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Direct Reduction of [illegible]PuO_2 and $^{239}PuO_2$ to Metal

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by

L. J. Mullins and C. L. Foxx

ABSTRACT

The process for reducing 700 g $^{239}PuO_2$ to metal is a standard procedure at Los Alamos National Laboratory. This process is based on research for reducing 200 g $^{238}PuO_2$ to metal. This report describes in detail the experiments and development of the 200-g process. The procedure uses calcium metal as the reducing agent in a molten $CaCl_2$ solvent system. The process to convert impure plutonia to high-purity metal by oxide reduction followed by electrorefining is also described.

I. INTRODUCTION

The conversion of impure $^{239}PuO_2$ to high-purity metal by direct oxide reduction (DOR) followed by electrorefining (ER) is a standard procedure at Los Alamos National Laboratory.[1] This process is based on earlier work for reducing 200 g $^{238}PuO_2$ to metal, followed by electrorefining, which was described in Los Alamos progress reports on the artificial heart program.[2,3] This report describes in detail the development of the 200-g process.

Preparation of medical-grade $^{238}PuO_2{}^{16}$ powder is based on converting metal of high chemical purity to $^{238}PuO_2{}^{16}$ (Refs. 4-7). In this process, based upon conventional ^{239}Pu technology, an oxide feed is first converted to metal, as shown in Fig. 1, and the metal is then purified by electrorefining. The electrorefining process is relatively insensitive to the purity of the feed metal and routinely produces ^{238}Pu metal having minimum neutron- and gamma-dose rates.[4,5] The procedure has been well established with ^{239}Pu; an electrorefining facility with a 10-kg/wk capacity has been operating in Los Alamos since 1965. The process also works well with ^{238}Pu, but the scale of operation is reduced from 4 kg ^{239}Pu/batch to 200 g ^{238}Pu.

The neutron radiation hazard of the $^{238}PuF_4$ intermediate is the greatest disadvantage of the process shown in Fig. 1. Because of the (α,n) reaction on ^{19}F [that is, $^{19}F(\alpha,n)^{22}Na$)], the fluoride has a neutron emission of 2×10^6 n/s·g ^{238}Pu. Dose rates at 10 cm measured through 0.76 mm of tantalum are 0.2 rem/h·g ^{238}Pu for neutron and 0.01 rem/h·g ^{238}Pu for gamma. Obviously, the fluoride poses a serious radiation problem and must be handled with extreme care.

To eliminate the radiation problems caused by $^{238}PuF_4$, we developed a process for the reduction of $^{238}PuO_2$ to metal. There were additional incentives for initiating the project.

- Economics—The 50-g process, consisting of dissolution of PuO_2, precipitation of plutonium peroxide, hydrofluorination, and reduction to metal, would be replaced by a one-step, high-yield 200-g PuO_2 reduction process. All chemical purification would be accomplished in the electrorefining operation.
- Waste generation—An oxide reduction process would generate less waste than conventional methods.
- Impact on ^{239}Pu processing—Successful development of the oxide reduction process would affect existing ^{239}Pu technology.

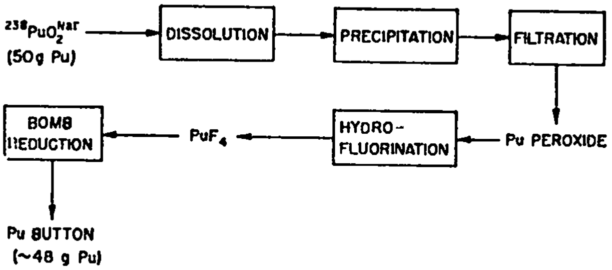

Fig. 1. Flow sheet showing conversion of $^{238}PuO_2$ to metal using conventional ^{239}Pu technology.

A flow sheet for the preparation of medical-grade plutonia ceramics is given in Fig. 2.

II. PLUTONIUM REDUCTION PROCESSES

Metallic plutonium was first prepared by R. D. Baker, using the reduction of PuF_4 with calcium in a sealed pressure vessel,[8] and this process is still used for most of the plutonium metal produced today.[9] However, at Savannah River plutonium metal is prepared by reducing a mixture of 75 mole % PuF_4-25 mole % PuO_2 with calcium.[10] The mixture is made by roasting PuF_3 in air.

In Baker's process, a mixture of PuF_4, calcium, and iodine is heated in a refractory-lined metal container. At approximately 325°C, calcium and iodine react, liberating heat.

$$Ca + I_2 = CaI_2 \qquad -\Delta H^\circ_{298} = 128 \text{ kcal}$$

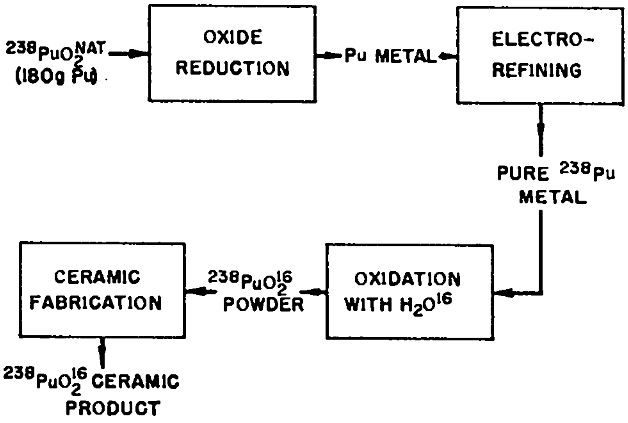

Fig. 2. Flow sheet showing preparation of high-purity $^{238}PuO_2^{16}$ ceramics.

