amps–Broke cup while troubleshooting														0.987
038	DOR buttons[3]	Metal/ceramic–salt/anode	+294	+120	60.6	36.2	62.8	–	–	–	–	–	–	–	–	–	0.964

[1] No initial holdup.

[2] Combined ER-029 and ER-029A.

[3] Analytical data not yet available.

either some physical/chemical characteristic of DOR production buttons or the generally higher level of impurities associated with them severely limit anode depletion for delta feed. Whether this would be true for impure alpha DOR buttons is unknown.

Non-plutonium-basis anode depletion experienced with production DOR feeds during the test program ranged from 59.2 to 62.5%, compared to a "lost amps" average of 55.3% (Table 6) and "good and lost amps" run-average of 67.3% (Table 1) for production ER. This represents reasonable agreement and substantiates the "poor" performance of production DOR buttons in the test program as well as during production operation.

Metallography/SEM/XRD results for DOR buttons used for feed to Runs ER-021 (pure alpha) (DOR/ER 1 to 4) and ER-025 (pure delta) (DOR/ER 9 to 12) show inclusions with:

1. Major calcium and magnesium concentrations with only minor or no chlorine associated.
2. Major calcium and chlorine together.
3. Magnesium and chlorine together.
4. Chromium inclusions.

No similar information is available for non-DOR or production DOR feed metal to ER runs.

Metallography/SEM/XRD studies were performed on anode heels from ER-018 (non-DOR feed) and ER-028. ER-018 heel showed inclusions with chlorine and plutonium associations, with no sodium, potassium, nor calcium identified in inclusions. Some carbon was also detected. ER-028 heel showed inclusions with major calcium-chlorine-magnesium associations, chlorine-calcium associations, and calcium-magnesium associations with little or no chlorine. No inclusions showing sodium or potassium were noted. The qualitative trend for anode heel inclusions was found to be mainly plutonium-chlorine associations when runs yielded high anode depletions, but calcium-chlorine-magnesium associations when runs yielded low anode depletions (e.g., <70%). This again supports the role of DOR-related (not necessarily oxide-feed related) chemical and physical impurities in limiting of ER anode depletions. Only trace amounts of tantalum, silicon, or iron were noted. Carbon was occasionally identified, but aluminum, tungsten, gallium, and nickel were not seen in the ER-018 or ER-028 anode heels.

Intermediate Treatment

Preliminary evaluation of four intermediate treatment schemes was made during the test program. ER Runs ER-019 and ER-022 were made on DOR metal that had been vacuum melted and drip cast prior to ER. Runs ER-023 and ER-032 were made on leached DOR buttons. Run ER-027 was made on vacuum cast DOR metal, and ER-020 was made on DOR metal that had been consolidated, with stirring, under a molten salt. Results are reported in the following sections.

Vacuum Melting and Drip Casting

Feed identity and analytical data for DOR materials fed to vacuum melting and drip casting are unavailable to assess the impact of this treatment on ER feed purity. Related analytical data are available from this program and are given in the Appendix, Table A5. Performance parameters are given in Table 10.

Results of the vacuum melting procedure show 7 and 34 g of condensate collected for VM-2 and VM-3, respectively. The larger value for VM-3 may have resulted from the higher vacuum and temperature used and also includes some physically splattered material from the melt. The only condensate sample available [VM-3(A)] shows considerable quantities of zinc* in addition to magnesium and calcium. The levels of these components back-calculated to feed would be 0.14, 0.5, and 0.3% for calcium, magnesium, and zinc, respectively—reasonable levels for all except zinc (seldom >25 ppm in DOR buttons).

*Could have been in furnace from previous Pyroredox work.

Drip casting of anodes showed a product yield of ~49 to 59% to cast product for vacuum-melted feed. Non-vacuum-melted DOR feed gave only about 33% yield to cast anode and was difficult to melt. The composition of casting skull and non-molten skin from AC-2 (Table A5) shows extremely high calcium content and high tantalum and carbon levels. Casting skull from AC-1 also shows high carbon but not an excessive calcium level.

ER results for ER-019 and ER-022 are given in Tables 11 and 13. Anode depletions achieved were 80.7 and 64.4% (non-plutonium basis) and 81.9 and 65.1% (plutonium basis) for ER-019 and ER-022, respectively. Feed analyses shown in Table 13 reflect an actual feed sample for ER-019 but only the top drilled AC-2 product surface for ER-022. In light of this, the analytical data do not suggest a cause for the vast difference in performance between the two vacuum-melt/drip-cast metals in ER. However, given the high calcium content in the drip cast skull and the known inhomogeniety of calcium in plutonium, one might suspect a higher concentration of calcium in ER-022. Run conditions given in Table 9 show that ER-019 feed weight is about one-half the normal anode size, resulting in about twice the ratio of $MgCl_2$ and total salt-to-feed-metal weight of that typical for other ER runs. A cracked anode cup was also experienced during ER-019; however, there was no evidence of metal leakage from the anode. The transfer rates (g Pu/A·hr—corrected to account for plutonium in salt) were 2.55 g/A·hr for ER-019 and 2.42 g/A·hr for ER-022.

Feeds to both VM-2 and VM-3 were production DOR buttons. Therefore, ER Runs ER-028, ER-030, and ER-031 represent the comparison to feeds without vacuum-melt/drip-cast intermediate treatment. On this basis, the results are mixed. In the case of ER-019, the treatment appears to have significantly improved performance: 81.9% anode depletion (plutonium basis) with treatment vs 59.5 to 63.4% (plutonium basis) without treatment. ER-022 anode depletion was 65.1% (plutonium basis), indicating no significant effect of treatment in this case.

Some insight into the ambiguous test results is offered by the metallography/SEM/XRD results for ER-019 feed and anode heel and ER-022 anode heel. Two key observations have been previously presented:

1. DOR buttons provided to ER characteristically show inclusions with major calcium-chlorine together and calcium-magnesium with zero to trace chlorine.
2. Anode heels from low anode depletions tend to show similar calcium-chlorine-magnesium inclusions related to DOR-introduced impurities, while high anode depletion runs show mainly plutonium-chlorine associated inclusion.

