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PRELIMINARY MOLTEN SALT EXTRACTION EXPERIMENTS
WITH DICESIUM HEXACHLOROPLUTONATE (Cs_2PuCl_6)

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U. S. DEPARTMENT OF ENERGY
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SUBJECT DESCRIPTORS

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J. L. Long, T. J. Humiston, and A. M. Murray

ABSTRACT

Dicesium hexachloroplutonate was prepared on a 200-gram scale and used as an oxidant in the molten salt extraction process to remove americium from plutonium metal. Single-pass extraction efficiencies exceeding 90% were achieved in molten calcium chloride.

INTRODUCTION

Problems in the foundry with magnesium contamination of molten salt extraction (MSE) products provided the motivation for considering oxidant salts other than magnesium chloride (MgCl_2). Among the possibilities were plutonium chloride (PuCl_3) and any metal chlorides less stable than americium chloride (AmCl_3). In a non-equilibrium environment, metal halides somewhat more stable than PuCl_3 react with americium metal; but the degree of americium extraction may be limited, and undesirable side reactions may occur. Dicesium hexachloroplutonate (Cs_2PuCl_6) was examined as an alternative to PuCl_3 because it is not hygroscopic and can be prepared by aqueous chemistry.¹ In contrast, PuCl_3 is somewhat hygroscopic and is prepared using highly toxic and corrosive gases.

The chemical reactions expected to occur during MSE utilizing Cs_2PuCl_6 are:

The free energy relationships are such that the conversion of quadrivalent plutonium (in Cs_2PuCl_6) to trivalent plutonium may be assumed

complete for most purposes. In essence, the same species oxidizes americium, whether PuCl_3 or Cs_2PuCl_6 is used. Therefore, it is reasonable to assign variations in extraction efficiencies to differences imparted to the diluent salt by the CsCl added, if the same diluent salt concentrations and the same final oxidant concentration are present.

It has been suggested that americium is oxidized from metal into the salt phase as divalent americium chloride in contrast with the trivalent americium chloride shown in Equations 2 and 3.^{2,3} This produces the following chemical reactions:

This changes the equilibrium constants for Equations 2 and 3. However, the same plutonium species oxidizes the americium.

Because no extractions had been performed on a small scale, experiments using the current MgCl_2 oxidant were done to obtain a baseline for comparison to extractions with Cs_2PuCl_6 . This permitted screening of the Cs_2PuCl_6 MSE parameters with less investment of time and materials than the large scale. Information obtained from the small-scale work was used to design the large-scale experiments. The behavior of Cs_2PuCl_6 upon heating was needed to determine whether undesirable decomposition products would be formed.

Some means of residue treatment were needed to provide a complete process.

EXPERIMENTAL

Small-scale experiments described in this report were performed in stationary furnaces with inner

Inconel wells 3-1/16-inch diameter The heat was provided through resistance coils insulated with alumino-silicate fibrous material The cell head, bearing housing, and furnace were used in the past for direct oxide reduction (DOR) ⁴ The large-scale furnaces are the same as those used in production with 5-3/4-inch id Inconel wells

The quantities of salt, metal, and oxidant shown in Tables 1 and 2 were placed in the tantalum or

magnesia (MgO) crucibles The metal was loaded first, followed by the salt and oxidant The charge was inserted into the furnace, and the furnace chamber was evacuated and backfilled with argon three times Contents of the furnace were heated to reaction temperature The stirrer was lowered to within 1/4 inch of the crucible bottom for small scale (one inch for large scale) Then stirring was initiated After stirring, the melt was held at temperature 15 minutes before cooling

