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Key Words

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INTER-OFFICE MEMORANDUM

SAVANNAH RIVER PLANT

DPSPU-86-272-60

April 25, 1986

TO: D. W. MURDOCH, 221-F

FROM: H. P. HOLCOMB, 772-F *HPH*DISSOLUTION & ANALYSIS OF HANFORD PLUTONIUM OXIDE SHIPMENT HRA-37INTRODUCTION AND SUMMARY

The Separations Technology Laboratory was requested to chemically examine samples of lot numbers 27, 28, and 29 from Hanford plutonium oxide shipment HRA-37. The oxide, 12% Pu²⁴⁰, was a product of oxalate conversion and was purportedly rather pure material based on emission spectrographic analyses accompanying it. Filtration difficulties produced by rather copious sludging had slowed processing of this oxide in Cabinets 6-8, Special Recovery, F B-Line.

Varying levels of impurities were found from SRP emission spectrographic analysis of the oxide lots. For example, lot #27 had 25 ppm iron impurity; lots #28 and #29, >500 ppm. Lot #27 had <10 ppm Sn; lots #28 and #29, 100 ppm. Analyses for Al, Cr, Ni, & Cu show similar differences between oxide lots.

Dissolution tests were made on samples of the oxide, as received, as well as on a sample of the process sludge taken during dissolution of lot #27. None of the oxide samples nor the sludge completely dissolved upon treatment with 14M HNO₃ - 0.15M HF at elevated temperature for an extended period of time. Analysis of the residual material by scanning electron microscopy/X-ray fluorescence (SEM/XRF) showed that Si, Ti, Fe, and Pu were components of the undissolved material from lot #27. For lots #28 and #29, the residue consisted of Si, Pu, Sn, Ti, Fe, Ca, Zr, and Al.

The total plutonium content of the oxide material was found to vary between lots. All three lots, according to Hanford data, should analyze 87.5-87.6 weight percent plutonium versus a theoretical 88.2%, if the oxide were pure PuO₂. Analysis of our test dissolver solutions yielded 86.7, 70.2, and 85.7 wt%, respectively, for lots #27, #28, and #29. The sample with the lowest Pu yield on dissolution also produced the greatest quantity of residual

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solids. The different plutonium yields are theorized to be caused by undissolved solids resulting from the presence of small quantities of higher-fired oxide. Lot inhomogeneity or nonrepresentative samples could also be factors.

The sludges encountered during oxide processing in Cabinets 6-8 result from the relatively intractable oxides, especially SiO_2 , of these impurities or of plutonium itself. Via SEM/XRF analysis, plutonium was confirmed to be a component of the residues from the dissolution tests on the process sludge and the oxide samples.

The use of a Dynel[®] cloth prefilter has provided relief from the sludge-caused pluggage of process filter frits. However, since plutonium is a sludge component, approximately 0.8 g Pu per mL sludge, proper loss controls and nuclear safety procedures should be in place as part of prefilter handling and disposal.

EXPERIMENTAL

Initial Test of Lot #27 Oxide and Process Sludge

Samples of the oxide from lot #27 and of the process sludge were furnished the Separations Technology Laboratory. Our testing philosophy for these initial samples was to determine their behavior under processing conditions, but to extend the heating period from the nominally used 2 hours to 4 hours. We employed 14M HNO_3 - 0.15M HF as the dissolvent.

For the oxide, 4.011 g was used in 20 mL of mixed acid, approximately the same ratio used in Cabinets 6-8 processing. These were placed in a 30-mL graduated centrifuge cone. Similarly, one mL of the sludge was placed in a cone together with 20 mL of mixed acid. Both containers were heated in a boiling water bath for a 4-hour period. Following the dissolution cycle, the containers and contents were cooled and centrifuged. Approximately 0.4 mL of gray-tan solids persisted in the cone originally bearing the oxide. For the sludge, the white solids remaining had a volume of 2 mL, double that of the original sludge sample! A sample of only the dissolution solution of the sludge was taken for total plutonium analysis by diode array spectrometry by W. L. Frazier of Laboratories. Analysis of dissolver solutions of oxides from all three lots was done in later tests incorporating a dissolution period (2 hrs.) similar to the one used in Cabinets 6-8 processing. The residues were thoroughly washed with 1M HNO_3 and dried on the surface of the hot plate. Each residue was primarily contained in a polystyrene vial. These residual solids were forwarded to D. F. Steedly of ADD, SRL, for SEM/XRF analysis. A sample of the original oxide, as received, was forwarded to J. T. Coleman of Laboratories for emission spectrographic analysis.