Vacuum-melt/drip-cast feed to ER-019 showed none of the typical DOR button inclusions (e.g., calcium-chlorine, calcium-magnesium, and calcium-chlorine-magnesium), possibly due to effective removal during intermediate treatment. No metallography/SEM results are available for ER-022 feed for comparison, but perhaps the vacuum melt/drip cast treatment did not effectively remove the DOR-related chemical impurities or physical carryover. The latter possibility is supported by results on the anode heels in which ER-019 anode heel showed mainly the plutonium-chlorine type inclusions characteristic of high anode depletion runs, while the ER-022 (low anode depletion) anode heel showed the calcium-chlorine inclusions characteristic of DOR-related physical and chemical impurities. Anode heel calcium levels for ER-022 and ER-019 in the Appendix, Table A4, support this observation.

This explanation may account for the difference between ER-019 and ER-022. If so, the data suggest that effective intermediate treatment by this technique (if it can be consistently accomplished) could enable typical DOR product to achieve anode depletions about 15 to 20% higher than the indicated 60 to 65% levels demonstrated without vacuum melt/drip cast. The results are not conclusive and indicate that "consistently" successful intermediate treatment requires further demonstration and, possibly, process development. The results also clearly show the large losses to side streams (40 to 50%), which may be associated with application of this technique.

Leaching

ER Runs ER-023 and ER-032 experienced anode depletions of 68.6 and 78.6%, respectively, on a plutonium basis and 65.7 and 76.1%, respectively, on a non-plutonium basis. The plutonium-basis values compare with 59.9 to 63.4% for non-leached production DOR buttons. If other feed and process variables are neglected, modest impact of leaching is shown for ER-023, while a significant improvement in ER performance is suggested by the results of ER-032.

No significant differences between ER-023 and ER-032 ER conditions are shown by the data in Table 11. Higher carbon and lower calcium are shown for ER-023 feed (Table 13). Otherwise, feed compositions are similar. Significantly higher plutonium loading in spent salt is indicated for ER-032, which results in a rather low value of plutonium transfer rate when salt plutonium correction is made: 2.07 g Pu/A·hr. It is noteworthy that visual observations made during the leaching process indicated the ER-023 DOR buttons to be much rougher and "dirtier" in appearance.

Although calcium and magnesium levels appear higher for the unleached production buttons than for the two leached buttons (before leaching), most other impurity levels are similar for both feed types. Unfortunately, buttons were not sampled after leaching, and leach solution analyses for estimation of impurity removal were inconsistent. The purest comparison of leaching effect, independent of feed composition, is given by ER-032 (leached) vs ER-031 (unleached). The same production DOR feed was used for the two runs, and results show 78.6% anode depletion (plutonium-basis) for the leached buttons compared to 63.4% (plutonium-basis) for the unleached.

If the ER-032/ER-031 comparison is assumed to be significant and reproducible, then about 15% anode depletion (plutonium-basis) may be attributed to this intermediate treatment. However, further demonstration of the effect is required to substantiate this preliminary result and resolve the failure of leaching to enchance ER-023 performance. It is possible that the very rough and dirty initial appearance of the ER-023 feed indicated a very high internal loading of inclusions with DOR-related impurities inaccessible to the surface leaching process. Thus, leaching was ineffective in improving ER performance, and some other type of intermediate treatment might have been more appropriate. No metallography/SEM/XRD results were obtained on anode heels from ER-023 or ER-032.

Vacuum Casting

Five production DOR buttons were vacuum cast. The analytical data given in Table A4 (ER-027) show the composition of metal before and after vacuum casting. Although no mass balance data were provided for the vacuum casting process, the feed weights to vacuum casting and subsequent ER indicate a metal recovery of about 73%. Although the calcium levels are similar for feed to and product from the casting operation, the mass loss suggests that a volatile metal or skull was removed. A massive pickup of tantalum, tungsten, and aluminum is also indicated.

ER results summarized in Tables 11 and 13 show anode depletions of 83.9% (plutonium basis) and 92.9% (non-plutonium basis) for the vacuum cast feed. These results compare to plutonium basis values of 59.9 to 63.4% and non-plutonium basis values of 59.2 to 62.5% for untreated production DOR buttons. Also for comparison, previously cited "successful" vacuum melt/drip cast and leaching intermediate treatments yielded non-plutonium anode depletions of 80.7 and 76.1%, respectively. If all these preliminary results are assumed reproducible, then vacuum casting pretreatment appears to offer about 20% anode depletion improvement. This is about the same as vacuum melt/drip cast treatment, but the data suggest that it may be achievable at a material loss of 35 to 40% to a side stream, compared to 40 to 50% for vacuum melt/drip cast. However, further tests are required to substantiate and further quantify the intermediate process.

Molten Salt Consolidation

One lot of production DOR buttons was remelted and stirred under a calcium chloride – magnesium

chloride salt cover to remove calcium metal and consolidate the metal for ER. Product analysis is given in Appendix-Table A4 and Table 13 as ER-020 feed. Both calcium and magnesium levels are high (>1000 ppm E-spec), carbon is somewhat high (776 ppm carbon), but other impurities are relatively low. Consolidated product yielded anode depletions of 49.6 (plutonium basis) and 48.1% (non-plutonium basis) for ER-020.

The consolidated button was composed of three phases. Metallography/SEM/XRD results showed the inclusions in the bottom phase to be mainly plutonium with nickel/iron impurities. The top and middle phases showed inclusions with magnesium-plutonium, magnesium-plutonium-chlorine, and magnesium-chlorine associations. X-ray diffraction results on an edge piece of the button identified minor/moderate PuC or PuN, as well as PuO_2 and oxychloride, in addition to delta plutonium. Major calcium-magnesium-chlorine associations were seen only in the edge piece analyzed.

This preliminary molten salt consolidation technique did not yield improved ER performance. The anode froze half way into the run. No explanation for the poor performance is suggested by the above results; further evaluation is required to yield any firm conclusion. Two special samples of the consolidated metal were separately analyzed spectrographically: (1) smooth, well-molten metal and (2) a rough, poorly-molten section of metal. Calcium ranged from 1.6 to 3.7% with 500 to 1000 ppm magnesium in the two separate samples, suggesting that (in spite of the SEM results) the feed to ER may still have been extremely high in DOR-related impurities as inclusions.

Tilt/Pour DOR Buttons

Two ER runs were made on buttons produced from DOR that had been performed in a tilt/pour furnace: ER-024 and ER-026. The best buttons, based on plutonium assay and general appearance, were selected for ER-024. The anode cup broke during ER-024, but the metal was rerun as ER-024A. Anode depletion of 79.2% (non-plutonium basis) and 80.2% (plutonium basis) were achieved for ER-024A. Anode depletions of 69.1% (non-plutonium basis) and 71.8% (plutonium basis) were achieved during ER-026. These DOR metal feeds show higher than typical tungsten levels (>150 ppm) and lower magnesium content (~100 ppm), probably both indications of the DOR equipment difference. Calcium, nickel, and iron in ER-026 feed also appear slightly higher than the normal ranges.