This heat immediately raises the temperature of the mixture, and the reduction of PuF_4 with calcium takes place at about 600°C.

$$PuF_4 + 2\,Ca = 2\,CaF_2 + Pu \qquad -\Delta H^\circ_{298} = 157 \text{ kcal}$$

This reaction also produces heat, and the temperature of the melt can increase to values as high as 2000°C; the actual temperature attained depends principally on the rate of heat loss. The CaF_2-CaI_2 slag (mp ~1320°C) (Ref. 11) remains molten long enough to permit the dense plutonium liquid to collect before the slag freezes. If a similar process is tried for the reduction of PuO_2, only plutonium powder or finely dispersed metal is produced. The high melting point of the CaO slag, 2600°C, precludes carrying out the reaction above that point; CaO also can be dissolved in molten salts such as $CaCl_2$ and $CaCl_2$-CaF_2. Jenkins et al. were among the first to try this approach using $CaCl_2$ as a flux to dissolve CaO;[12] however, they were not successful in obtaining massive plutonium metal. Runnals used a flux of $AlF_3 \cdot 3NaF$ to dissolve the Al_2O_3 produced in reducing PuO_2 to metal with aluminum,[13] but in this case the product was an aluminum-plutonium alloy. Alloys containing as much as 25 wt % plutonium have been prepared. Knighton and Steunenberg[14] used a solvent consisting of alkali and alkaline earth chlorides and fluorides to dissolve the by-product MgO that occurs when reducing PuO_2 to metal with magnesium metal. The product was a dilute solution of plutonium in magnesium-zinc. Wade and Wolf were apparently the first to prepare massive plutonium metal from PuO_2 (Ref. 15). They used $CaCl_2$ as a solvent for CaO in their experiments and reported excellent yields with approximately 50 g plutonium. Encouraging results were also reported by R. E. Felt, who reduced PuO_2 to metal in a $CaCl_2$-CaF_2 flux.[16] In 1970, workers at Dow Chemical's Rocky Flats Plant (RFP) also reported PuO_2 reduction experiments using a flux of $CaCl_2$-CaF_2 (Ref. 17). Although the results obtained by all these workers showed great promise, the experimental procedures were not converted to practice, and no further work has been reported.

The present work at Los Alamos was initiated in 1975. Results of the first 18 experiments were summarized in Ref. 2, and additional results were reported in late 1977.[3]

III. EXPERIMENTAL

A. Experimental Plan

We anticipated that the principal problems in the $^{238}PuO_2$ reduction process using a salt flux to dissolve the CaO would be

(a) thorough mixing of the multiphase system, including

  top phase—calcium, solid or liquid (mp 839°C),
  middle phase—liquid salt or flux, and
  bottom phases—solid PuO_2 and liquid plutonium;

(b) quantitative collection of plutonium metal in a dense, easily isolated mass; and

(c) dissipation of heat resulting from ^{238}Pu decay by alpha emission.

Thorough mixing can be achieved by proper design and operation of the agitator or stirrer. Quantitative collection involves many parameters, the most important of which are crucible geometry, flux composition, temperature, stirring, and chemical impurities.

The following items were identified for study in the development of the plutonia reduction process.

(a) Crucible material and geometry
(b) Mode of mixing
(c) Salt flux composition and preparation
(d) Temperature
(e) Determination of the maximum ratio of g PuO_2/g $CaCl_2$
(f) Minimization of contamination by impurities
(g) Specifications for oxide feed
(h) Salt recycle

Most of the development runs were done with $^{239}PuO_2$. For economic reasons, the experiments were done in existing ^{239}Pu electrorefining facilities. The objective was to develop a process for the direct reduction of 200 g $^{239}PuO_2$ to metal and then to use the process for $^{238}PuO_2$. The 200 g of oxide was selected as the batch size because that is the size of the usual Savannah River $^{238}PuO_2$ lot.

B. Equipment

The equipment used for the oxide reductions is shown schematically in Fig. 3. In a typical run, 200 g of PuO_2 powder, a 1-kg cylinder of $CaCl_2$, and 85 g of calcium were loaded into the MgO crucible. The furnace tube was evacuated and then filled with argon to 3 psig. The furnace was heated at a rate of ~200°C/h to the melting point of $CaCl_2$ (775°C). A nickel thermocouple sheath, protected by a tantalum sleeve, was lowered to the bottom of the crucible. The stirrer was lowered when melting was complete and activated at the desired temperature; the reaction was monitored by measuring the neutron flux and the salt temperature. Upon completion of the reduction and metal collection, the stirrer and thermocouple sheath were raised from the melt and the furnace was cooled to room temperature. The MgO crucible was then removed from the furnace and the metal button was removed from the salt.

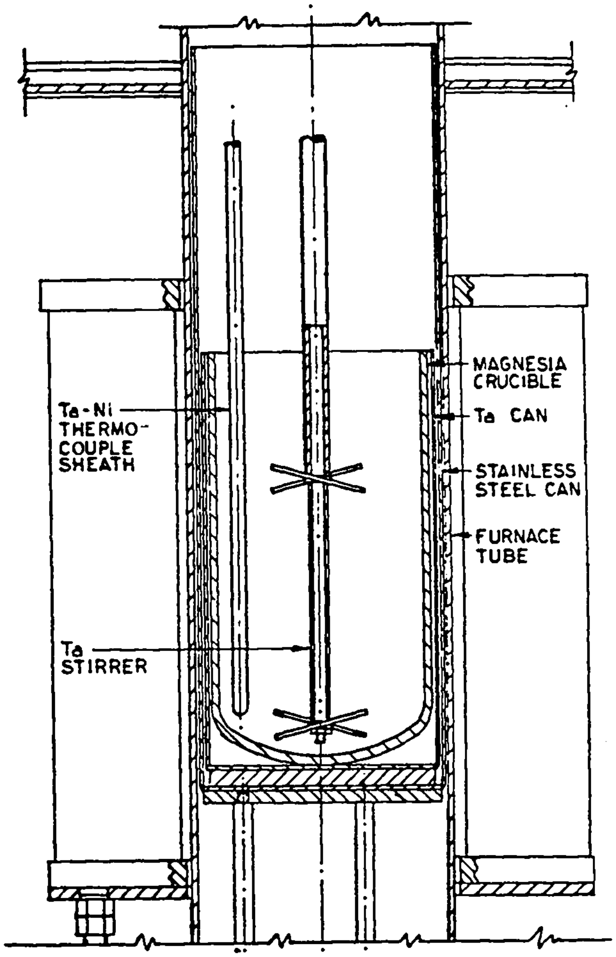

Fig. 3. Plutonia reduction equipment.

C. Reagents and Materials

- Calcium—Pfizer's redistilled grade 6 mesh nodules were ground in a Wiley Mill, and the 180- to 1000-micron fraction was used.

- CaF_2—MCB's reagent grade anhydrous CaF_2 was dried to constant weight at 150°C before mixing with $CaCl_2$.
- $CaCl_2$—Baker's analyzed reagent grade, anhydrous $CaCl_2$ was used. The salt was dried for several days at 225°C under vacuum (~0.1 torr) before vacuum melting or isostatic pressing.
- $^{239}PuO_2$—most of the oxides were obtained from the Los Alamos Group CMB-11 plutonium recovery section and had been prepared by the ignition of plutonium (III) oxalate. Before being used, the oxides were dried at 750°C in an air atmosphere.
- Crucible—the crucibles used in this study were fabricated by Los Alamos Group CMB-6 and were all MgO-3 wt % Y_2O_3 bodies. The crucible used in most of the runs is identified by the shape number A-247 and is shown in Fig. 3.
- Stirrers—the stirrers were fabricated from Ta-10 wt % W rod and tantalum sheet.