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Dissolution Tests of Oxide from Lots #27, #28, and #29

Another sample of lot #27 oxide together with samples from the next two lots were obtained. On comparing the 3 samples of oxide, that from lot #27 was a shade darker than those from #28 and #29. Dissolution tests of these were made as described above, except that the heating cycle in the mixed acid was the same, 2 hours, as that used in full-scale processing. Small quantities of tannish-gray solids persisted: 0.05 mL for #27, 0.1 mL for #28, and about 0.03 mL for #29. Figure 1 in the Appendix is a Polaroid photo showing these residues following washing and centrifugation. Analyses, similar to those run during the initial investigation described above, were performed on the as-received oxides, on the dissolution solutions, and on the residues.

Determination of Silicon Blank

The test dissolutions were carried out in Kimax® glassware with a PVC-lined screw cap. Because of the potential for HF to react with the glassware, two of the cones used for the test dissolutions were subjected to a 4-hour dissolution cycle with conditions the same as those used for the tests except no solids were included. After this test, no solids were observed, nor were the interiors of the centrifuge cones noted to have been etched. The mixed acid was submitted for silicon analysis by direct current argon plasma spectrometry (DCAP) by H. M. Forrest of Laboratories. Analysis of each solution showed a total of 10 mg soluble silicon (500 ppm) in each 20-mL mixed acid aliquot. Some silica was rendered soluble by the mixed acid attack, but no residual solids were produced. The residues being formed from the test dissolutions were therefore considered an intrinsic part of the initial oxide sample rather than originating from dissolution of the glass container.

RESULTS AND DISCUSSION

Table 1 lists the analytical results from emission spectrographic analysis of the oxide samples, as received.

TABLE 1

EMISSION SPECTROGRAPHIC ANALYSIS OF HRA-37 Pu OXIDES

Element	DPM			
	Initial #27	#27	#28	#29
Al	7	13	>200	>200
Cr	10	<10	100	75
Ca	50	25	25	15
Ni	<10	<10	200	100
Mg	<10	<10	25	25
Fe	200	25	>500	>500
Si	10	<5	15	15
Cd	<10	<10	<10	<10
B	<1	<1	10	5
Ti	<Faint Trace	-	-	-
Ga	<10	<10	20	20
Zn	<50	50	50	50
Cu	2	5	50	50
Sn	<10	<10	100	100
Be	<0.5	<0.5	<0.5	<0.5
Pb	<10	<10	10	10
Mn	5	5	10	10

The impurity levels in the three oxide lots are not compositionally consistent. Also, there is some disagreement between the two samples of lot #27, particularly for the iron impurity. The relatively high tin levels in lots #28 and #29 are manifested later in the residues from their dissolution tests. These latter two lots have much higher levels of contamination by aluminum and by stainless steel corrosion products: Fe, Cr, and Ni. Iron, chromium, and aluminum, whose oxides are rather intractable in nitric acid, were all components of the dissolution residues as well.

Analysis of Dissolution Solutions for Total Plutonium

Aliquots of the dissolver solution (two-hour) for each lot were analyzed for total plutonium content by diode array spectrometry. Table 2 shows the data involved in determining total Pu content.

TABLE 2DETERMINATION OF Pu CONTENT OF OXIDES AND PROCESS SLUDGE

	Process Sludge	#27 Oxide	#28 Oxide	#29 Oxide
mg Pu/mL Diss. Sol. by Diode Array Spec.	40	166.4	134.8	155.0
Vol. Diss. Sol., mL	20.0	21.0	21.0	14.0
g Total Pu in Diss. Sol.	0.8	3.49	2.83	2.17
wt. sample, g	(1 mL)	4.032	4.031	2.532
wt% Pu	(0.8 g/mL)	86.7	70.2	85.7
wt% Pu-Hanford data	-	87.6	87.5	87.5
(mL residue	2	0.06	0.1	0.09)

These data show that the samples of the oxide lots were not consistent in the quantity of process-soluble plutonium oxide. The lot yielding the smallest quantity of soluble plutonium also yielded the largest volume of residual solids. There are two major factors to consider: 1) homogeneity of the material within a lot so that replicate grab samples would be representative of the whole, 2) presence of undissolved, Pu-containing solids that would diminish the yield. Possibly undetected "hot spots" are forming during oxalate calcination and are producing small quantities of higher-fired and, therefore, less tractable oxide.