It is difficult to say whether the 9 to 10% improvement over stationary furnace DOR button performance indicated by this single test represents a real effect. Further test work is indicated and recommended. Tilt/pour DOR physical processing, specifically the pouring sequence with associated holdup, may provide a mechanism for inclusion removal, high-melting impurity removal, or viscous-phase removal, as holdup, sufficient to enchance the ER process.

Anode Stirring

Stirring of the anode metal was evaluated as a mechanism to increase anode depletion for DOR feed metal. Anode stirring was also intended to provide improved back-EMF measurement capability and decrease impurity transfer.

Metal Stirrer

Initial stirring tests were conducted using a tantalum metal stirrer with a single impeller. The anode metal and the salt phase were stirred in the typical 160 to 170 rpm range. To avoid electrolyzing the tantalum metal, the cell was operated at a significantly lower voltage (2.5 to 2.6 V) and amperage (15 to 19 A). Runs ER-029 and -029A, ER-030H, and ER-033 were conducted in this fashion.

Run ER-029 experienced an induction heating failure during initial operation. The initial run was terminated for repairs, and the anode heel restarted and completed as Run ER-029A. It is significant to note that the salt was reused with a ~100 g increase in holdup (possibly due to moisture pickup outside the furnace). The combined results for ER-029 and ER-029A show anode depletions of 83.9% (non-plutonium basis) and 94.9% (plutonium basis). ER-033 was conducted using

the mixed pure/impure delta DOR metal prepared in DOR/ER Runs 14, 15, 17, 20, and 21. Run ER-033 achieved anode depletions of 60.9% (non-plutonium basis) and 65.2% (plutonium basis). ER-030H was conducted on the spent anode heel from ER-030 in an attempt to demonstrate the ability to remelt and achieve additional electrolysis by virtue of the stirred anode. The anode heel would not remelt and no restart could be accomplished.

The results of using a metal stirrer in the anode are inconclusive. The results of ER-029 (and 029A) indicate a beneficial increase in anode depletion. This is particularly clear when compared with the results of ER-030 (plutonium-basis anode depletion = 59.9%), which used identical feed metal. However, the results cannot be clearly attributed to anode stirring since cell electrical conditions (e.g., voltage and current density) were also significantly different for the metal-stirrer runs. There is also the potential effect (good or bad) of the ER-029 shutdown/startup procedure. What is suggested by the single comparison is that a lower voltage/current operation with metal-stirred anode may yield a significant improvement in anode depletions for DOR metal during ER.

Based on the above results, the performance of ER-033 was surprisingly poor. A possible explanation is indicated by analytical data for metal feed. Extremely high calcium (>3%) and magnesium (~3500 ppm) are shown in Tables 13 and A4, pointing to very high levels of DOR-related impurities in the buttons. This is supported by a comparison of the average "100% minus" plutonium assay–0.9787 g/g–with the calorimetric value–0.9336 g/g. Further, DOR results show two of the five DOR runs produced significant quantities of black salt, one run was made with extremely high excess calcium addition, and one button was noted as being poorly consolidated. The presence of DOR-related impurities is confirmed by the frequency of their observation in metallography/SEM/XRD results for DOR/ER Buttons 15, 17, and other buttons to ER-033. No metallography/SEM results were obtained for ER-029 or ER-033 anode heels.

It is noteworthy that back-EMF readings upon termination for ER-029 (and 029A) and ER-033 were 0.025 to 0.091 V, compared to nearly one volt for ER runs stirred only in the salt phase.

Metal/Ceramic Stirrers

Five ER runs were conducted using a combined metal/ceramic paddle stirrer designed to stir both the salt phase (with the upper metal portion) and the metal anode (with the lower ceramic portion). These runs served a dual purpose as part of the DOR/ER test program and the initial phase of an ongoing stirrer-development program. ER Runs ER-034 through ER-038 were made using the metal/ceramic stirrer. Use of the ceramic lower section for anode stirring made it possible to electrorefine at cell parameters typical of unstirred-anode conditions: 5.8 to 6.0 V and 46 to 60 A, since tantalum was not in contact with the anodic molten plutonium. Two ER runs were made on DOR feeds (ER-035 and ER-038), two runs on non-DOR feeds (ER-034 and ER-037), and one run on a mixture of DOR/non-DOR feed (ER-036).

Only one of the two ER runs on non DOR feed was completed successfully. Run ER-037 was terminated early in the run because of increasing resistance. The anode cup was broken during troubleshooting. Run ER-034 was successfully completed and achieved anode depletions of 96.3 (non-plutonium basis) and 97.8% (plutonium basis). The run was made on MSE delta metal and was continued about 50 minutes beyond the normal termination, as indicated by back-EMF. Final back-EMF reading was 0.56 V. No gallium analysis was obtained on the product, but other impurities (e.g., iron, nickel) do not appear to have been carried over at exceptional levels. The 95+% anode depletions achieved compare to approximately 80% average anode depletions in production for non-DOR feeds (Table 1). Results require confirmation by the ongoing stirrer development program, but this preliminary test supports the expectation that significant improvement in ER treatment of non-DOR feed may be possible through combined salt and anode stirring.

Runs ER-035 and ER-038 show mixed results for DOR metal feed. ER-035 achieved anode depletions of 83.7% (non-plutonium basis) and 87.8% (plutonium basis), while ER-038 showed anode depletions

of only 60.6% (non-plutonium basis) and 62.8% (plutonium basis). The results compare to salt stirred DOR metal ER results of 59.9 to 63.4% plutonium basis anode depletions. ER run sheets indicate that ER-038 lost current at 15 minutes after the back-EMF indicated termination. This suggests that the anode was indeed beginning to solidify; however, no feed analyses are available to confirm anticipated exceptional impurity levels. Also, no metallography/SEM/XRD results were obtained to support the possibility of very high DOR-related impurity/inclusion levels.

