



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Operation of the Oxide Washer for Water-Washing Solubles out of Impure Pu Oxide

K. E. Dodson, W. L. Close, O. H. Krikorian,
H. V. Summers III

January 30, 2006

Disclaimer

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

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Operation of the Oxide Washer for Water-Washing Solubles out of Impure Pu Oxide

Karen E. Dodson, Walter L. Close, Oscar H. Krikorian and Harry V. Summers III

University of California, Lawrence Livermore National Laboratory,
Livermore, CA 94551

Abstract

An evaluation has been made for using the Oxide Washer to wash water-soluble materials out of impure Pu oxide. It is found that multiple washes are needed to reduce the water-soluble materials to very low levels in the impure Pu oxides. The removal of the wash water from the Oxide Washer is accompanied by particulates of the impure Pu oxide, which subsequently need to be filtered out. In spite of the additional filtration needed, the overall level of manpower required for processing is still only about one third of that for an all-manual operation.

Introduction

The Oxide Washer was developed by the Research Institute of Atomic Reactors (RIAR) in Russia to remove soluble chlorides from cathode deposits that are generated during pyrochemical operations for reprocessing nuclear fuel, and also to wash out salts from U and Pu oxide fuels in hot cell operations. An Oxide Washer (also called a RIAR Washer) was purchased from RIAR for use at the Lawrence Livermore National Laboratory (LLNL) for washing out solubles, such as chlorides, nitrates, and hydroxides, from impure Pu oxide materials. Removal of the solubles would (1) reduce the affinity of the impure Pu oxide for absorbing moisture, (2) reduce the volume of impure Pu oxide that needs to be packaged for storage, and (3) eliminate the problem of chloride volatilization during calcination and loss on ignition (LOI) measurements when preparing the material for Department of Energy approved packaging.¹ It was hoped that the Oxide Washer would substantially reduce the level of effort required for removal of solubles as compared with a manual operation. This report describes our experiences with the Oxide Washer.

Process Flow Sheet

The process flow sheet for Oxide Washer processing of impure Pu oxide is given in Fig. 1. In the first process step, an approximately 1 kg batch of impure Pu oxide is loaded into the Oxide Washer and washed with about 800 ml of deionized or distilled water. After the wash, the wash water is removed and its electrical conductivity is measured. If the conductivity is above 450 $\mu\text{S}/\text{cm}$, another wash is made and the conductivity is again checked. The process of washing and checking the conductivity is repeated until the conductivity drops to