Due to lack of sample, less of lot #29 oxide was treated. However, the volume of dissolvent was reduced accordingly. For lot #29, less undissolved material resulted, but the residue/sample volume ratio was the same as that for lot #27. The ratio for lot #28 was twice that of #27 & #29. A corroborating effect for lot #28 is the appearance of less plutonium in its dissolver solution.

SEM/XRF Analysis of Residues

The washed and dried residues from the four oxide samples and from the process sludge following their dissolution treatment were forwarded to D. F. Steedly of ADD, SRL, for SEM/XRF analysis. SEM photos and XRF scans of these are contained in Figures 2-6 in the Appendix. Table 3 summarizes the qualitative analysis

of these residues with the component elements listed in approximately decreasing order of peak height.

TABLE 3

XRF QUALITATIVE ANALYSIS OF DISSOLUTION RESIDUES

<u>Initial Sludge</u>	<u>Initial Lot #27</u>	<u>Lot #27</u>	<u>Lot #28</u>	<u>Lot #29</u>
Si	Si	Si	Si	Si
Ti	Pu	Ti	Pu	Pu
Fe	Fe	Fe	Sn	Sn
Pu	Ti	Pu	Ti	Ti
	Al		Zr	Fe
	Zn		Fe	Ca
			Al	Al

The residues consist primarily of elements whose oxides are, or can be, rather intractable under the dissolution conditions employed.

The residue from lot #27 (initial sample) following the four-hour mixed acid contact is structurally different from the others and appears to be mainly silica with only relatively small quantities of other elements. I suggest that the reason for this is the longer contact time in the mixed acid has, to some extent, dehydrated the soluble silicon ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$ or $\text{H}_2\text{SiF}_6 \cdot x\text{H}_2\text{O}$), thereby reducing its solubility and precipitating it from solution. Less dehydration would be produced by the shorter contact time which would yield less insoluble silica. Silica dehydration can be quantitatively effected by heating in concentrated mineral acids such as perchloric, sulfuric, or hydrochloric.¹ Nitric acid (or $\text{HNO}_3\text{-HF}$) is just not as efficient.

The residue from the process sludge dissolution contained intractable oxides of primarily Si and Pu. In the SEM photo, they appeared to be less hydrated (i. e., less "fluffy") than the solids from initial lot #27 oxide dissolution. The appearance of traces of chloride in the XRF scans is due to attack of the PVC cap liner by the mixed acids.

The residue particles obtained from the two-hour dissolution period for lots #27, #28, and #29 appear to be structurally similar. They consist of rather anhydrous oxides of the less tractable elements. Note the appearance of tin in dissolution solids from

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lots #28 and #29. Tin's occurrence in the residues parallels its presence in the as-received oxide, reported in Table 1 as found by emission spectrographic analysis.

CONCLUSIONS

The three lots of shipment HRA-37 of Hanford plutonium oxide were not compositionally consistent as determined by dissolution behavior and component analysis. The kinds and amounts of impurities in the oxide vary.

A small part of the plutonium oxide remains intractable to SRP dissolution conditions. I suspect that this material has been exposed to calcination temperatures ("hot-spots") higher than those nominally used for conversion at Hanford.

Silicon (or SiO_2), as a Pu oxide impurity, is the prime source of the filtration problems that cause throughput hindrance. Our study indicates that too long a heating period during dissolution could even promote formation of jelly-like $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ via dehydration of soluble silicon. Such compounds exacerbate filtration difficulties. Therefore, even shorter dissolution periods should be considered.

In conversation² with Rocky Flats Plant staff concerning aqueous solution processing of highly-impure plutonium oxide, I was told that they became resigned to filtering to remove insolubles and to changing filters often due to pluggage. We may have to assume a similar processing philosophy even for relatively pure Hanford oxide. The use of Dynel® prefilters and changing them as necessary has appeared to alleviate part of the pluggage problem in Cabinets 6-8, thereby improving processing. However, our test with process sludge found a relatively high content of accompanying plutonium. Its recovery as well as nuclear safety concerns for the use of these prefilters should have already been addressed.

ACKNOWLEDGMENTS

The analytical assistance from D. F. Steedly of ADD, SRL, in providing the SEM/XRF analyses is appreciated.