The results of ER-035 show high anode depletions (87.8% plutonium basis) compared to unstirred DOR metal feeds and are supportive of the positive impact of anode stirring. It should be noted, however, that DOR metal fed to ER-035 showed an unusually high value of ~0.987 g Pu/g total material. This plutonium content is more typical of non-DOR metal than DOR metal and may account for the difference between ER-035 and ER-038 performance. Furthermore, prior to ER-037 an experimental "*in-situ* furnace clean-out" was attempted using 200 g of calcium and 3026 g $CaCl_2$. This procedure may well have left DOR-type material (calcium and $CaCl_2$) in the furnace and may be the cause for the anomalous behavior of ER-037. Further work is necessary to confirm the positive effect of anode stirring.

Analytical data for ER-034 through ER-036 feeds (Table 13) show the generally purer nature of the non-DOR feed, although the 1000 ppm magnesium (E-spec) level for non-DOR is unusual. Electrical characteristics for all three runs show back-EMF greater than ~0.2 V at termination and a somewhat lower value of transfer rate (2.132 g Pu/A·hr) for the DOR buttons (ER-035). Spent-salt plutonium contents ranged from 4.4 to 6.0% for ER-034 through ER-036, slightly higher than for most unstirred runs.

Overall ER Analytical Results

The overall analytical results for the ER test program are given in Appendix Table A4. In view of the absence of analytical data for all major feed and process streams and the expected wide variations in anode heel data due to inhomogeneity, no mass balances can be calculated for the ER tests. Preliminary comparisons of IN–OUT masses for iron, nickel, gallium, and carbon confirmed the inability to produce meaningful results without further analytical data.

The data in Table 13 show feed compositions and ER performance for all ER runs made during the test program. Although no computer analyses of the data have been conducted, no significant correlations were identified by examination of the results for carbon, tantalum, tungsten, aluminum, chromium or their totals in feeds. The absence of overall correlations with feed composition, even if a signficiant effect existed, is not surprising in view of the major changes in other process variables made throughout the test program. If only the successful runs made with salt-phase stirring are considered, the above composition parameters still show no significant correlations with anode depletion.

The role of DOR-related impurities indicated by the analysis of individual test groups suggests that calcium or calcium and magnesium may yield some correlation with performance. With the exception of ER-022 (for which feed data were approximated by an anode casting sample), calcium and magnesium content of feed is plotted against percent anode depletion in Figure 3 for all successful ER runs for which analytical data are available. No statistical fit to the data was made; however, a rather good correlation appears to exist between total calcium and magnesium in feed versus achieved anode depletion for delta DOR feed to ER. A similar correlation is seen if only plutonium-basis anode depletion or only calcium content is used. The negative impact of these DOR-related components is clearly shown and results in about 10% (absolute) loss of anode depletion per 1000 ppm of indicated total calcium plus magnesium.

The limited results with other feeds suggest that non-DOR and alpha metal do not participate in the apparent deleterious impact of DOR-related impurities; however, this conclusion will require confirmation by further test work. Other run data also suggest that anode stirring significantly

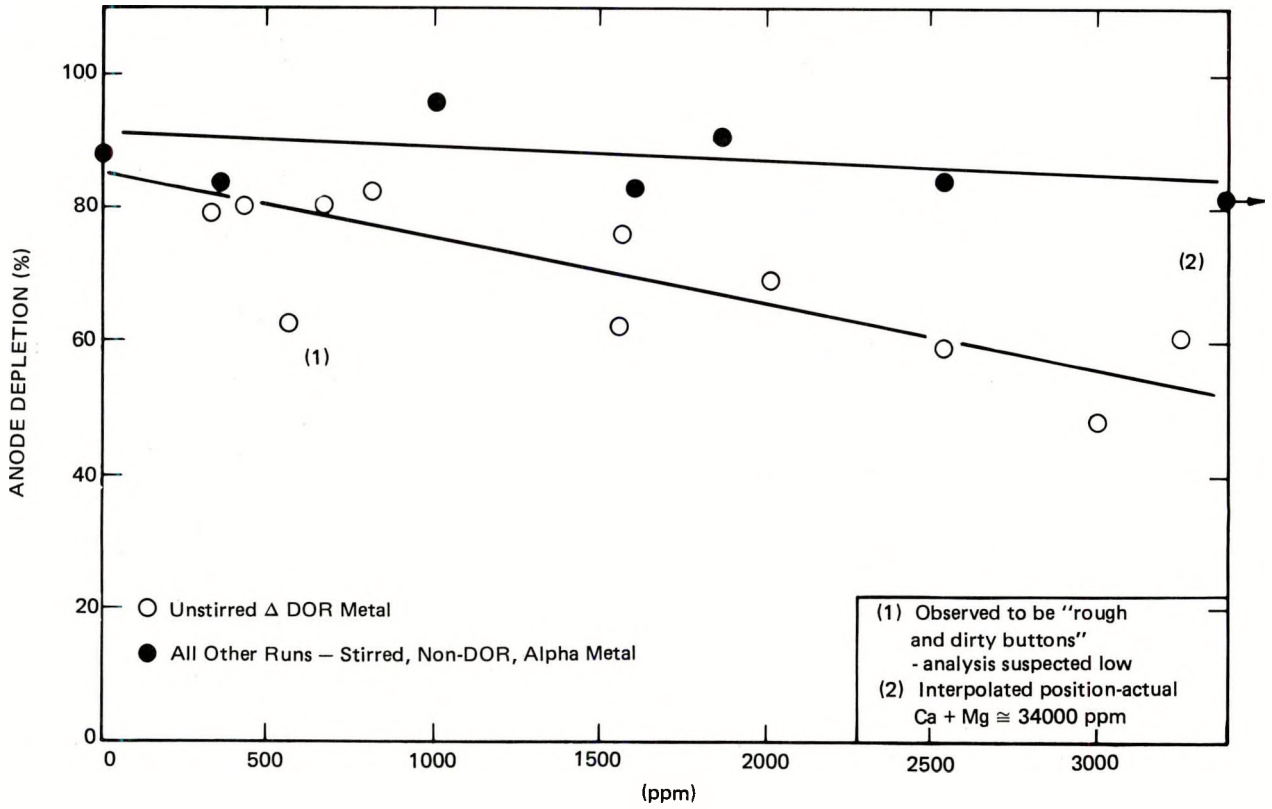


FIGURE 3. Relationship Between Calcium and Magnesium Content of ER Feed and Anode Depletion

dampens out the deleterious effect, although this should also be confirmed by further tests. Neither of the lines shown on Figure 3 is fitted statistically but is simply included to show the trend indicated by the data.

To improve the correlation, additional relationships using non-calcium/magnesium impurities in conjunction with the data in Figure 3 may be possible. However, data evaluation using a computer is recommended if this is desired. Based on results previously discussed, a gallium term was evaluated in various forms but failed to improve the apparent correlation. Future evaluations should include the effect of a carbon term.