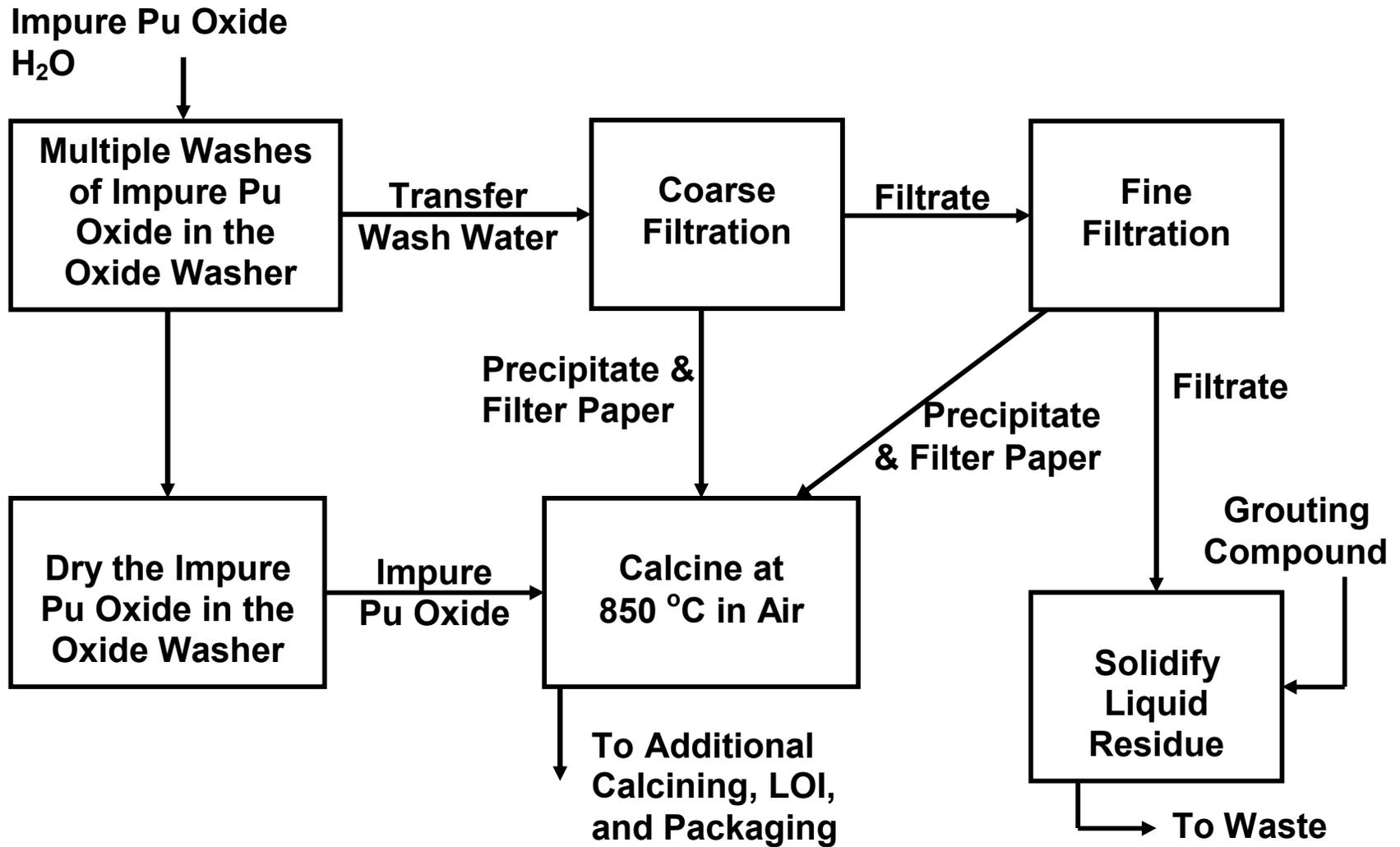


Figure 1. Flow sheet for Oxide Washer processing of impure Pu oxide.

below 450 $\mu\text{S}/\text{cm}$. Typically, about 8 washes are needed to reduce the conductivity to below 450 $\mu\text{S}/\text{cm}$.

After the last wash, the impure Pu oxide is dried using a built-in heater in the Oxide Washer, and the impure Pu oxide is removed from the Oxide Washer using a Dustless Transfer Unit (vacuum cleaner) and sent to the calcining furnace where it is calcined in air at 850 $^{\circ}\text{C}$. Meanwhile, the accumulated wash waters are put through a coarse low-ash paper filter to remove carryover of impure Pu oxide particles from the oxide washer. The filtrate is then put through a fine low-ash paper filter to remove most of the fine particles that came through the coarse filtration. The precipitates and filter papers from the two filtrations are sent to the calciner, and the final filtrate is sent to be solidified with a grouting compound and then sent out as waste. The calcined materials are sent out for a higher temperature calcining (1000 $^{\circ}\text{C}$) and an in situ LOI evaluation with a thermal balance, and are finally packaged in a Department of Energy approved 3013 container.¹ The 1000 $^{\circ}\text{C}$ calcining and succeeding processes are not covered in this report. All of the operations described here are carried out in air-flow gloveboxes.

Experimental Equipment

Oxide Washer:

The Oxide Washer is illustrated in a simplified cross sectional view in Fig. 2 and is shown in the photographs given in Figs. 3 and 4. The washing is carried out in a Ti crucible that serves as the wash tub. The Ti crucible is nominally 15 cm in dia X 21 cm high. During the wash operation, a thick slurry of the oxide powder to be washed is laid onto the inside walls of the Ti crucible and held there by centrifugal force from the rotation of the Ti crucible at ~ 930 rpm. Wash water placed in the Ti crucible flows through the slurry similarly to flow through a filter bed. Because of the sloped walls of the crucible, the wash water reaching the walls migrates upward and flows into a larger diameter notch in the Ti crucible (see Fig. 2). When the notch is filled with water, the excess water flows inward along the upper contour of the Ti crucible and is thrown forward and falls toward the bottom of the crucible. The water is again thrown out by centrifugal force against the slurry and migrates again through the slurry and up to the notch. The water thus continues to recycle and pick up soluble salts. When it is desired to remove the wash water, a water pickup tube is rotated into the notch in the Ti crucible to scoop up and remove the water. The water pickup tube has a right angle bend (see Fig. 4) that positions the tube opening toward the centrifugal flow of water in the notch in the Ti crucible. If it is desired to observe the murkiness of the water without removal of the water, the water pickup tube is only partially rotated into the notch in the Ti crucible. The water then flows up to the glass observation dome and is continuously returned to the Ti crucible through a central hole in the rotation fixture (see Figs. 2 and 4).