IV. RESULTS OF $^{239}PuO_2$ REDUCTION

The results of all of the runs are given in the Appendix, Table A-I, and are best understood by considering them in the context of the following discussions.

A. Crucible Material and Geometry

The choice of crucible material was limited to metal containers (tantalum, tungsten, and tantalum-tungsten alloys) or ceramic containers [magnesia, thoria, and alumina (for all chloride melts only)].

We selected magnesia for our studies; the choice was based on the availability of magnesia bodies and the excellent record of magnesia bodies in PuF_4 reductions and electrorefining operations.

Crucible geometry in $^{238}PuO_2$ reductions is important for two reasons. First, the geometry must permit good mixing of the reactants and collection of the product in an easily isolated form. Second, because of the high heat output of ^{238}Pu (0.56 W/g ^{238}Pu), the ratio of the metal's surface area to volume should be large to promote dissipation of heat and ensure solidification of the low-melting plutonium (mp 640°C). Thus, with 170 g ^{238}Pu, for example, a thin, flat metal disk would be the best form to handle.

Crucible geometry was the major parameter studied in the first 10 runs (Table A-I). Flat-bottom, conical-bottom, and hemispherical-bottom crucibles were tested. Although high yields were obtained with the flat-bottom crucible (Runs 1, 2, 6, and 8) the best-formed ingots and the cleanest separation of salt and metal were obtained with the hemispherical-bottom crucible. Salt and metal products from a reduction in the hemispherical crucible are shown in Fig. 4. The flat-bottom crucible probably would be adequate for larger amounts of plutonium; however, with 170 g plutonium and also with 274 g plutonium (Table A-I, Run 8), the casting is too thin to ensure one coalesced-metal piece. Yields were poor with the conical-bottom crucible because of mixing problems. The hemispherical crucible was used in all runs subsequent to 8.

B. Mode of Mixing

A combination of unidirectional and reverse motion stirring[18] was used in the first 10 experiments to ensure thorough mixing of solid PuO_2, molten $CaCl_2$-CaF_2, and calcium. This procedure gave good mixing but sometimes resulted in a loss of plutonium to the upper crucible walls. Only unidirectional stirring was used in Run 11. In this mode of stirring, the upper impeller pushes the calcium toward the bottom of the crucible, and the bottom impeller lifts the solid PuO_2 to the top. The 98% reduction yield of Run 11 indicates that unidirectional stirring is effective in obtaining good mixing; in addition, examination of the crucible walls showed no splashing. Undirectional stirring is the preferred mode and was used in all runs after Run 10.

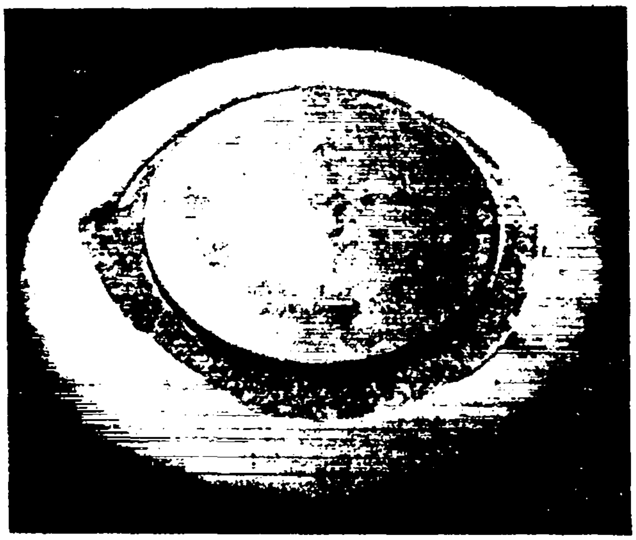

Fig. 4. Direct oxide reduction metal product with residues.

C. Salt Flux Composition

Two solvents have been used for dissolving CaO: molten $CaCl_2$ (Ref. 15) and molten $CaCl_2$-CaF_2 (Refs. 16 and 17). We chose the the $CaCl_2$-CaF_2 system for the first 11 experiments because we thought good metal collection would be more easily achieved with fluoride present. Good metal collection was achieved with $CaCl_2$-26 mole % CaF_2; however, good metal collection was also achieved with $CaCl_2$ (see results of Run 12, Table A-I). The procedures were identical in Runs 11 and 12, except that $CaCl_2$-CaF_2 was used in 11, and $CaCl_2$ was used in 12. Metal collection was good in both experiments. The reduction yields were 98.1% in Run 11 and 99.3% in Run 12.

$CalCl_2$ has been used in all runs subsequent to Run 11. We prefer this salt system for the following reasons.

(1) Lower neutron flux—the measured neutron flux is lower with the $CaCl_2$ salt.

(2) Nondestructive evaluation of wastes—both the waste salt and crucible can be evaluated accurately for plutonium content by neutron coincidence counting in the $CaCl_2$ system.

(3) Simpler salt recycle—if a salt recycle were used (that is, convert CaO to $CaCl_2$ with HCl and reuse the salt), the $CaCl_2$ system would be simpler because analysis and adjustment of the CaF_2 concentration would not be required.

The advantage of the $CaCl_2$-CaF_2 system is that it forms a peritectic with CaO at 670°C (Ref. 19) and is therefore capable of being used at a lower temperature than $CaCl_2$. However, in the temperature range used in our studies (800-875°C), neither salt system offers a distinct weight or volume advantage with respect to its capacity to dissolve CaO.

D. Temperature

Continuous measurement of the melt temperature is essential when following the progress of the plutonia reduction. A thermocouple sheath, consisting of an outer tantalum tube and an inner nickel tube, is lowered into the magnesia crucible. The reaction rate is controlled by observing the temperature rise and slowly increasing the stirring rate. The composite tantalum/nickel sheath was not available for the first 12 runs. Nickel was used in the first run and tantalum in the next 11 runs. Because nickel is not compatible with the molten reaction mixture, and the inside of tantalum is oxidized by air at temperatures above 700°C, only brief temperature measurements were made in the first 12 runs. The progress of the reaction in these runs was monitored by neutron flux measurements. These measurements did indicate the progress of the reduction, but they were not definitive; we could not ascertain when the reaction was complete. Salt temperature measurements, however, are most definitive, and the reaction rate can be controlled by observing the salt temperature and adjusting the stirring rate. The melt temperature profile for Run 23 is given in Fig. 5.