Relationships between the plutonium content of ER feed and ER performance were explored and showed a weak correlation between plutonium concentrations in the feed and anode depletion.

Groups of anode heels were burned and subsequent oxide samples analyzed for rough comparison with anode heel analytical data. Results are given in Appendix Table A6. The results do not show excessive levels of aluminum in the anode heels and only moderate levels of carbon. However, carbon analyses after button oxidation reflect the oxidation and loss of carbon as CO or CO_2. The calcium level is lower in the first group (which was composed of one non-DOR and two vacuum melt/drip cast feeds out of five ER runs) than in subsequent groups. The highest calcium levels shown are for ER-023 through ER-028, 1.25 to 1.55% calcium in the oxide. This could correspond to 40 to 60 g of calcium in this group of heels, or greater than 1% calcium in a typical anode heel.

Tilt/Pour ER Holdup

Since holdup in the tilt/pour furnace is a primary contributor to loss of product, it is of interest to examine holdup levels experienced during the test program. Net new holdup ranged from -498 to +889 g per run during the test series, with the

average at 155 g/run. This compares to the average production level of 620 to 640 g/run (Table 1). Holdup was removed twice from the test tilt/pour furnace—after ER-024 and after ER-026. In both cases, new holdup in the next run was 880 to 890 g, the highest levels for the test sequence.

Analytical data for the oxide produced from burning both holdup batches are given in the Appendix, Table A7. Also shown are analytical data for as-sampled holdup after ER-025. The samples uniformly show very high tungsten, potassium, and magnesium levels. These probably reflect normal ER salt inclusions and contamination by crucible metal during scrapeout. None of the other impurities appear at exceptionally high levels and offer no special guides to the source of the carryover buildup.

Two samples of holdup were examined by metallography/SEM/XRD and showed multiple phases. In most cases, chlorine, potassium, and sodium were present, often with moderate plutonium and/or trace-minor silicon, magnesium, and iron. X-ray diffraction indicated the presence of minor PuC/PuN in one case with major amounts of NaCl, KCl, PuOCl, and PuO_2. In a sample chipped from the furnace prior to heatup and scrapeout, major PuC or PuN was identified with moderate PuO_2 and PuOCl and minor to trace amounts of KCl and NaCl.

For those ER runs with unstirred DOR anode metal, 57% showed gains in holdup and 43% showed a decrease in holdup. Three of the six runs showing decreases in holdup were vacuum treated before ER and one was pure alpha metal feed. The average non-plutonium anode depletion for those showing a decrease in holdup was 78.0%, compared to 67.4% for those showing gains in holdup. Those ER runs with anode metal stirred showed an average loss of 44 g/run for holdup, suggesting the possiblity of lower holdup if anodes are stirred. There is insufficient data to comment on the cause for this; but it may be an indirect result of improved impurity control (and improved product purity) resulting from successful back-EMF operation and less anode polarization.

SUMMARY AND DISCUSSION OF KEY RESULTS

Analysis of production ER operating data for DOR and non-DOR feeds during 1983 confirmed that DOR metal feed experiences significantly lower anode depletions and yields than non-DOR metal feed to ER. For "good" ER runs and "amps lost" runs combined, non-plutonium basis anode depletions averaged 67.3% for DOR feed and 79.3% for non-DOR feed. Non-plutonium basis product yields for the same runs averaged 37.0 and 57.9% for DOR feed and non-DOR feeds, respectively. Evaluation of the production data shows that about one-quarter of ER runs initiated on DOR feed failed to start, reportedly due to incomplete melting or low fluidity. Twenty percent of the ER runs on DOR feed were prematurely terminated due to "amps lost" at anode depletions lower than similar early terminations on non-DOR feed. One-half of the ER runs on DOR feed went to normal termination but achieved significantly lower anode depletions than normal runs on non-DOR feeds.

The production data do not provide firm information on the cause of these shortfalls but focus attention on DOR button quality (i.e., DOR-related impurities) for runs failing to start or terminating prematurely. The data confirm the higher impurity content of metal feed from DOR and thereby support a possible relationship between these contaminants and premature run termination. A relationship also appears possible between DOR feed and lower plutonium transfer rate, which may account for lower anode depletion during normally terminated ER runs.

Results of the DOR/ER test program have provided good preliminary information to guide future experimental work to identify the specific causes of DOR/ER incompatibility. The initial comparison of non-DOR, pure-α DOR, and delta-DOR metal in ER suggests that the presence of gallium coupled with DOR-processing (presumably, the resulting DOR-related impurities) gives poorer anode depletion. However, subsequent tests showed that DOR buttons may perform quite differently in ER depending on their source and

probably their content of DOR-related impurities. Thus, an underlying assumption of the initial test sequence—that pure-α DOR and delta-DOR feeds were similar with respect to the DOR contribution—may not have been valid.

The results of metallography/SEM/XRD showed that:

1. DOR buttons contain inclusions of magnesium-calcium with little or no chlorine, major calcium-chlorine together, and major calcium and chlorine associated.

2. Non-DOR buttons to ER, pure-α DOR, and some "successfully" treated DOR buttons (e.g., vacuum melt/drip cast) did not contain inclusions with these associations and performed well in ER.

3. Anode heels from ER runs on DOR metal with low anode depletions showed typical DOR-type inclusions (calcium, magnesium, chlorine), while those with high anode depletions showed an absence of inclusions with these associations, showing mostly the plutonium-chlorine types.

Test work on production DOR buttons suggested that they may have contained more typical DOR-related impurities on average than some of the DOR buttons produced during the test program. Intermediate treatments of production DOR buttons gave somewhat mixed ER results. However, contradictory results could often be resolved by analysis of the status of DOR-related impurities in feeds. Vacuum melting and drip casting, when successful, gave ~15 to 20% (absolute) increased anode depletion at a cost of 41 to 51% plutonium loss during treatment. Leaching of buttons appeared to yield ~15% absolute increase in anode depletion, while vacuum casting achieved an increase of ~20% (absolute) anode depletion at a cost of 27% plutonium loss during treatment. The leaching and vacuum melt treatments did not enhance anode depletion in some trials.

All of these techniques require further evaluation if warranted by the preliminary results. Limited test results on tilt/pour DOR buttons were supportive of the remelt/pour/holdup procedure (e.g., vacuum cast and vacuum melt/drip cast) in enhancing ER performance.