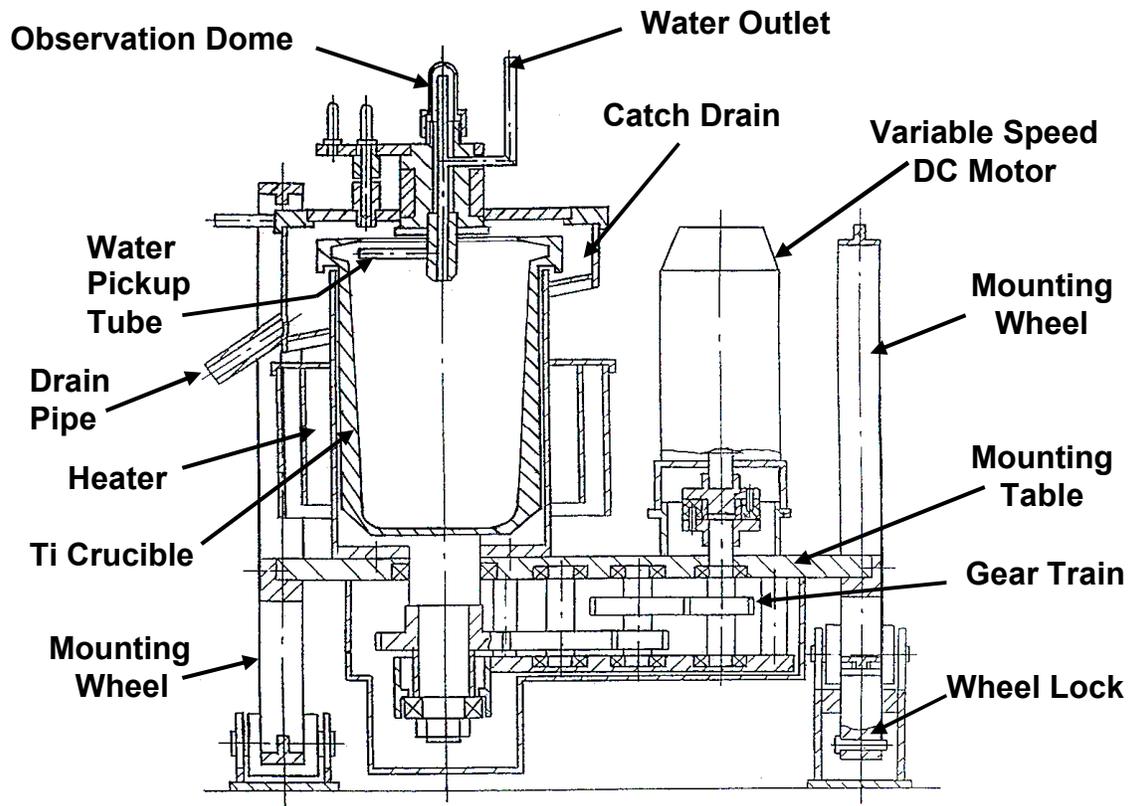


Figure 2. Simplified cross sectional view of the Oxide Washer.



Figure 3. View of the Oxide Washer mounted in vertical position.



Figure 4. Oxide Washer in 45° position with the cover removed and showing the bottom side of the cover.

Other features of the Oxide Washer are as follows. The lid to the chamber is placed on the chamber rim and fitted into 3 matching slots (see Fig. 4). The lid is then rotated into grooves in the slots and locked into place with hand screws. A drain system for catching any wash water lost from the top of the Ti crucible is provided by a surrounding catch tank with a sloped bottom and a drain pipe (see Figs. 2 and 3). A Calrod heater is built into a chamber that surrounds the back half of the lower part of the Ti crucible (see Figs. 2 and 3). The heater provides uniform heating to the Ti crucible by maintaining a slow rotation (~60 rpm) in the crucible during drying of the washed oxide. The heater is rated at 1 kW of power and is capable of heating the lower part of the Ti crucible to a maximum temperature of 140 °C. A 410 W DC permanent magnet servomotor (this is a replacement of a 230 VAC Russian made motor) provides a variable speed with a maximum rotation rate of 8000 rpm to power the rotation of the Ti crucible through a 5.46:1 speed reduction gear train. The gear train is maintained in a bath of transmission oil. The motor, gear train and chamber assembly are supported on a mounting table, which is in turn supported on two sides by rotatable wheels (see Figs. 2 - 4). The wheels allow the assembly to be tilted and locked into 3 positions: (1) vertical, (2) 25° from vertical, and (3) 45° from vertical.

Three additional features built into the lid but not used here are: (1) a second water inlet tube on a rotation fixture (see Fig. 4) for collecting samples of

the wash water from the notch during the wash operation, (2) an opening in the lid for adding wash water to the Ti crucible during operation, and (3) an opening in the lid with a cover cap to be used for adding solids to the Ti crucible during operation.

Dustless Transfer Unit:

The Dustless Transfer Unit is a vacuum cleaner that has been specifically designed for the vacuum transport of dry powders. The vacuum is supplied by a 3450 rpm regenerative blower with a 1/3 hp permanent split capacitor brushless motor. A stainless steel tube (3/8" in dia) attached to reinforced plastic tubing is used as a vacuum wand to pick up the dry impure Pu oxide and transport it to a convenience can. A metal frit filter (5 or 10 μm pore size) prevents loss of the impure Pu oxide into the vacuum and allows the ash to settle into the convenience can. Pneumatic solenoid-actuated back-pulse valves allow the filter to be back flushed every few minutes during use, or at the end of the operation, in order to prevent blockage of the filter. Experience shows the transport of Pu oxide material powders takes about a minute per 1000 g, and the transfer is quantitative to within a few tenths of a gram.

Conductivity Measurements:

The conductivity meter is made by GLI International as Model 53. It gives a digital readout to within 1 $\mu\text{S}/\text{cm}$ in the range of 0 - 1999 $\mu\text{S}/\text{cm}$. Data are illustrated in Fig. 5 on the conductivities at 25 °C for most of the expected dissolved salts and hydroxides as a function of their concentrations given in g/l. The data are taken from the International Critical Tables,² and have been corrected to 25 °C as needed. With concentrations expressed in g/l, NaNO_3 and Na_2SO_4 have the highest concentrations, and KOH and NaOH have the lowest concentrations. Salts such as NaCl, KCl, CaCl_2 , Na_2CO_3 , NaF and MgCl_2 are grouped together in the middle. Assuming that halides and carbonates are the main solubles, the amount of dissolved solubles at 450 $\mu\text{S}/\text{cm}$ is ~0.2 g/l and the amount of solubles left in the impure Pu oxide can be estimated to be about 0.1 g.