Examination of magnesia crucibles from runs in which stirring was initiated at temperatures higher than 840°C indicated that the following parasitic reaction took place above the melting point of calcium metal (839°C),

$$Ca\ (\ell) + MgO\ (s) = CaO\ (s) + Mg\ (\ell)\ .$$

To minimize this reaction, the melt should be well stirred before the temperature reaches 839°C. Of course, keeping the melt temperature below 839°C would virtually eliminate the reaction, but to ensure a high solubility of CaO in $CaCl_2$, the temperature should be 835°C or higher.[19] Thus the ideal temperature range is 835-839°C. Because of the heat generated by the reduction of PuO_2, keeping the temperature in this range is very difficult. We therefore permit the temperature to rise above 839°C, but we go to the final stirring speed before this temperture is reached.

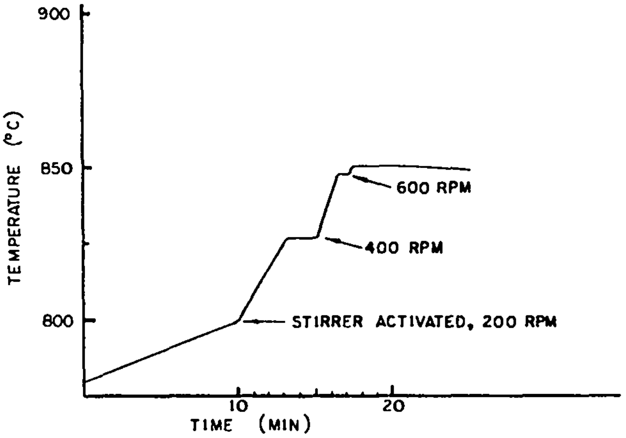

Fig. 5. Temperature profile, Run 23.

E. Calcium Metal Excess

The first 13 runs were made with a 50% excess of calcium metal, that is, 1.5 times the amount required for the reduction of PuO_2. Although the optimum calcium excess is not a crucial issue, it is desirable to keep the excess to a minimum for operational convenience.

The purpose of Run 14 was to accomplish the oxide reduction with a 25% excess of calcium in place of the 50% excess used in Runs 1-13. The procedure in other respects was essentially that of Run 13.

The physical appearance of the reaction products from Run 14 was excellent. The metal product and salt slid easily out of the MgO crucible. The salt was of uniform appearance with no calcium occlusions. A small amount of calcium was on the lid. Nondestructive analysis of the salt and crucible gave a value of 1 g plutonium. The reduction yield was 99.4%. Thus, reducing the calcium metal excess to 25% had no deleterious effect on the process.

The optimum calcium excess is primarily a function of the furnace heating rate and the chemical purity of the oxide feed and $CaCl_2$ salt. For process control, a small excess of calcium should always be clearly observable either on the furnace lid or on top of the $CaCl_2$-CaO salt. If this excess cannot be observed, the calcium excess should be increased.

F. Maximum Ratio of g PuO_2/g $CaCl_2$

The phase diagram for the $CaCl_2$-CaO system[19] shows that the solubility of CaO in $CaCl_2$ at 835°C is 18.5 mole %. Little additional solubility is achieved above 835°C. For example, the solubility at 950°C is only 20 mole %. Thus, we can expect that the limit of loading for the reduction of pure PuO_2 at 835°C is 0.245 g plutonium/g $CaCl_2$. Most of the runs were made at a loading of ~0.17 g plutonium/g $CaCl_2$. We attempted to increase this loading in Runs 17 and 18 to values of 0.234 and 0.267. For comparison, the results of Runs 16, 17, and 18 are summarized in Table I. The same purity of oxide feed (99.4%) was used in all runs. Increasing the ratio to values of 0.234 and 0.267 decreased the reduction yields to values of 94.6 and 87.9%. Plutonium-rich black solids were observed in Runs 17 and 18 (see Table A-I). Because of these solids and the poor reduction yields, a loading of 0.17 g plutonium/g $CaCl_2$ (that is, 5 g $CaCl_2$/g oxide feed) was used for most of the runs after Run 18. Black solids were also observed in Runs 3, 9, and 10, where poor stirring was clearly evident. Thus, it appears that black solids are formed when we have undissolved CaO.

G. Preparation of $CaCl_2$ Cylinders by Isostatic Pressing

The low bulk density of $CaCl_2$ powders does not permit loading adequate amounts of $CaCl_2$ into a reduction crucible. The salt was therefore melted and frozen in quartz tubes for Runs 1-15. The melting was done under vacuum to remove traces of water and other volatile impurities. Although this method was generally satisfactory, it suffered from (1) introduction of ~1000 ppm silicon into the salt, and (2) breaking of the 90-mm-ID quartz tube (two castings at most could be obtained per tube).

To eliminate these problems, isostatic pressing procedures were developed for $CaCl_2$ cylinder preparations. These procedures were used for several of the later runs and became the recommended method of preparation.

H. Reaction Time

Most of the runs (1-21) were done with reaction or stirring times from 1-6 h. These long times were used to ensure complete reduction of oxide. The temperature traces, however, indicated that reaction was complete in less than 20 min. Reaction times of 15 min were used in Runs 22 and 23, and the results of these $^{239}PuO_2$ runs are summarized in Table II. The procedure used is outlined in Sec. VII. The reduction yields were calculated by measuring the plutonium content of the reduction residues by neutron coincidence counting; that is,

$$\text{Yield} = 100 \times \left(\frac{\text{g Pu in feed} - \text{g Pu in residues}}{\text{g Pu in feed}} \right) .$$

For example, in Run 22, assay of the salt residues gave a value of 1.84 g plutonium, and assay of the crucible residues gave a value of 1.19 g plutonium. The total loss was therefore 3.03 g plutonium or 1.7% of the plutonium feed. The reduction yield was 98.3% in Run 22 and 99.7% in Run 23. The crucible residue in Run 23 contained 0.30 g plutonium, and the salt contained 0.23 g. The low plutonium contents of the residues indicated that a reaction time of 15 min is adequate to achieve good reduction yields.