Anode stirring with a metal stirrer gave mixed results, which could again be resolved by assessment of the "dirtiness" of the feed with respect to DOR-related impurities. Stirring salt and anode with the metal/ceramic stirrer yielded generally good results for both DOR and non-DOR feeds. The limited preliminary results suggest that stirring of the anode may decrease the sensitivity of the ER process to DOR-related impurities.

Calcium and magnesium in delta DOR feed was shown to correlate well (inversely) with anode depletion, although no other correlations with specific feed impurities could be identified. The correlation with calcium/magnesium supports the apparent relationship between the amount of DOR-related impurities carried over and ER performance.

In terms of ER results, no firm conclusions can be drawn and recommendations can be based upon "suggested" effects only. Nevertheless, a number of key observations can be made, which should guide future test work on this problem.

In the anode heels examined, the relative absence of high melting phases, which derive from impurities initially soluble in the anode (e.g., aluminum, carbon, tantalum, tungsten, silicon, and gallium), suggest that this source of the problem is not particularly significant. However, it is important to note that average values of impurity content, for feeds to those ER runs for which anode heels were examined, were lower than the averages for DOR metal to Building 371 during 1983 (Table 2). There are specific feeds to particular production ER runs for which the presence of "high melters" at low anode depletions is a controlling, limiting factor. Minimum practical impurity content in the DOR feeds is felt to be desirable.

The common thread suggested throughout the test results is the role of impurities in DOR product, both mechanically entrained and chemically present, in the ER process. Our test results give no

direct evidence of the specific species causing problems, or the mechanism involved. However, the results do qualitatively comment on the calcium-magnesium, calcium-chlorine, calcium-magnesium-chlorine associations present. Other DOR-related soluble impurities (e.g., magnesium) may also be involved. Both two-phase liquids (plutonium-magnesium system) and liquid-solid two-phase systems often show drastic increases in viscosity over their single-phase counterparts. This effect, coupled with possible higher melting ranges of a second phase concentrated at the anode-salt interface (e.g., $CaO/CaCl_2$, $MgO/CaO/CaCl_2$ compounds) may be related to a failure to successfully initiate an ER run. No fresh feed used during the Research and Development test program failed to initiate in ER runs. However, AC-3 (drip cast), which failed to fully melt, or ER-030 heel, which could not be remelted, may be our closest examples.

One working hypothesis, as a guide for future test work and production observations, is that extremely high loadings of the mechanically entrained or surface-related DOR impurities (whatever their exact source and identity) may lead to failure of the anode to melt. Moderate levels permit initiation, but in concert with other high impurity levels (perhaps gallium), lead to premature termination of the ER run. The presence of DOR-related species in the anode feed results in premature solidification of the anode, thus preventing attainment of anode depletions comparable to non-DOR feed.

Although test results do not prove this hypothesis or identify the specific mechanisms, the results are qualitatively supportive in that effective minimization of the DOR-related impurities appeared to improve ER performance. On this basis, improvement of DOR/ER compatibility depends upon (1) operation of the DOR process to minimize carryover of DOR-related impurities, (2) effective reduction of the quantity or nature of the impurities by intermediate treatment, or (3) modification of the ER process to accept the undesirable materials without effect.

Based on these observations and our preliminary test results, an intermediate treatment strategy may be variable depending on the quality of the DOR button produced. A relatively clean looking, well consolidated button may best be leached simply for surface cleanup, while a very rough, poorly consolidated button (which may contain high internal loadings of mechanical impurities) may require some treatment involving remelting with material loss to a side stream (e.g., vacuum melting or casting) to generate high-yield metal for ER. The limited production data for DOR feed also suggest that higher $MgCl_2$ loadings in ER salts could raise yield by lowering holdup for DOR fed to ER.

REFERENCE

1. W. S. Moser and J. D. Navratil, *J. Less Common Metals, 100,* p 171, 1984.

TABLE A1. Analytical Data – Calcination Feeds and Products

Run No.		Composition										
		Cr (ppm)	Ga (wt %)	Al (ppm)	W (ppm)	Ca (ppm)	C (ppm)	Ta (ppm)	Fe (ppm)	Ni (ppm)	Mg (ppm)	Zn (ppm)
Pure α Oxide												
95	Feed oxide (green cake)	43		13	<10	500	132	<10	94	<10	5	<10
	Calcined oxide	138		22	<10	1000	100	<10	29	14	25	<10
109	Feed oxide (green cake)	50	0.0144	<5	<10	1000	48	<10	205	19	50	10
	Calcined oxide	50	0.0028	<5	<10	1000	21	<10	56	<10	50	<10
Pure Δ Oxide												
767733	Metal–before burn	100	1.085	25	<10	<10	157	<10	375	225	100	<10
	Burned oxide	36	0.8550	47	<10	665	198	<10	700	300	<5	<10
	Calcined oxide	56	0.6150	69	<10	<393	118	<10	550	215	1000	<10
767736	Metal–before burn	250	1.071	25	<10	<10	239	<10	235	195	100	<10
	Burned oxide	25	0.7350	25	<10	720	197	<10	720	485	500	<10
	Calcined oxide	149	0.8550	75	<10	183	104	<10	710	520	<5	<10
Combined Oxides to "pure Δ DOR"		500	–	<92	50	1730	95	20	800	1000	3150	–
Impure Δ Oxide												
110	Feed oxide	33		29	<10	<10	473	<10	225	33	25	150
	Calcined oxide	32		35	<10	<10	243	<10	145	26	10	<10
111	Feed oxide	32		113	<10	<10	380	<10	240	52	25	<10
	Calcined oxide	33		124	<10	<10	270	<10	245	47	50	<10
112	Feed oxide	130		69	<10	<10	347	<10	605	170	<5	<10
	Calcined oxide	110		70	<10	<10	347	<10	545	165	<5	<10