Calcining Furnaces:

Calcining of the washed impure Pu oxide and calcining of the impure Pu oxide precipitates and the burning off of the filter papers are carried out in ambient air in Thermoline type 1400 muffle furnaces. The furnace chambers are 5" wide X 4.25" high X 6" deep and alumina dishes are used to contain the materials being calcined. The furnaces are programmable and have an upper temperature limit of 1100 °C.

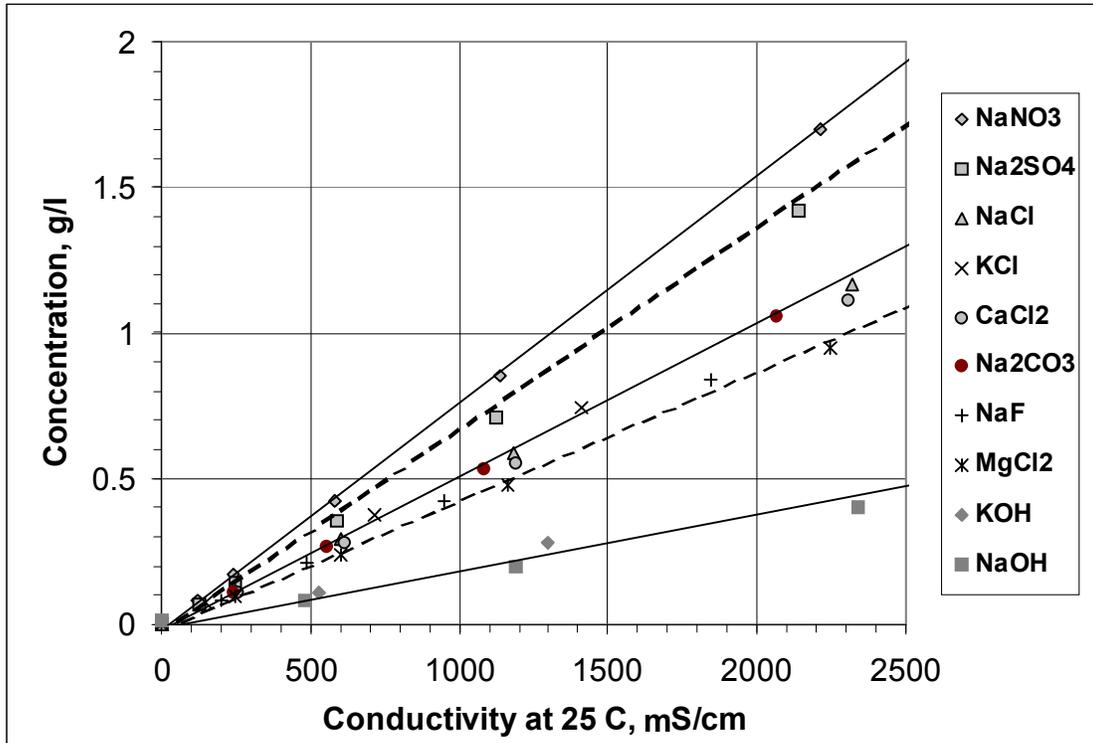


Figure 5. Conductivities are given at 25 °C for soluble salts and hydroxides that are likely to be present in impure Pu oxide materials.

Oxide Washer Operating Procedure

The Oxide Washer operating procedure consists of six steps, which are as follows:

1. Mixing of Impure Pu Oxide and Water.
2. Forming of Side-Wall Layer.
3. Washing/Filtering.
4. Water Removal.
5. Drying of Impure Pu Oxide
6. Removal of Impure Pu Oxide.

Steps 1 through 4 complete a wash cycle. At the end of step 4, a decision is made as to whether to run another wash cycle with fresh water or to proceed to step 5 and dehydrate the impure Pu oxide. Details on the six steps will now be described.

To begin step 1, the mixing step, first make sure that the impure Pu oxide to be washed is in powder form. If not, remove any chunks of foreign material (such as pieces of ceramic or graphite crucibles) and then run the impure Pu oxide in a ball mill until pulverized to pass a 65 mesh screen (-210 μm). With the impure Pu oxide in powder form, take a small sample of the Pu oxide material and add some water to it. Swirl for a few minutes and then test the pH with litmus paper. If the pH is 7 or

greater, then remove the lid of the Oxide Washer chamber, set the washer in the 45° position and load approximately 1 kg of impure Pu oxide and 800 ml of water into the Oxide Washer. If the pH of the sample is less than 7, then add a mixture of 6N NaOH and water to the impure Pu oxide in the Oxide Washer to obtain a pH of 7 or somewhat greater, but do not exceed a total volume of 900 ml of wash water.