TABLE I. EFFECT OF RATIO PLUTONIUM/$CaCl_2$ ON REDUCTION YIELD

Run	Oxide Feed (g Pu)	$CaCl_2$ (g)	Ratio (g Pu/g $CaCl_2$)	Reduction Yield
16	175	1037	0.169	98.5
17	243	1039	0.234	94.6
18	277	1037	0.267	87.9

TABLE II. RESULTS OF $^{239}PuO_2$ REDUCTIONS IN 15 MIN REACTION TIME

	Oxide Feed		Metal Product		Reduction
Run	wt (g)	Pu (g)	wt (g)	Pu (g)	Yield (%)
22	200	175	165	165	98.3
23	200	175	171	170	99.7

I. Chemical Purity of Reduced Metal

Little if any purification can be expected in the plutonia reduction process because virtually all of the metallic impurities will be reduced to metal by calcium and will concentrate in the plutonium metal. The purity of the metal product will therefore be determined by the purity of the oxide feed, the $CaCl_2$, and the calcium metal. The magnesia crucible and tantalum hardware (stirrer and thermocouple sheath) are additional sources of contamination.

Analyses of feeds and products for the $^{239}PuO_2$ reductions are given in Table A-II. The principal impurities introduced into the metal in the oxide reduction process were magnesium, aluminum, silicon, and calcium. The magnesia crucible and calcium metal were the source of magnesium and calcium. However, because they are removed in subsequent vacuum casting operations, these elements present no problem. Melting the $CaCl_2$ salt in quartz was the principal source of silicon contamination. The use of isostatically pressed cylinders in Runs 16, 17, 22, and 23 resulted in less silicon contamination of the metal. The source of the aluminum contamination is not known. Nonmetallic elements such as carbon and nitrogen were not analyzed in this study.

J. Specifications for PuO_2 Feeds

Most of the experiments were done with $^{239}PuO_2$ prepared by the calcination of plutonium (III) oxalate. This type of oxide is known to be quite reactive and is therefore readily reducible to metal, as our results have shown.

The oxide feed for Run 8 was prepared by burning casting skulls from our plutonium foundry. This oxide was quite unreactive; only 50% of it could be dissolved in HNO_3-HF. Attempts to dissolve it in sealed tubes with $HClO_4$ were also unsuccessful. In spite of its low reactivity, however, this oxide was reduced to metal with a yield of 99.3%. The results of this run suggest that the reduction process could be used to reduce refractory or ceramic PuO_2 to metal.

K. Salt Recycle

No experiments were done in this area. The recycle of $CaCl_2$-CaO salt by reaction with HCl, that is

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \ ,$$

would offer considerable economic advantage, particularly from the waste disposal aspect.

V. RESULTS OF $^{238}PuO_2$ REDUCTIONS

Runs 15, 21, and 24 were made with $^{238}PuO_2$. Details of these runs are given in Table A-I, and results are summarized in Table III. Run 15 was made with Savannah River oxide. The oxide feed for Runs 21 and 24 was made by calcining plutonium peroxide. The

TABLE III. SUMMARY OF $^{238}PuO_2$ REDUCTIONS

	Oxide Feed		Metal Product		Reduction
Run	wt (g)	Pu (g)	wt (g)	Pu (g)	Yield (%)
15	202[a]	174	169	165	99.0
21	176[b]	144	140	135	97.7
24	202[b]	178	171	169	99.7

[a]Savannah River oxide lot.

[b]Oxide prepared by calcining plutonium peroxide.

reduction yields for the three runs were 99.0, 97.7, and 99.7%.

Analysis of feeds and metal products for the $^{238}PuO_2$ reductions are given in Table A-III. The results are in general agreement with the ^{239}Pu analytical data; however, boron appeared as an additional impurity in the ^{238}Pu metal. The source of this contamination was not known at the time of the experiments, but later work has shown that the boron was a contaminant in the $CaCl_2$ salt.

VI. DEMONSTRATION OF OXIDE REDUCTION-ELECTROREFINING FLOW SHEET

The process flow sheet for preparing high-purity $^{238}PuO_2$ ceramics is given in Fig. 2. The oxide is reduced to metal with calcium, and the metal is then purified by electrorefining. The metal is subsequently converted to the ceramic product by the procedures reported in Ref. 5. Demonstration of the oxide reduction-electrorefining steps was first done with $^{239}PuO_2$. In reduction Run 8 (see Table A-I), 322 g of $^{239}PuO_2$ containing 274 g plutonium was reduced to metal with a yield of 99.3%. Approximately 200 g of this metal was then electrorefined, using the standard ^{238}Pu electrorefining process, to yield a product ring weighing 146 g. Plutonium metal was first oxidized at the anode to generate Pu^{+3}, and Na^+ was reduced at the cathode.

Anode reaction: $Pu(\ell) \rightarrow Pu^{+3} + 3e^-$

Cathode reaction: $3Na^+ + 3e^- \rightarrow 3Na$

After $PuCl_3$ generation, the stirrer was activated and electrorefining was initiated.

Anode reaction: $Pu(\ell)$, impure $\rightarrow Pu^{+3} + 3e^-$

Cathode reaction: $Pu^{+3} + 3e^- \rightarrow Pu(\ell)$, pure

Loss of plutonium to the NaCl-KCl electrolyte and crucible as $PuCl_3$ and uncollected metal was 26 g or 13%. (Anodes are recycled to electrorefining feed in ^{238}Pu electrorefining operations.) The purities of the oxide feed, reduced metal, and electrorefined product are given in Table IV. The oxide feed purity was 96.5%; however, this value is suspect because extreme difficulty was encountered in dissolving the sample for analysis (see Sec. IV. J). The true value was probably closer to 99%. The purities of the metal from the oxide reduction and electrorefining were 99.1% and 99.94%, respectively. These experiments demonstrate that a relatively impure unreactive oxide can be reduced directly to metal in good yield and that a pure metal can be obtained by electrorefining.

The second demonstration of the process flow sheet was done with $^{238}PuO_2$. In Run 15, 202 g $^{238}PuO_2$ containing 174 g plutonium was reduced to metal with a yield of 99.0% (see Table A-I). Approximately 164 g of this metal was electrorefined to yield 105 g of product metal. Loss of plutonium to the electrolyte and crucible in this run was approximately 27 g or 16%. This loss is high compared to the usual loss of 2-3% on the 200 g scale; however, the run does demonstrate the effectiveness of the chemical purification. Chemical purities of the oxide feed, the reduced metal, and the electrorefined metal are compared in Table V. The oxide feed contained 87% plutonium with the principal impurities being ^{234}U (from decay of ^{238}Pu), thorium, ^{237}Np, and calcium. The 87% plutonium value corresponds to an oxide purity of 98.7%. The fluorine content was 20 ppm by chemical analysis and 55 ppm by gamma spectrum analysis. The reduced metal purity was 97.8% plutonium and the purity of the electrorefined metal was 99.5%. Radiation measurements made on the oxide, reduced metal, and electrorefined metal are given in Table VI. The neutron emission rate of the electrorefined metal was 3080 n/s·g ^{238}Pu. This compares to a value of 3080 ($\pm$30) n/s·g ^{238}Pu for our old process,[4] consisting of oxide dissolution, precipitation of plutonium peroxide, conversion of peroxide to PuF_4, reduction of PuF_4 to metal, and electrorefining.[5] The (β,γ) dose rate of 0.27 mr/h·g ^{238}Pu compares favorably to the usual value of 0.2.[4] Detailed analysis of the gamma spectrum of the oxide, reduced