I also wish to recognize and thank H. M. Forrest, J. T. Coleman, and W. L. Frazier, all of 772-F Laboratories, for their help in obtaining the data that is included in this report.

N. W. McGabee, my technical analyst, did his usual fine job in running the glove box dissolution tests. His perceptive attention to job conditions and to contamination control permitted this work to be done safely and without release of radioactivity.

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FIGURE 1

WASHED RESIDUES FROM LOTS #27, #28, & #29 (l. to r.)

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900X
#83806

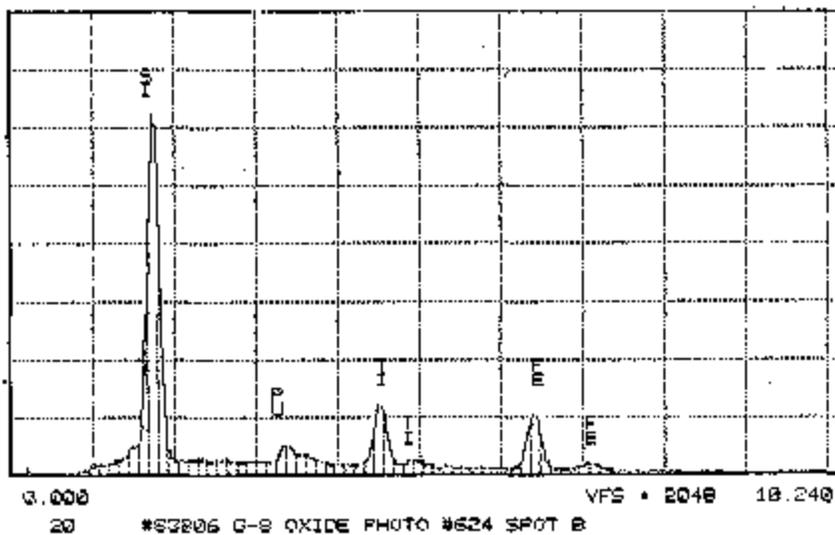
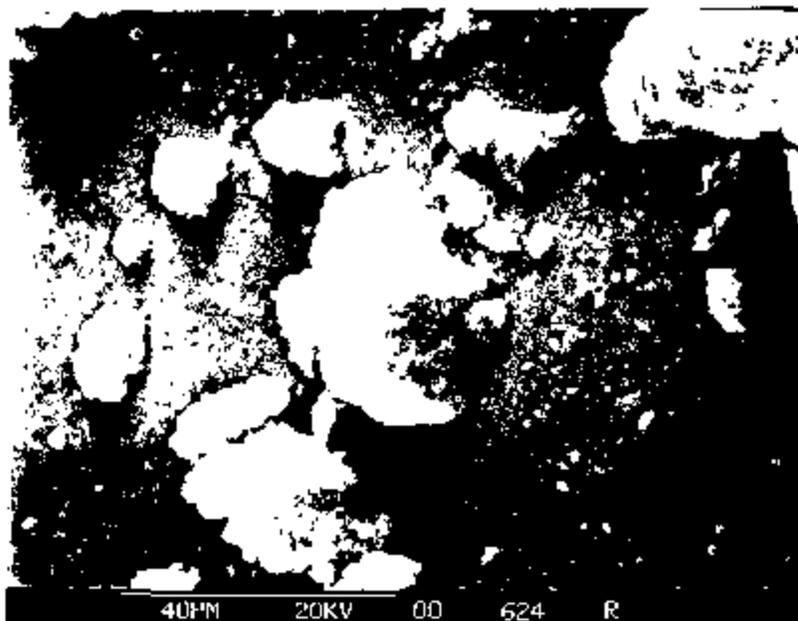
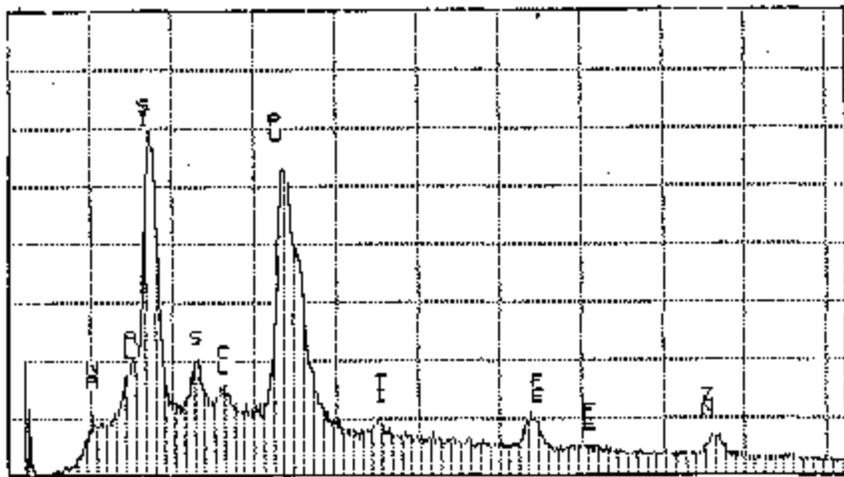
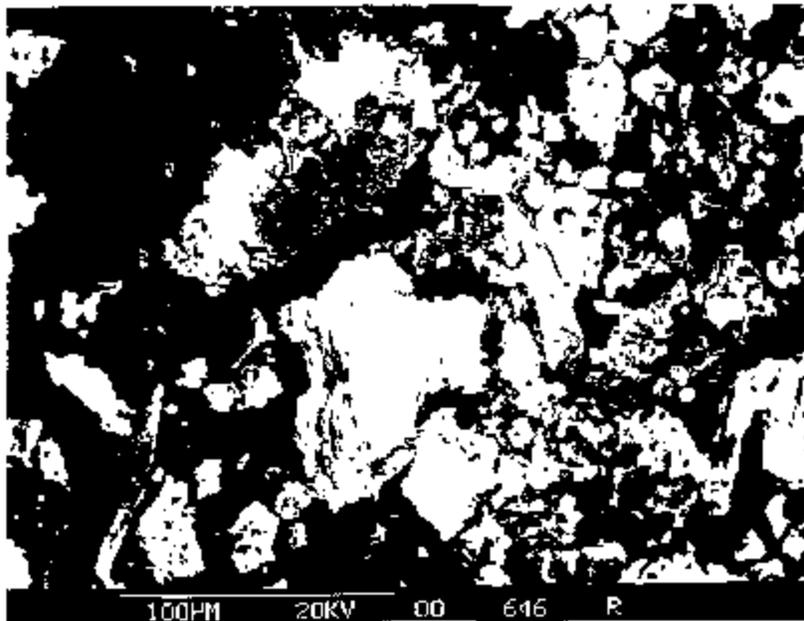