With the chamber lid off, the Oxide Washer set at 45° and loaded with impure Pu oxide and wash water, set the rotation rate at ~60 rpm and allow the impure Pu oxide and water to thoroughly mix for about 5 minutes. Use a rubber spatula (such as used for cake batters) to smooth out any lumps in the mixture. When the mixture is free of lumps and has run for 5 minutes it is ready for step 2, the layer-forming step.

For step 2, bring the Oxide Washer up from 45° from vertical to 25° from vertical, while it is still running at 60 rpm. Now gradually increase the rotation rate to ~200 rpm. This will allow the slurry layer to form about half way up the wall of the Ti crucible. The crucible should be free of any excessive vibration at this point. If vibration is excessive, reduce rotation rate to 60 rpm, reset the Oxide Washer to 45°, and recheck the mixture for lumps with the spatula. Now return to 25° from vertical, gradually increase the rotation rate to 200 rpm, and once again check for excessive vibrations. It requires some experience to successfully complete this step. Proceed now to step 3, the washing and filtering step.

In step 3, set the chamber lid in place making sure that the water pickup tubes are rotated away from the notch in the Ti crucible. Set the Oxide Washer in the vertical position, and gradually increase the rotation rate to 950 rpm (takes about 15 minutes) and hold there. Here, also, vibrational intensity should be minimal in order to minimize carryover of solids when withdrawing the wash water. Set the water pickup tube for the observation dome partially into the notch of the Ti crucible and sample the effluent wash water in the observation dome. Some murkiness is always present in the wash water and tends to decrease when held at 950 rpm for about 5 minutes. If the vibrational intensity and hence the murkiness are unusually high, the process needs to be returned to step two and the wall layer reformed more carefully. Otherwise, after 5 minutes set the water pickup tube fully into the notch of the Ti crucible and withdraw the wash water into a flask. About 8 minutes are needed to withdraw the water, leaving about 50 ml of residual water behind in the Oxide Washer.

Check the electrical conductivity of the wash water that was withdrawn into the flask. If the electrical conductivity exceeds 450 $\mu\text{S}/\text{cm}$, one or more wash cycles will need to be run (i.e., steps 1 - 4). Before adding water in step 1, the impure Pu oxide remaining in the notch region and the side walls of the Ti crucible needs to be returned to the bottom of the Ti crucible. This can be done in the 45° position at 60 rpm by first scraping or rubbing the Pu oxide ash off with the rubber spatula, and then rinsing it down with water from a squirt bottle.

The wash waters collected from the washings are all filtered through coarse and fine filters and further processed as will be described below.

When the last washing gives an electrical conductivity of less than 450 $\mu\text{S}/\text{cm}$, proceed to step 5, the drying step. With the chamber lid off and the Oxide Washer in the 45° position with a rotation rate of 60 rpm, proceed to clean off the impure Pu oxide from the notch region and the side walls using the rubber spatula and water from a squirt bottle. While retaining the chamber lid off, the 45° position and the 60 rpm rotation rate, program the heater to heat the lower part of the vessel to 120 °C for 4 hours. When the heating cycle is completed and the impure Pu oxide is dried and cooled down, proceed to step 6, the oxide removal step.

In step 6, shut off the rotation and use the dustless transfer unit to vacuum the impure Pu oxide out of the Ti crucible and transfer it into a convenience can. The impure Pu oxide is then sent to be calcined.

Filtration Procedures

The first filtration of the wash water is carried out with a Buchner funnel using a coarse filter paper, e.g., Whatman No. 41 ashless filter paper, 20 - 25 μm porosity. The filtration is rapid and removes most of the carryover particulates. After filtration the precipitate and filter paper are allowed to air dry and then sent to be calcined.

The filtrate from the coarse filtration still contains fine particulates and needs further filtration with a finer filter. Before filtration, a sufficient amount of NaOH pellets are added to the filtrate to increase the pH into the 12-14 range, and thus promote precipitation of any Pu ions still in the filtrate. A second filtration is then carried out with a Buchner funnel using a fine filter paper, e.g., Whatman No. 42 ashless filter paper, 2.5 μm porosity. An aspirator is used on the Buchner funnel to reduce the filtration time. After filtration, a water rinse is used to wash out the residual NaOH in the precipitate. The precipitate and filter paper are allowed to air dry and are sent to the calciner. The filtrate, which contains a small trace of fine particulates and excess NaOH, is neutralized with HCl. It is then solidified with grouting material (Aquaset) and sent out to waste.

Description of the Impure Pu Oxide to be Processed

The impure Pu oxide material that is being processed here has been described by Van Konynenburg et al.³ The material was accumulated at LLNL from Pu residues from 1970 to the present time. The sources of Pu residues have included machine turnings, research samples, metallographic samples, X-ray samples, residues from chemical analyses of Pu, Pu-containing solutions, crucible residues, cleaning tissues (e.g., Kimwipes) used to mop up chemical spills, glovebox sweepings, and a number of other residues. When the Pu material was present in quantities on the order of a gram or more in the residues, the material

was usually processed by dissolution in acid, and then precipitated with NaOH to form Pu hydroxide. The precipitate was filtered and allowed to dry and then calcined at ~450 °C in ambient air to form an impure Pu oxide. These calcined materials were ball milled into a powder and then packaged for storage. A more detailed description of the historical processing and storage problems of the Pu residues (see Van Konynenburg et al.³ for a complete overview) will now be given so that there will be more insight as to impurity effects.