TABLE IV. COMPARISON OF $^{239}PuO_2$ FEED, DOR METAL, AND ER METAL

Element	Concentration[a] (ppm) Oxide	DOR Metal	ER Metal
B	[b]Est. 25-50	4	<1
Na	Est. 250-5000	<10	<10
Mg	100	Est. 240-4000	15
Al	300	Est. 500-1000	20
Si	Est. 500-3000	Est. 500-2000	130
K	Est. 100-500	<4	15
Ca	45	Est. 250-2000	10
Cr	100	210	10
Mn	10	40	3
Fe	Est. 500-3000	Est. 500-1000	85
Co	6	10	<1
Ni	380	Est. 500-1000	30
Cu	20	25	2
Mo	5	65	8
La	Est. 50-1000	8	<1
Ta	500	Est. 1000-4000	<100
W	300	Est. 1000-4000	80
^{241}Am	221	211	16
Th	40	16	<15
U	50	200	10
Pu (wt%)	85.1	99.1	99.94

[a] g element/10^6 g sample.
[b] Estimated values by spectroquantitative analysis.

metal, and electrorefined metal shows essentially complete removal of nitrogen, fluorine, sodium, and magnesium. Thus the new process, in which Savannah River oxide is reduced directly to metal and the metal is electrorefined, yields a product that is equivalent to the conventional product.[5]

VII. RECOMMENDED PROCEDURE FOR REDUCTION OF PuO_2 TO METAL

As the result of the 24 runs summarized in Table A-I, the following procedure is recommended for the reduction of $^{238}PuO_2$ and $^{239}PuO_2$ to metal.

A. Equipment (Los Alamos Drawing 26Y-79293)

Crucible—$MgO\text{-}Y_2O_3$, Los Alamos Shape Number A-247
Furnace—6012 S Lindberg Furnace
Stirrer—tantalum, double impeller
Thermocouple Sheath—tantalum outer tube, nickel inner tube

B. Reagents

200 g $^{238}PuO_2$ or 200 g $^{239}PuO_2$—oxide calcined in air at 800°C for 2 h before use

Calcium—74 g of ground calcium (25% excess)

$CaCl_2$—1 kg Bakers analyzed reagent grade, predried and isostatically pressed into 3.5-in.-diam cylinders.

TABLE V. Comparison of Chemical Purities of Savannah River $^{238}PuO_2$ Feed (90 at % ^{238}Pu), DOR Metal (Run 15), and ER Metal (Run 238-200-4).

	Concentration (ppm)		
Element	SR PuO_2	DOR Metal	ER Metal
B	<1	4	5
Na	10	4	20
Mg	2	200-800	10
Al	25	120	<5
Si	50	870	30
K	<5	5	20
Ca	500-2000	5	10
Cr	20	25	<5
Mn	2	4	2
Fe	55	170	20
Ni	10	75	7
Cu	2	3	1
Zn	15	25	5
Mo	<2	100	4
Pb	<5	5	<5
^{241}Am	120	112	15
^{237}Np	1030	1170	195
U	15 200	17 600	60
Th	1600	1200	75
F, chemical	20[a]	---	---
Pu (wt%)	87.0	97.8[b]	99.5

[a] Gamma spectrum analysis gave a value of 55 ppm.

[b] By difference value.

C. Procedure (see Fig. 3)

(1) Place PuO_2 in A-247 crucible.

(2) Place $CaCl_2$ cyclinder in crucible.

(3) Place calcium metal on top of $CaCl_2$ cylinder.

(4) Place A-247 crucible in tantalum safety can.

(5) Place tantalum safety can in stainless steel loading can.

(6) Lower loading can into furnace.

(7) Place cover flange on furnace tube and check tube for gastight integrity by pulling a vacuum to 24 in. Hg and closing valve. Gauges should show no increase in pressure over a 1-min period.

(8) Fill furnace with argon gas to 3 psig. Evacuate and back fill with argon twice.

(9) Program furnace controller to heat contents of furnace to 850°C at a rate of 200°C/h.

(10) When the crucible temperature reaches 790°C, lower the thermocouple into the melt, 1 in. off bottom of crucible.

(11) Lower the stirrer slowly at 800°C and initiate stirring when a temperature of 800°C is regained.

(12) Stir at 200 rpm for 2 min, 400 rpm for 2 min, 600 rpm for 2 min, and finally 700 rpm for 9 min. (These stirring times are approximate. Control of the reaction is

TABLE VI. COMPARISON OF RADIATION MEASUREMENTS FOR $^{238}PuO_2$ FEED, DOR METAL (RUN 15), AND ER METAL (RUN 238-200-4)

	SR $^{238}PuO_2$ Lot HA 304040	DOR Metal	ER Metal
Neutron emission rate (n/s·g ^{238}Pu)	17 865	8410	3080
(β, γ) dose rate at 10 cm (mr/h·g ^{238}Pu)	9.70[a]	0.61[b]	0.27[b]
Gamma spectrum impurities (ppm)			
N, ^{238}Pu basis	765	672	10
F, ^{238}Pu basis	55	27	0
Na, ^{238}Pu basis	41	13	ND[c]
Mg	ND[c]	927	<100

[a] Measured through 0.050 in. stainless steel.
[b] Measured through 0.030 in. tantalum.
[c] Not detected.

achieved by observing the salt temperature. The objective is to achieve a smooth temperature rise from 800 to 840°C. Stirring at 700 rpm should be done before the temperature rises above 840°C.

(13) At the end of the 15-min stirring period, raise stirrer .5 in. and permit it to drain for 5 min. Raise stirrer and thermocouple from melt; shut off furnace.

(14) Unload furnace when it has cooled to ambient temperature.

15) The metal button is removed by breaking away the bottom of the magnesia crucible.

VIII. CONCLUSIONS

The direct reduction of impure $^{238}PuO_2$ to impure metal, followed by electrorefining, permits the use of a new cost-effective flowsheet for preparing high-purity ^{238}Pu metal. This process provides the following advantages:

(1) radiation exposures from $^{238}PuF_4$ are eliminated,

(2) generation of process wastes is decreased, and

(3) manpower requirements for preparing pure metal are decreased.