TABLE 1 Small-Scale Molten Salt Extraction Screening Experiments

MSE Run	Feed		Product		Salt Product		Extraction*	Kd	Feed Salt/Metal Ratio**		Crucible Material
	(g)	Am (ppm)	(g)	Am (ppm)	(g)	Am (ppm)					
1	603	3330	570	890	114	13164	0.747	14.79	0.14	48 g NaCl KCl + 38 g MgCl ₂	Ta
2	611	3460	584	660	108	16006	0.818	24.25	0.14	48 g NaCl KCl + 38 g MgCl ₂	Ta
3	600	3390	586	770	127	12463	0.778	16.19	0.20	60 g NaCl KCl + 60 g Cs ₂ PuCl ₆	Ta
4	599	3406	582	1167	101	13478	0.667	11.55	0.15	30 g NaCl KCl + 60 g Cs ₂ PuCl ₆	Ta
5	599	3360	576	267	150	12392	0.924	46.41	0.20	60 g CaCl ₂ + 60 g Cs ₂ PuCl ₆	Ta
6	600	3430	576	853	120	13056	0.761	15.31	0.15	30 g CaCl ₂ + 60 g Cs ₂ PuCl ₆	MgO
7	601	3290	517	870	131	11660	0.773	13.40	0.10	60 g Cs ₂ PuCl ₆	Ta
8	601	3505	570	869	105	15345	0.765	17.66	0.17	60 g CaCl ₂ + 15 g MgCl ₂ + 25 g Cs ₂ PuCl ₆	MgO
9	600	3565	555	183	120	16981	0.953	93.05	0.23	50 g CaCl ₂ + 60 g Cs ₂ PuCl ₆ + 25 g MgCl ₂	MgO
10	601	3445	561	275	153	12548	0.925	45.63	0.20	60 g CaCl ₂ + 60 g Cs ₂ PuCl ₆	MgO
11	601	3480	574	396	115	16195	0.891	40.90	0.15	30 g CaCl ₂ + 60 g Cs ₂ PuCl ₆	MgO
Average		3424	568	654	122	13935					

$$* \text{Extraction (\%)} = \frac{\text{ppm Am in feed} - \text{ppm Am in product}}{\text{ppm Am in feed}}$$

$$** \text{Salt to metal ratio S/M} = \text{weight of salt/weight of metal}$$

TABLE 2 Large Scale Molten Salt Extraction Experiments With Cs₂PuCl₆

MSE Run	Feed		Product		Salt Product		Extraction*	Kd	Feed Salt/Metal Ratio**		Pu Invested (g)***	Crucible Material
	(g)	Am (ppm)	(g)	Am (ppm)	(g)	Am (ppm)						
1	1838	2440	1786	156	340	12371	0.938	79.30	0.17	179 g CaCl ₂ + 132 g Cs ₂ PuCl ₆	96	Ta
2	1850	3244	1752	215	369	15243	0.937	70.90	0.17	179 g CaCl ₂ + 133 g Cs ₂ PuCl ₆	142	Ta
3	1830	3214	1780	220	357	15378	0.933	69.90	0.17	175 g CaCl ₂ + 133 g Cs ₂ PuCl ₆	94	Ta
4	1827	3175	1769	432	352	14308	0.868	33.12	0.17	247 g CaCl ₂ + 67 g Cs ₂ PuCl ₆	80	Ta
Average		3018	1772	256	355	14325					103	

$$* \text{Extraction (\%)} = \frac{\text{ppm Am in feed} - \text{ppm Am in product}}{\text{ppm Am in feed}}$$

$$** \text{Salt to metal ratio S/M} = \text{weight of salt/weight of metal}$$

$$*** \text{Pu invested} = \text{grams Pu in feed} - \text{grams Pu in product} + \text{grams Pu in Cs}_2\text{PuCl}_6$$

Small-scale experiments included the use of a new stirrer design (Figure 1) and stirring time of 30 minutes. Stirring speed was 250 rpm. Temperature was maintained between 720 and 760 °C in the melt. Both tantalum and magnesium oxide crucibles were used.

DOR stirrers (Figure 2) were used for the large-scale experiments. The blades were positioned to mix both the metal and salt. The stirrer was operated at 200 rpm for 90 minutes in these full-scale

experiments, and tantalum round-bottom crucibles were used. The melt temperature was held at approximately 850 °C and was monitored with an immersed thermocouple.

The residue salts generated from large-scale extraction during Experiments 1 and 2 were combined and scrubbed with aluminum and magnesium. The same salt scrub procedure used for production was applied to this run. The aluminum and magnesium weights used in the experiment were calculated as follows:

Weight of magnesium = $0.23 \times$ total actinide weight in the salt

Weight of aluminum = $1.89 \times$ total actinide weight in the salt

The aluminum and magnesium were loaded into a flat, step-bottom MgO crucible. The salt was then added onto the metals. A 1-1/2 by 2-inch flat-paddle tantalum stirrer was used to mix the contents at 250 rpm in one direction for two hours. Inside temperature was maintained at 850 °C during stirring and that temperature was maintained one hour after stirring before cooling the contents.

RESULTS AND DISCUSSION

The results of the small-scale experiments are presented in Table 1. The Cs_2PuCl_6 was prepared as described in Appendix A. All reagents used

FIGURE 1 Stirrer for Small-Scale Experiments

FIGURE 2 Stirrer for Large Scale Experiments

in the preparation of Cs_2PuCl_6 are available in production quantities at a cost comparable with other commonly used reagents. Single extractions of approximately 93% are needed to obtain product containing less than the foundry specification of 200 ppm americium. The exact percentage depends upon the concentration of americium in the feed metal from retired weapon parts (site returns).