FIGURE 2
PHOTOMICROGRAPH & XRF SCAN OF LOT #27 OXIDE (Initial)
RESIDUE

345X

#83807

BSE



0.000 20 #83807 G-B CRLO-PHOTO #646 VFS = 1024 10.240

FIGURE 3

PHOTOMICROGRAPH & XRF SCAN OF PROCESS SLUDGE RESIDUE

500X

#85639

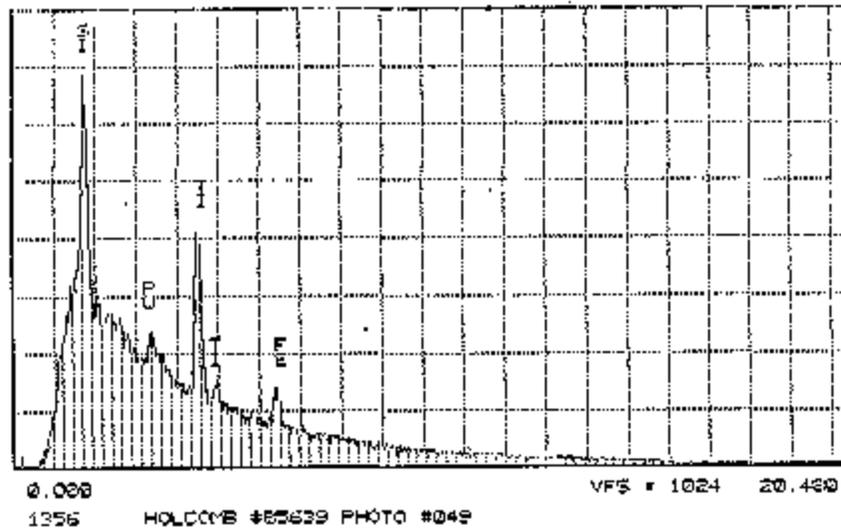
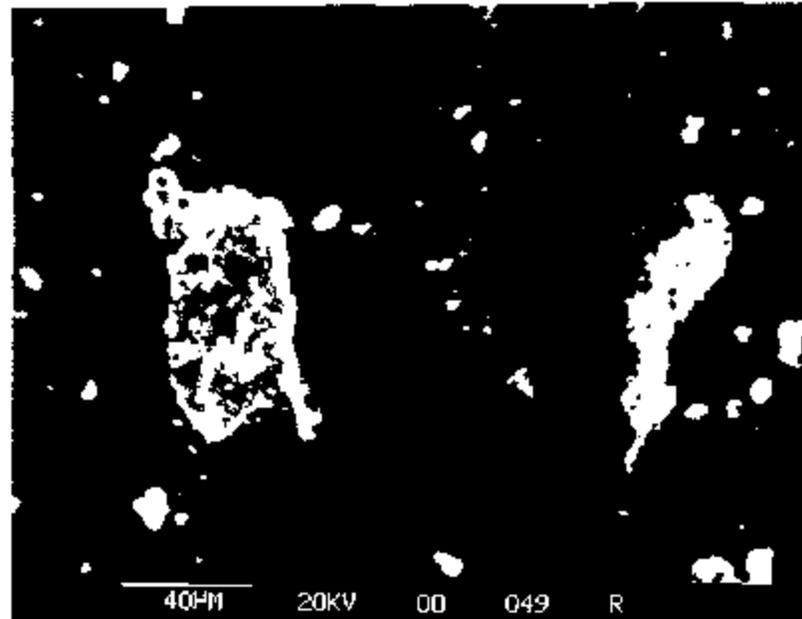


FIGURE 4
PHOTOMICROGRAPH & XRF SCAN OF LOT #27 OXIDE RESIDUE

300X

#85640

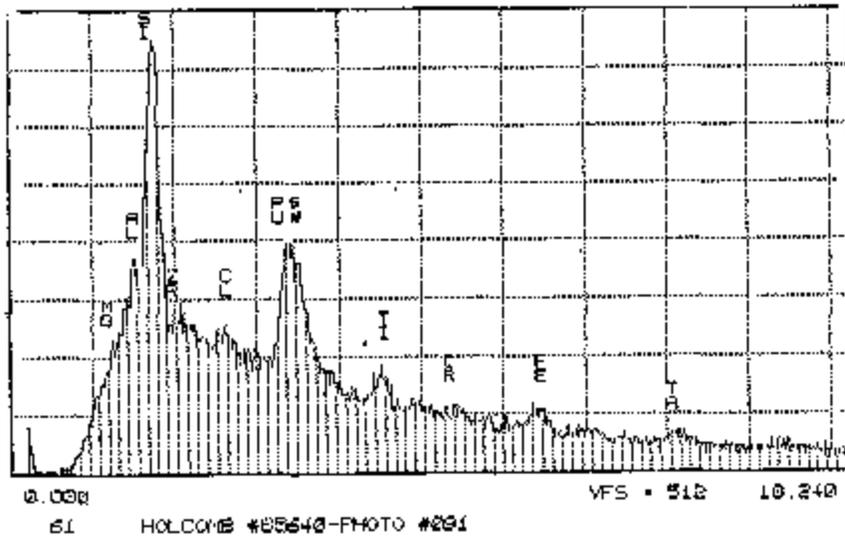
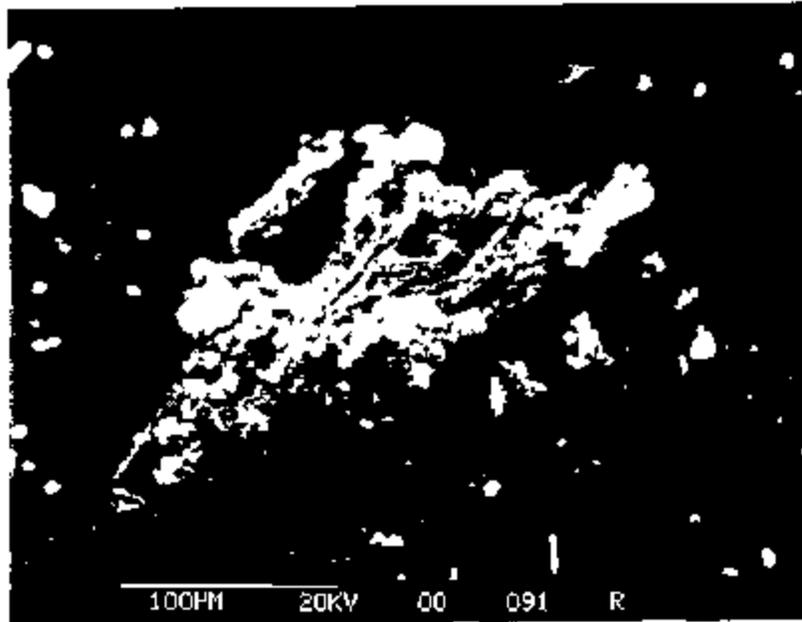