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APPENDIX

TABLE A-1. COMPILATION OF PLUTONIA REDUCTION RUNS

Experiment Conditions

Feed - $^{239}PuO_2$ in all runs except 15, 21, and 24
$^{238}PuO_2$ in runs 15, 21, and 24.

Stirring - Reverse and unidirectional motion in Runs 1-10, unidirectional only, in Runs 11-24.

Salt Composition - $CaCl_2$-26 mol % CaF_2 in Runs 1-11. $CaCl_2$ in Runs 12-24.

Salt Cylinders - Vacuum cast in all runs, except Runs, 16, 17, 18, 22, and 23, isostatically pressed cylinder in Runs 16, 17, 18, 22, and 23.

Salt Thermocouple Sheath - Ni in Run 1, Ta in Runs 2-12, Ni/Ta composite in Runs 13-24.

Reduction progress measured only by neutron flux measurements in Runs 1-12 and by continuous salt temperature measurement in Runs 13-24.

		Oxide Feed				Salt Temperature (°C)				Product Ingot			
Run No.	Crucible Geometry[a]	wt (g)	Pu (g)	Salt (g)	Ca (g)	Start of Stirring	Maximum	Stirring Time (h)	Plutonium Appearance	wt (g)	Pu (g)	Observable Black Solids	Reduction Yield (%)
1	FB	200	173	1009	85	805	860[b]	1	Partial disk	181[c]	171[e]	No	99.4[d],99.6[fg]
2	FB	200	173	1004	85	735	785[b]	1	3-4 mm thick disk, ring, shot	142	139[h]	No	83.2[d]
3	Furnace heating elements burned out.												
4	C	230	200	1005	85	717	855[b]	1	Button	115	113[h]	Yes[i]	70[d]
5	C	200	172	1018	85	800	890[b]	4	Button	113	110[h]	No	75[d]
6	FB	200	176	1006	85	—	890[b]	4	Partial disk	172	171[e]	No	99.5[d]
7	C	200	176	1015	85	833	895[b]	5	Button	150	149[h]	No	89.9[d]
8	FB	322	274	1707	137	848	900[b]	5	Partial disk	270	268[h]	No	99.3[d]
9	H	200	172	1000	85	893	943[b]	5	Button	149	145[b]	Yes[i]	91[d]
10	H	200	172	1008	85	854	900[b]	6	Button	161	160[e]	Yes[i]	96.3[d]
11	H	200	169	1000	85	—	—	5	Button	108	105[e]	No	98.1[f]
12	H	200	168	1028	85	850	903[b]	5	Button	169	169[e]	No	99.3[d]
13	H	200	175	1030	85	807	848[j]	3	Button	179	178[e]	No	101.8[d],98.7[fk]
14	H	200	175	1030	74	810	856[j]	3	Button	173	173[e]	No	100.6[d],99.4[fk]
15	H	202	174	1023	74	790	848[j]	3	Button	169	165[h]	No	99.0[fk]
16	H	200	175	1037	74	810	846[j]	2	Button	156	153[e]	No	98.4[d],98.5[fk]
17	H	277	243	1039	110	806	874[j]	2	Button	220	219[e]	Yes	95.7[d],94.6[fk]
18	H	313	277	1037	122	810	865[j]	2	Button	224	223[e]	Yes	88.4[d],87.9[fk]
19	H	200	175	1013	74	788	867[j]	1	Button	173	172[e]	No	99.4[fk]
20	H	200	175	1024	74	815	844[j]	2	Button	170	169[h]	No	98.6[fk]
21	H	176	144	1027	74	813	880[j]	2	Button	140	135[e]	No	97.7[fk]
22	H	200	175	1049	74	760	850[j]	0.25	Button	165	165[e]	No	98.3[fk]
23	H	200	175	1035	74	770	840[j]	0.25	Button	171	170[e]	No	99.7[fk]
24	H	202	178	1029	74	840	860[j]	0.25	Button	171	169[e]	No	99.7[fk]

[a] FB = flat-bottom crucible, C = conical-bottom, H = hemispherical bottom.

[b] Estimated value.

[c] Metal contaminated with nickel from thermocouple sheath.

[d] Reduction yield = 100 × g Pu product metal + g Pu metal on stirrer/g Pu in Oxide Feed.

[e] Pu values based on chemical analysis of product.

[f] Reduction yield = 100 × (g Pu in feed - g Pu in salt and crucible)/g Pu in oxide feed.

[g] Pu values in salt and crucible based on chemical analysis.

[h] Product assumed to be of same purity as feed.

[i] Poor mixing clearly evident.

[j] The salt temperature was measured continuously during this run.

[k] Pu values in salt and crucible determined by neutron coincidence counting in thermal neutron counter (TNC). Value for Run 14 was 1.0 g Pu. Chemical analysis value also was 1.0 g Pu.