Processing Methods and Storage Problems of Pu Residues:

During the period of 1970 through mid 1992, the processing and storage of Pu residues was carried out as follows. Pu residues, except for cleaning tissues and glovebox sweepings, were generally dissolved in concentrated HCl. Occasionally, concentrated HNO₃ with added HF was used to speed up the dissolution process. Once dissolved, the solution was made basic with excess NaOH to give a pH of 12 or greater. This allowed the Pu to precipitate out as the hydroxide. Some of the impurities also precipitated out as the hydroxides. The solution was then filtered using an ashless filter paper. However, the filter cake was not rinsed in order to minimize the amount of filtrate produced. As a result of not rinsing, some unknown amounts of NaOH, chlorides, nitrates, and fluorides remained with the filter cake. Also, some of the salts may have exceeded saturation when NaOH was added, and precipitated out, adding to the salts retained with the precipitate.

The next process step was calcining. When dry, the filter cakes together with the filter papers from the precipitations, were inserted into a stainless steel beaker. Pu-contaminated cleaning tissues and glovebox sweepings were also added to the beaker. The beaker was placed on a stand in a vertical-axis clamshell electrical resistance furnace and the furnace was heated to 650 °C. The furnace heating element was monitored and controlled at 650 °C for several hours to calcine the Pu residues. The temperature inside of the beaker was not monitored, but was estimated to be at least 450 °C. Air was allowed to flow up around the stainless steel beaker (chimney effect) during the heating. However, access of air into the inside of the beaker was restricted by diffusion. Therefore, the material inside of the beaker was periodically stirred during a run to allow exposure of the bottom material to air. It is expected that the Pu hydroxide and most other hydroxides converted to oxides. Organic materials either distilled off or pyrolysed to form chars, which may not have burned off completely. If graphite was present as an impurity, it is unlikely that it burned off. Residual NaOH and chloride salts would have remained. Nitrate salts may have partially or totally decomposed into oxides. Calcining was done at a low temperature because it was anticipated that Pu recovery operations would be carried out at some future date and that the lower temperature calcination would make it easier to dissolve the Pu oxide.

After calcining, the impure Pu oxide was left in the furnace to cool overnight (or longer). It was then removed and sieved through a 65 mesh (-210 μm) screen. Material not passing through the screen was ball-milled (or ground) and sieved again, and size reduction repeated as necessary until all of the material passed through the screen. The impure Pu oxide powder was then blended for 4 hours in a V-blender to homogenize the material in preparation for Pu determination by calorimetry and gamma counting. All of these operations were carried out in ambient air and it is expected that water absorption occurred in the NaOH and salt impurities from the humidity in the air.

From 1970 until late 1992 the impure Pu oxide powders were stored in 0.5 liter "Kaufman cans." Kaufman cans are tin-plated steel cans incorporating screw-on lids with neoprene rubber gaskets. The rubber gasket limited exchange of gases between the interior and the environment but did not provide a completely hermetic seal to gases. No bulging of Kaufman cans from internal gas generation was observed during storage of the impure Pu oxide powders.

From November 1992 through July 1993, a program was undertaken to combine the impure Pu oxide powders into larger batches and seal them in doubly contained food-pack cans. The intent was to consolidate these for shipment to the Savannah River Site for reprocessing and reclamation of the plutonium. Most of the new batches were made up of pairs of batches from the Kaufman cans. In June 1994, two of the new packages were found to exhibit bulges in the outer food-pack lids. Shortly thereafter, another 6 packages were found with bulges. As a temporary expedient to secure the inventory of the packages, both food-pack cans were punctured to allow gas release and then packaged inside of a larger can with a carbon frit filter in the lid to allow gas exchange with the environment. Several of the food-pack cans were analysed for gases and the interiors checked for corrosion. In most cases the cans showed corrosion although the corrosion was not deep enough to penetrate the can walls. Gases evolved included H_2 , O_2 , CO and CO_2 . Radiolysis would have led to formation of H_2 and O_2 from residual water, and CO and CO_2 would occur because of the presence of char, H_2O , and O_2 in the radiolytic environment. Also, considering the presence of impurities and humidity in the cans and the radiolytic conditions, it can be expected that hydrochloric acid, nitric acid, formic acid, oxalic acid, and hydrogen peroxide would form with time and lead to a progressive corrosion of the cans.

This history of temporary storage of these impure Pu oxide materials suggests that the problems of gas generation and corrosion that have occurred can be eliminated by treating the impure Pu oxide by: (1) washing out the soluble impurities, and (2) calcining in air at 850 $^\circ\text{C}$ and higher temperatures to remove water and organics and to burn off residual char and graphite.