TABLE A2. Analytical Data – Product DOR Buttons

DOR/ER Run No.	Oxide Feed Type	Composition Cr (ppm)	Ga (wt %)	Al (ppm)	W (ppm)	Ca (ppm)	C (ppm)	Ta (ppm)	Fe (ppm)	Ni (ppm)	Mg (ppm)
1	Pure alpha	1,000	0.047	250	<10	<48	145	200	515	435	100
2	Pure alpha	1,000	0.136	25	<10	185	158	75	575	635	1,000
3	Pure alpha	500	0.082	50	<10	720	102	150	570	1,700	500
4	Pure alpha	1,000	0.032	100	<10	5,000	148	<10	445	265	50
5	Pure alpha	224	0.037	100	<10	430	127	20	360	320	<55
6	Pure alpha										
7	Pure alpha	500	0.039	50	<10	1,265	84	20	380	340	<52
8	Pure delta	50	0.709	170	<10	440	78	100	495	455	650
9	Pure delta	100	0.736	190	20	195	88	2,000	645	505	43
10	Pure delta	45	0.875	165	<10	14,500	108	<10	635	565	2,250
11	Pure delta	95	0.764	120	<10	1,080	79	200	540	495	115
12	No. 8 metal–rerun										
13	Pure delta	134	0.881	225	<10	3,955	226	1,000	905	1,200	265
14	Pure delta	137	1.227	415	<10	7,950	169	<10	1,050	1,550	1,600
15	Pure delta	90	0.600	710	<10	6,200	287	20	1,250	1,450	6,400
16	Pure delta	21	1.078	323	<10	9,050	142	<10	905	1,600	1,195
17	Impure delta	21	0.979	205	<10	65,500	126	50	735	905	1,550
18	Impure delta	Analytical data unavailable									
19	Impure delta										
20	Impure delta	24		165	<10	48,750	285	50	320	105	8,400
21	Impure delta	52		86	<10	14,475	149	3,000	415	71	1,080
22	Impure delta										

TABLE A3. Analytical Data–$CaCl_2$ DOR Feed Salt
(semiquantitative E-spec.)

DOR/ER Run No. Salt Form	Composition (ppm) 1 Loose	5 Loose	6 Cake
C	95	87	44
Ca	200,000	200,000	200,000
K	20,000	20,000	20,000
Rb	5,000	5,000	5,000
Sr	10,000	10,000	10,000
Ga	<1,000	<1,000	<1,000
W	<1,000	<1,000	<1,000
Fe	500	500	500
Ni	<50	<50	<50
Ta	<50	<50	<50
Al	500	100	100
Mg	10	10	10

TABLE A4. Analytical Results – Tilt/Pour ER
(Sheet 1)

ER Run No.		Assay Source	Composition (ppm) Cr	Al	W	Ca	C	Ta	Fe	Ni	Mg
ER-018	Feed	Sample	765	31	<10	10	175	<10	340	78	<5
	Heel	Sample	424	<5	20	<46	162	10	3,000	435	500
	Product	Sample	275	15	100	250	243	<10	153	38	>1,000
	Salt	Sample	<10	<500	<1,000	490	–	<50	100	<50	7,350
ER-019	Feed	Sample	100	500	<10	400	–	500	1,300	408	25
	Heel	Sample	123	50	<10	72	230	20	5,200	1,500	500
	Product	Sample	435	67	20	100	286	20	185	55	500
	Salt										
ER-020	Feed	Sample	54	32	<10	>1,000	776	20	1,200	420	>1,000
	Heel	Sample	140	100	50	14,188	–	100	1,650	550	9,500
	Product	Sample	180	15	200/50[1]	<47	78	1,500/100[1]	97	36	1,330
	Salt										
ER-021	Feed	–[2]	880	106	<10	1,450	139	106	527	745	420
	Heel	Sample	865	>1,000	50	6,775	–	500	1,350	1,500	510
	Product	Sample	48	9	1,000/100	<45	52	1,000/50[1]	32	25	120
	Salt										
ER-022	Feed	–[3]	284	163	–	<45	81	–	664	250	<45
	Heel	Sample	650	15	<10	6,250	847	<10	8,100	6,050	179
	Product	Sample	165	70	200/100[1]	<19	79	3,000/20[1]	31	26	125
	Salt										
ER-023	Feed	–[4]	148	26	32	347	1,510	880	2,690	734	215
	Heel	Sample	740	14	<10	11,850	4,442	2,000	3,500	1,005	890
	Product	Sample	<205	17	<10	<42	56	<10	33	25	110
	Salt	Sample	<10	<500		840	–	<50	1,000	<50	5,950
ER-024	Feed	–[5]	136	27	180	229	708	454	1,139	1,896	100
	Heel										
	Product										
	Salt										
ER-024A	Feed	–[6]	129	25	178	228	715	497	1,144	1,822	100
	Heel	Sample	–	–	2,000	8,200	–	>4,000	2,650	3,400	850
	Product	Sample	11	3	2,000	<44	41	10	21	15	89
	Salt										
ER-025	Feed	–[7]	73	161	6	4,050	88	575	579	503	765
	Heel										
	Product	Sample	35	15	4,000/100	25	20	<10/<10	120	140	99
	Salt										

[1] Original assay/recheck assay.
[2] Calc. from DOR Button 1-4 assays.
[3] Anode Cast 2–top drilled sfc assay.
[4] Calc. from DOR button assays before leaching.
[5] Weight average of TPR-13 & 14 button.
[6] Weight average of TPR-13 bal. and ER-024 feed.
[7] Arithmetic average of DOR/ER Buttons 8, 9, 10, 11; DOR/ER 12 not available.

TABLE A4. Analytical Results – Tilt/Pour ER
(Sheet 2)

ER Run No.		Assay Source	Composition (ppm) Cr	Al	W	Ca	C	Ta	Fe	Ni	Mg
ER-026	Feed	–[8]	307	147	169	1,902	396	338	1,722	3,954	104
	Heel	Sample	911	801	2,000	17,500	1,433	2,000	1,400	3,133	2,050
	Product	Sample	25	10	1,000	<49	55	<10	17	13	260
	Salt										
ER-027	Feed	–[9]	66.1	65.7	8.4	499	492	27.7	700	467	307
	Feed	–[10]	128	355	100	490	239	2,500	695	485	<47
	Heel	Sample	134	275	500	12,000	560	2,000	1,950	985	130
	Product	Sample	6	20	100/100	<20	43	20/<10	65	52	1,000
	Salt										
ER-028	Feed	–[11]	237	64.4	<10	1,591	645	201	1,031	784	1,680
	Heel										
	Product	Sample	24	22	150	<21	48	20	120	100	3,750
	Salt										
ER-029	Feed	–[12]	753	338	37.9	1,840	900	1,599	701	436	696
& –029A	Heel (A)	Sample	470	149	200	14,500	7,039	<10	4,500	2,200	424
	Product (029)	Sample	13	12	500/500	<42	23	<10/<10	63	57	100
	Product (029A)	Sample	8	9	500/200	<45	22	<10/<10	71	69	71
	Salt										
ER-030	Feed	–[12]	753	338	7.9	1,840	900	1,599	701	436	696
	Heel										
	Product	Sample	9	8	150	<44	36	<10	21	29	120
	Salt										
ER-031	Feed	–[13]	349	123	1.9	1,012	428	1,032	1,572	1,766	555
	Heel	Sample	727	89	<10	15,000	727	>1,000	1,900	<1,000	2,300
	Product	Sample	9	6	200	<45	28	<10	56	25	120
	Salt										
ER-030H	Feed										
	Heel	Sample	171	77	<10	13,250	1,584	>1,000	1,200	792	2,950
	Product										
	Salt										
ER-032	Feed	–[13]	349	123	1.9	1,012	428	1,032	1,572	1,766	555
	Heel	Sample	500	250	<10	18,000	506	>1,000	1,550	1,065	435
	Product	Sample	47	24	100	<45	66	<10	170	78	2,900
	Salt										
ER-033	Feed	–[14]	62	295	<10	30,430	194	674	735	293	3,507
	Heel	Sample	<10	<5	<10	71,500	592	>1,000	1,850	10	11,500
	Product	Sample	52	21	1,000	<48	118	10	140	67	653
	Salt										