TABLE A-II. CHEMICAL PURITY OF OXIDE FEEDS AND METAL PRODUCTS IN $^{239}PuO_2$ REDUCTION RUNS

Element	Run 1 (ppm)		Run 6 (ppm)		Run 8 (ppm)		Runs 10 and 11 (ppm)			Run 12 (ppm)	
	Oxide	Metal	Oxide	Metal	Oxide	Metal	Oxide	10 Metal	11 Metal	Oxide	12 Metal
Li	—	—		<5	<5		<2	<4	<4	<2	<2
Be	<1	<1		<1	<1		<1	<1	<1	<1	<1
B	1	1		2	25-50	4	<1	4	1	<1	8
Na	<50	<50		<10	250-5000	<10	30	<10	10	30	<20
Mg	<2	50		9	100	250-4000	60	250	250-8000	60	250
Al	8	20		160	300	500-1000	30	40	160	30	65
Si	6	1000		1000-4000	500-3000	500-2000	65	500-2000	500-2000	20	1000-4000
K	...	—		<5	100-500	<4	6	<4	<4	6	<4
Ca	130	500-1000		35	45	250-2000	140	250	250-4000	140	15
Ti	10	<5			<1		5	<10	8	<2	<5
V	5	5		2			2	<1	3	5	5
Cr	45	40		180	100	210	60	50	140	130	140
Mn	1	50		15	10	40	15	10	20	15	10
Fe	8	20		290	500-3000	1500	400	370	540	490	490
Co	<2	15		2			2	<2	<2	2	2
Ni	6	52 000		260	380	500-1000	70	310	230	75	150
Cu	2	<1		2	20	25	4	3	15	4	3
Zn	<5	5		4	4	4	10	5	15	5	5
Rb	...	...		<5			<2	<4	<4	<2	<4
Sr	<5	<5		<5			10	<2	<2	<2	<5
Y	—	—					<2	<2	40	<2	20
Zr	200	100		2			60	<1000	<1000	60	400
Nb	<10	20		<10	5	65	<25	<25	<25	<25	<10
Mo	80	75		1000-4000			500	250-1000	500	500	500-2000
Cd	15	<10		<1			<2	<10	<10	<2	<10
Sn	8	<5		<1			5	10	10	10	5
Ba				<1			<2	<2	<2	<2	<4
La	—	...		<1	50-1000	8	<2	<2	<2	<2	<4
Hf	...	—		<1			<2	<2	<2	<2	<4
Ta	<100	<100		<100	500	1000-4000	<100	300	<100	<100	<100
W	<10	40		10	300	1000-4000	<10	<10	10	15	10
Re	—	—		<1			<2	<2	<2	<2	<4
Pb	3	<5		<1			<2	2	40	5	5
Bi	<1	<1		<1			<1	<1	<1	<1	<1
U	<10	220		45	50	200	<10	<10	40	<10	10
Th	75	55		168	40	16	15	<15	68	40	25
Am	26	23	30	67	221	211	11	40	51	21	45
Pu (wt%)	86.44	94.24	87.83	99.58	85.1	99.1	85.84	99.43	96.75	84.32	99.81
Chemical purity (%)	98.06	94.24	99.64	99.58	96.5	99.1	97.38	99.43	96.75	95.66	99.81

TABLE II. (Cont) CHEMICAL PURITY OF OXIDE FEEDS AND METAL PRODUCTS IN $^{239}PuO_2$ REDUCTION RUNS

	Runs 13, 14, 16, and 17 (ppm)					Runs 19, 20, 22, and 23 (ppm)				
	Oxide	13 Metal	14 Metal	16 Metal	17 Metal	Oxide	19 Metal	20 Metal	22 Metal	23 Metal
Li	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Be	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
B	1	2	5	<1	5	10	10	50	45	45
Na	60	5	<2	6	<2	100	<2	<2	<2	<2
Mg	4	1000-4000	85	100-400	>100	40	530	30	>100	>100
Al	<5	200	120	450	90	15	70	140	110	70
Si	4	750	740	150[a]	120[a]	35	740	500-2000	130[a]	340[a]
K	15	<5	<5	<5	<5	15	<5	<5	<5	<5
Ca	15	1000-4000	9	500-2000	2000-8000	1000-4000	150	<3	1800	1000
Ti	5	10	...	<5	<5	<5	<5	<5	20	<5
V	<2	<2	<2	<5	<5	<2	<3	<3	<3	<3
Cr	20	25	35	<5	20	9	20	<5	10	15
Mn	3	5	6	4	10	2	4	5	2	3
Fe	50	120	90	190	150	55	120	190	95	90
Co	<2	<2	<2	<2	<2	<2	<3	<3	<3	<3
Ni	110	220	190	660	140	35	90	70	110	80
Cu	45	5	5	4	10	5	<2	1	3	<1
Zn	<5	6	6	10	10	5	7	5	65	<5
Rb	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Sr	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Y	<25	150	<25	<25	<25	<25	<25	<25	<25	<25
Zr	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Nb	<10	--	...	<10	<10	...	<10	<10	<10	<10
Mo	90	200	150	200	75	2	20	<3	4	3
Cd	9	<10	<10	<10	<10	<10	<10	<10	<10	<10
Sn	9	8	10	<5	5	<5	<5	10	<5	<5
Ba	<2	<2	<2	<2	<2	5	<2	<2	<2	<2
La	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
Hf	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
Ta	<100	500	100	<100	<100	<100	<100	<100	<100	<100
W	75	<10	<10	<10	<10	<10	...	<10	25	<10
Re	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
Pb	9	8	6	<5	<5	25	...	15	20	<5
Bi	<1	<1	<1	<1	<1	8	...	<1	<1	<1
U	<10	...	25	30	15	340	255	280	265	260
Th	75	...	30	63	60	930	720	225	640	960
Am	--	42	40	58	71	66	127	112	235	188
Pu (wt%)	87.62	99.5	99.76	98.2	99.56	87.5	...	--	99.8	99.4
Chemical purity (%)	99.40	99.5	99.76	98.2	99.56	99.3	--	--	99.8	99.4

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[a] $CaCl_2$ isostatic pressing used.

TABLE A-III. CHEMICAL PURITY OF OXIDE FEEDS AND METAL PRODUCTS IN $^{238}PuO_2$ REDUCTION RUNS

Element	Run 15 (ppm) Oxide[a]	Run 15 (ppm) Metal	Run 21 (ppm) Oxide[b]	Run 21 (ppm) Metal	Run 24 (ppm) Oxide[b]	Run 24 (ppm) Metal
Li	<1	<1	<1	<1		<1
Be	<1	<1	<1	<1		<1
B	<1	4	<1	400		100-400
Na	10	4	150	50		15
Mg	2	200-800	50	20		100-400
Al	25	120	40	520		64
Si	50	870	15	1000		247
K	<5	5	60	75		40
Ca	500-2000	5	350	5000		500-2000
Ti	20	25	20	15		<5
V	<3	<3	<3	<3		<3
Cr	<5	<5	<5	<5		<5
Mn	2	4	1	3		3
Fe	55	170	15	290		121
Co	<3	<3	<3	<3		<3
Ni	10	75	10	75		23
Cu	2	3	<2	20		2
Zn	15	25	<5	<5		10
Rb	<2	100	<10	<10		<10
Sr	<5	5	15	75		<5
Y	<25		<25	100		<25
Zr	<100		400	<100		<100
Nb	<10		<10	<10		<10
Mo	<10		3	<3		<3
Cd	<10		<10	<10		<10
Sn	<5		10	15		<5
Ba	<2		4	<2		<2
La	<25		<25	<25		<25
Hf	<25		<25	<25		<25
Ta			300	2500		100
W			50	50		<10
Re			<25	<25		<25
Pb			7	10		5
U	15 200	17 600	---	2400		1200
Th	1600	1200	---	3400		1200
Am	120	112	---			
Pu (wt%)	87.0	93.8	---	97.9		98.8
Chemical purity (%)	98.7	93.8		97.9		98.8

[a] Savannah River Oxide Lot HA 304040.

[b] Oxide prepared by calcining Plutonium Peroxide.

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