FIGURE 5

PHOTOMICROGRAPH & XRF SCAN OF LOT #28 OXIDE RESIDUE

250X

85641

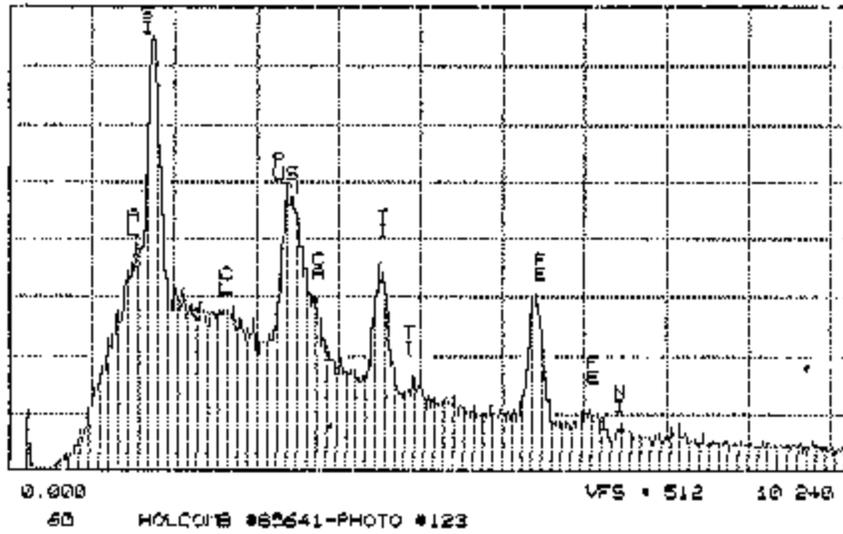
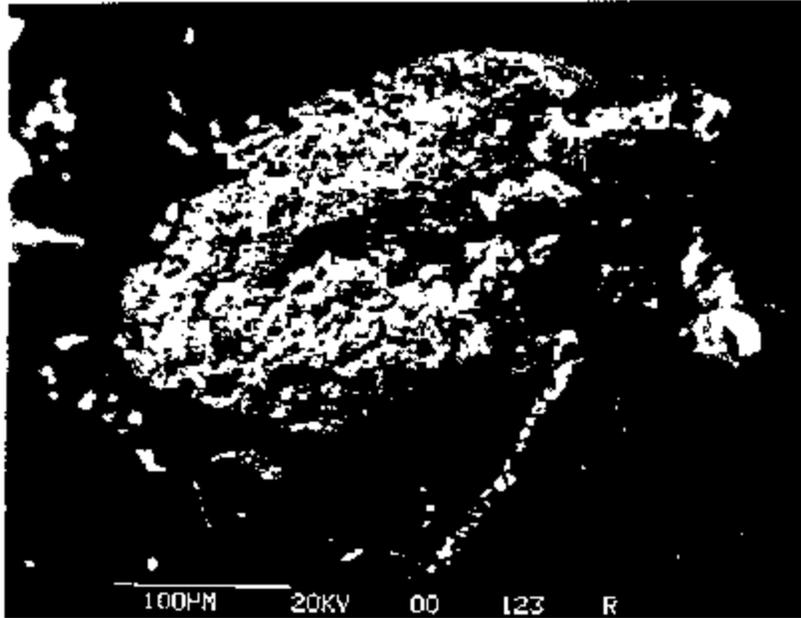


FIGURE 6

PHOTOMICROGRAPH & XRF SCAN OF LOT #29 OXIDE RESIDUE

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DISSOLUTION & ANALYSIS OF HANFORD PLUTONIUM OXIDE SHIPMENT HRA-37

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