[8] Weighted average of DOR buttons used as feed.
[9] Weighted average of DOR Buttons 188, 189, 190, 191, 192 before vacuum casting.
[10] ER-027 feed after vacuum casting.
[11] Weighted average of DOR Buttons 352, 353, 354, 361, 379.
[12] Weighted average of DOR Buttons 391, 394, 395, 397, 399, 405, 406, 411, 413, 415.
[13] Weighted average of DOR Buttons 417, 419, 422, 424, 425, 362, 365, 383, 387.
[14] Weighted average of DOR/ER Buttons 14, 15, 17, 20, 21.

TABLE A4. Analytical Results – Tilt/Pour ER
(Sheet 3)

ER Run No.		Assay Source	Composition (ppm) Cr	Al	W	Ca	C	Ta	Fe	Ni	Mg
ER-034	Feed	Sample	600	<5	<10	10	357	<10	1,300	240	1,000
	Heel										
	Product	Sample	9	3	1,000	200	40	10	41	12	1,060
	Salt										
ER-035	Feed	–[15]	148	48.5	<10	154	307	143	887	201	213
	Heel										
	Product	Sample	50	5	100	<44	76	50	73	280	530
	Salt										
ER-036	Feed	–[16]	520	170	4	971	578	875	1,032	616	632
	Heel										
	Product	Sample	81	10	200	<44	51	<10	16	28	210
	Salt										
ER-037	Feed	Sample	86	35	<10	<10	419	<10	785	330	255
	Heel										
	Product										
	Salt										
ER-038	Feed										
	Heel										
	Product	Sample	17	3	500	<46	69	20	88	44	180
	Salt										

[15] Weighted average of DOR Buttons 21, 24, 26, 27, 194.
[16] Approximate by arithmetic average of 029/30, 031, 034, 035 feeds; this is a very rough approximation.

TABLE A5. Analytical Results – Vacuum Melt/Drip Cast Intermediate Treatment Products

Run No.	Sample ID	Composition (ppm) Cr	Al	W	Ca	C	Ta	Fe	Ni	Mg	Zn
VM-2 (A)	–	–	–	–	–	–	–	–	–	–	–
VM-2 (B)	Surface flake	–	–	–	1,300	–	–	–	–	–	–
AC-1	Casting skull	41	24	–	220	1,064	–	192	150	70	330
(to ER-019)	Product metal	100	500	<10	400	–	500	1,300	408	25	–
VM-3 (A)	Drill top sfc	100	10	–	6,100	629	–	334	869	1,485	33
	Drill bottom sfc				12					118	<10
	Surface nodule	30	9	–	8,100	751	–	49	821	1,006	20
	Condenser	<10	<5	<10	10.5%	2,926	<10	<10	120	37.0%	23.5%
VM-3 (B)	Top sfc	587	129	<10	555	179	<10	200	175	<48	<47
	Bottom side	347	136	<10	12,500	498	<10	200	150	<44	<44
	Side Chunk	100	25	10	24.5%	738	4,000	520	120	<43	<43
	Skin metal	100	25	10	24.5%	928	4,000	520	120	<75	<46
AC-2	Drill top sfc–initial	1,000	500	<10	100		<10	270	250	25	
(to ER-022)	Drill top sfc–return	284	163		<45	81		664	250	<45	<45
	Surface bead				183					<44	<44
	Casting skull	500	80	<10	12.5%	662	100	242	234	47	<47
	Nonmolten skin	800	25	20	25.0%	992	500	200	250	<49	<49
AC-3 (sfc bead)		161	4	<10	90,500	1,791	20	2,444	4,612	250	<10

TABLE A6. Analytical Results – Anode Heel Oxides

Material Type	ER Runs Included	Composition (ppm) K	Cr	Ga	Al	W	Ca	C	Ta	Fe	Ni	Mg
Anode heel Oxide 1	ER-018, -019, -020, -021, -022	10 Na = 8,000	120	–	19	<10	2,100	254	100	107	65	5,300
Anode heel Oxide 2	ER-023, -024, -025, -026, -027, -028	>1,000	291	>2,000	109	100	12,500	579	<10	>1,000	>1,000	2,300
Anode heel Oxide 3	ER-023, -024, -025 -026, -027, -028	>1,000	289	>2,000	80	200	15,500	536	(10,000)* 500	>1,000	>1,000	2,950
Anode heel Oxide 4-1	ER-029A, -030H, -031, -032	3,000	168	>10,000	181	100	6,450	518	(10,000)* >4,000	491	845	1,900
Anode heel Oxide 4-2	ER-029A, -030H, -031, -032	1,500	154	>10,000	261	200	5,600	488	(10,000)* >4,000	493	790	1,950

*Semiquantitative E-spec tantalum results on the same sample.

TABLE A7. Analytical Data – Tilt/Pour Furnace Holdup Produced During the DOR/ER Test Program

	Holdup Source	Composition (ppm) K	Cr	Ga	Al	W	Ca	C	Ta	Fe	Ni	Mg
Holdup Oxide	Thru ER-024	–	–	465	–	74,000	930	–	20	–	–	24,000
Holdup (unburned)	After ER-025	>1,000	<10	805	<5	20,000	<10	104	<10	<10	<10	25
Holdup Oxide	After ER-025	20,000	35	–	25	>4,000	200	132	200	437	250	15,550