Processing of Impure Pu Oxide

Results of 44 of the first 46 Oxide Washer runs are summarized in Table 1. Net weight is the total weight of the material in each stage of the process. Pu weight is usually the weight determined by calorimetric and gamma counting measurements. Net weight and Pu weight are estimated at times because several samples were combined at the time of measurement. Estimated values are also given at times when no direct measurement was available. Washer recovery refers to the material removed from the washer after washing had been completed and the material had been calcined at 850 °C. Filtration recovery refers to the particulate materials filtered out of the wash water and then calcined at 850 °C with burnoff of the filter paper. The total recovery is the sum of the washer recovery and the filtration recovery. The net weight of the solubles removed is taken as the difference in net weight between the starting material and the total recovery. The Pu weight in the solubles removed is either measured, estimated, or taken as the difference between the starting material and the total recovery. Table 1 also lists the calculated wt % Pu in the starting material and in the total recovery material, and gives average values for all of the entries in the 44 runs.

Wash Water Requirement:

The amount of wash water used was not documented for every run. For the runs that had documentation, the amounts of wash water used were: 4.2 liters in W-1, 8.4 liters in W-2, 6.9 liters in W-3, 8 liters in W-4, ~5 liters in W-5, 8 liters in W-11, 4 liters in W-12, ~4 liters in W-13, and 6 liters in W-14. These amounts of water are roughly proportional to the net weights of solubles removed (see Table 1), and on the average 1 liter of water will remove 55 g of solubles.

Oxide Washer Recovery of Material:

The amount of material recovered in the Oxide Washer (see Washer Recovery column in Table 1) is determined as the material collected in the convenience can in the Dustless Transfer Unit. However, the material collected in the convenience can may not be a quantitative measure of the material produced in the Oxide Washer since residual material may remain from run to run in the Oxide Washer and in the components of the dustless transfer unit. This holdup of material was especially apparent in run W-6, when an estimated 54 g of material was held up on the metal frit filter of the dustless transfer unit because the oxide powder in the Oxide Washer was not fully dry when it was vacuumed out. The material held up on the filter in run W-6 later dried out in situ and was recovered from the filter and transferred into the convenience can for run W-7. An estimated correction has been made for the transfer of this material from run W-6 to run W-7.

Based on the average values in Table 1, the material recovered in the oxide washer shows a net material weight of 789 g, of which 417 g are Pu. The

Table 1. Recovery of impure Pu oxide materials after Oxide Washer treatments. Estimated values are in parentheses.

Batch #	Starting Material, Before Washing			Washer Recovery, After Calcination		Filtration Recovery, After Calcination		Total Recovery, After Calcination			Solubles Removed, By Wt. Difference	
	Net wt. (g)	Pu wt. (g)	Wt.% Pu	Net wt. (g)	Pu wt. (g)	Net wt. (g)	Pu wt. (g)	Net wt. (g)	Pu wt. (g)	Wt.% Pu	Net wt. (g)	% of orig. wt.
W-1	1212	764	63.0	926	716	(93)	(24)	(1019)	(740)	72.6	(193)	15.9
W-2	1414	721	51.0	898	674	(86)	(22)	(984)	(696)	70.7	(430)	30.4
W-3	1379	708	51.3	972	692	(27)	(8)	(999)	(700)	70.1	(380)	27.6
W-4	1533	735	47.9	1056	702	(18)	8	(1074)	710	66.1	(459)	29.9
W-5	1104	661	59.9	762	588	108	58	870	646	74.3	234	21.2
W-6	1279	647	50.6	(872)	(573)	(117)	63	(989)	(636)	64.3	(290)	22.7
W-7	1264	660	52.2	(903)	(632)	50	17	(953)	(649)	68.1	(311)	24.6
W-8	1269	525	41.4	933	500	47	18	980	518	52.9	289	22.8
W-9	1370	259	18.9	361	236	98	26	459	262	57.3	911	66.5
W-10	1316	308	23.4	797	291	67	17	864	308	35.6	452	34.3
W-11	1188	437	36.8	552	389	(88)	47	(640)	436	68.1	(548)	46.1
W-12	1397	637	45.6	993	597	65	37	1058	634	59.9	339	24.3
W-13	1013	468	46.2	776	457	32	10	808	467	57.8	205	20.2
W-14	1232	545	44.2	824	518	32	23	856	541	63.2	376	30.5
W-15	1300	509	39.2	989	496	(5)	2	(994)	498	50.1	(306)	23.5
W-16	1698	617	36.3	1112	598	(50)	15	(1162)	613	52.8	536	31.6
W-17	889	324	36.4	716	322	17	3	733	325	44.3	156	17.5
W-18	856	354	41.4	577	332	98	17	675	349	51.7	181	21.1

Table 1. (Continued)

Batch #	Starting Material, Before Washing			Washer Recovery, After Calcination		Filtration Recovery, After Calcination		Total Recovery, After Calcination			Solubles Removed, By Wt. Difference	
	Net wt. (g)	Pu wt. (g)	Wt.% Pu	Net wt. (g)	Pu wt. (g)	Net wt. (g)	Pu wt. (g)	Net wt. (g)	Pu wt. (g)	Wt.% Pu	Net wt. (g)	% of orig. wt.
W-19	958	385	40.2	633	366	20	5	653	371	56.8	305	31.8
W-20	1051	395	37.6	726	374	21	9	747	383	51.3	304	28.9
W-21	1046	344	32.9	576	311	79	29	655	340	51.9	391	37.4
W-22	970	285	29.4	407	225	118	65	525	290	55.2	445	45.9
W-23	1065	310	29.1	854	315	15	2	869	317	35.4	196	18.4
W-24	836	243	29.1	607	237	32	7	639	244	38.2	197	23.6
W-25	1057	305	28.9	744	302	19	8	763	310	40.6	294	27.8
W-26	1120	460	41.1	789	450	34	7	823	457	55.5	297	26.5
W-27	1171	328	28.0	732	327	26	3	758	330	43.5	413	35.3
W-28	1009	305	30.2	769	296	26	8	795	304	38.2	214	21.2
W-29	1223	343	28.0	744	326	43	5	787	331	42.1	436	35.7
W-30	1366	372	27.2	872	350	60	24	932	374	40.1	434	31.8
W-31	1363	246	18.0	1017	238	20	5	1037	243	23.4	326	23.9
W-32	1245	317	25.5	843	310	40	5	883	315	35.7	362	29.1
W-33	1063	265	24.9	526	258	15	6	541	264	48.8	522	49.1
W-34	1074	235	21.9	671	228	(25)	(6)	(696)	(234)	33.6	(378)	35.2
W-36	1213	242	20.0	724	236	24	5	748	241	32.2	465	38.3

Table 1. (Continued)

Batch #	Starting Material, Before Washing			Washer Recovery, After Calcination		Filtration Recovery, After Calcination		Total Recovery, After Calcination			Solubles Removed, By Wt. Difference	
	Net wt. (g)	Pu wt. (g)	Wt.% Pu	Net wt. (g)	Pu wt. (g)	Net wt. (g)	Pu wt. (g)	Net wt. (g)	Pu wt. (g)	Wt.% Pu	Net wt. (g)	% of orig. wt.
W-37	1505	247	16.4	1312	242	(25)	(4)	(1337)	246	18.4	(268)	17.8
W-38	1232	545	44.2	824	518	92	23	916	541	59.1	316	25.6
W-40	1051	395	37.6	726	381	21	9	747	390	52.2	304	28.9
W-41	1698	617	36.3	1112	598	(170)	(15)	(1282)	(613)	47.8	(416)	24.5
W-42	1046	344	32.9	576	311	79	29	655	340	51.9	391	37.4
W-43	1013	468	46.2	776	457	(50)	(10)	(826)	(467)	56.5	(187)	18.5
W-44	958	385	40.2	633	366	20	5	653	371	56.8	305	31.8
W-45	1188	437	36.8	552	393	91	47	643	440	68.4	545	45.9
W-46	1517	631	41.6	970	602	(25)	(10)	(995)	(612)	61.5	(522)	34.4

filtration recovery adds an additional 52 grams of material recovered and contains 17 grams of Pu. Total recovery is therefore 841 grams of material that contains 434 grams of Pu. The wt. % Pu increases from 36.6 % in the original material to 51.6 % in the recovered material. The average loss of material as solubles by the average weight differences is 360 grams, which represents 30.0 % of the original weight. represents 93.2 % of the total recovery of 895 g. The average amount of Pu remaining in the wash water is estimated by difference to be $439 - 434 = 5$ grams.

Discussion:

The Oxide Washer does not give a clean separation of the wash water from the particulates in the bed. When the wash water is removed from the Oxide Washer, it carries particulates with it in slurry form. With the typical use of eight washes for a given batch, about 6 % of the batch material is carried over as slurry material in the wash water (see Table 1). Manual work is therefore still required to filter the slurry. However, there is a major savings in the manpower effort required to process a batch of material when using the oxide washer as compared with an all manual operation. This is because the Pu mass limit for working with Pu in a wet chemistry glovebox is much lower than for the Pu mass allowed in the oxide washer contained in a separate glovebox. We estimate that the overall level of effort required for the oxide washer plus auxiliary filtration reduces the level of effort by about a factor of 3 as compared to an all manual operation.

The limit of $<450 \mu\text{S}/\text{cm}$ for the conductivity of the final wash leaves only about 0.1 g of solubles in the impure Pu oxide. If this limit is raised to $<1999 \mu\text{S}/\text{cm}$, or just on scale for the conductivity meter, then the amount of solubles left in the impure Pu oxide will be on the order of 0.5 g, which is still a very low amount. Raising the conductivity limit will serve two purposes. It will reduce the level of effort required for processing, and will also reduce the volume of waste generated by reducing the amount of wash water that needs to be grouted. For future operations, we plan to use the higher conductivity limit of "on-scale" on the conductivity meter ($<1999 \mu\text{S}/\text{cm}$) as the cutoff point for Oxide Washer processing.

References

1. "DOE Standard - Stabilization, Packaging and Storage of Plutonium-Bearing Materials," U. S. Department of Energy Report, DOE-STD-3013-2000, U. S. Department of Energy, Washington, D. C. 20585, Sept. 2000.
2. International Critical Tables of Numerical Data - Physics, Chemistry and Technology, Vol. VI, editor-in-chief Edward W. Washburn, McGraw-Hill Book Company, Inc., New York, 1929.

3. R. A. Van Konynenburg, D. H. Wood, R. H. Condit, and S. D. Shikany, "Bulging of Cans Containing Plutonium Residues--Summary Report," Lawrence Livermore National Laboratory Report, UCRL-ID-125115, March 1996.