Four experiments in Table 1 (Nos. 5, 9, 10, and 11) yielded the greatest extraction efficiencies. Evidently, extraction was enhanced by replacing NaCl-KCl with CaCl_2 . Experiments 10 and 11 were repeats of Experiments 5 and 6, respectively; however, Experiments 6, 10, and 11 were performed in MgO while Experiment 5 was performed in tantalum. Results of Experiments 5 and 10 were nearly identical. In contrast, Experiment 11 attained a higher extraction efficiency than Experiment 6. The MgO crucible failed during Experiment 6, apparently causing the lower extraction. Experiment 10 (with a higher CaCl_2 concentration by a factor of 1.5) yielded a slightly higher extraction efficiency than Experiment 11. Thus, the extraction efficiency is not a sensitive function of the CaCl_2 concentration.

Experiments 8 and 9 were done to determine whether mixed oxidants increase extraction efficiency. Replacing part of the Cs_2PuCl_6 with MgCl_2 was of no benefit. Experiment 7 was with Cs_2PuCl_6 alone. The extraction was significantly lower than that obtained with CaCl_2 in the mixture. Evidently, the ionic species (necessary for reaction and/or complex formation with the americium) is present in lower concentration in the absence of CaCl_2 . The distribution coefficients (K_d) are presented for comparison purposes. Note that the distribution coefficient changes by a factor of more than two, while the extraction percentage changes less than 3% in the 90% extraction range.

The results of the large-scale Cs_2PuCl_6 experiments are presented in Table 2. The first extraction utilized site return metal. Subsequent extractions were made with foundry reject metal to which americium was added via a master alloy by casting. This metal was higher in americium than the site return metal used.

Extractions 1 and 2 were made with oxidant prepared with filtrate recycle. (See Appendix A.) The third extraction was made with oxidant prepared without filtrate recycle. The extraction efficiency for Experiment 3 in Table 2 is the same as Experiments 1 and 2. Thus, using Cs_2PuCl_6 prepared with filtrate recycle had no detrimental effect.

The fourth extraction contained half the amount of Cs_2PuCl_6 , but CaCl_2 was added to maintain the same salt-to-feed-metal ratio. The extraction efficiency was reduced. However, the decrease was only 7% for a factor of two reduction in Cs_2PuCl_6 concentration.

The plutonium investment shown in Table 2 is essentially the same (approximately 90 grams per two-stage cycle) as incurred with the current production process utilizing MgCl_2 . Apparently, the high investment in Extraction 2 was caused by impure metal feed. This resulted in a very rough and irregular top surface, which was partially removed during separation of metal and salt.

Among the concerns about using Cs_2PuCl_6 was the issue of cesium metal contamination of the plutonium metal. A comparison of the free energies of formation at 900 °C of CsCl, KCl, and NaCl (Reference 5) shows that CsCl is 1.3 kcal/mole more stable than KCl and 6.5 kcal/mole more stable than NaCl (Table 3). This information indicates that cesium metal contamination would be less detrimental than either sodium metal or potassium metal contamination. One large-scale MSE product button made with Cs_2PuCl_6 was analyzed, and it contained less than 50 ppm of cesium.

Another question was whether corrosive chemicals (such as chlorine gas) would be released when

TABLE 3. Comparison of Free Energy Formation

Compound	Free Energy of Formation at 900 °C (kcal/mole)
CsCl	-85.1
KCl	-83.8
NaCl	-78.6

Cs_2PuCl_6 is heated. Thermograms made in air and in argon show significant differences. The trace made in air shows a relatively sharp weight loss and then a level portion. The initial weight loss was attributed primarily to the following reaction:

Subsequent weight loss was attributed to loss of CsCl by volatilization. The trace made in argon exhibited lesser, gradual weight loss at lower temperatures with the weight loss rate increasing at higher temperatures. This behavior was attributed to some oxidation caused by oxygen contamination of the argon followed by volatilization of salt at higher temperatures. To estimate the oxygen contamination, the argon stream was bubbled through an iodide solution. The amount of chloride formed by oxidation of the iodide ion was determined by ion chromatography. From this, the concentration of oxygen in the argon stream was sufficient to oxidize approximately one-third of the total chloride available for oxidation to chlorine.

Additional information was gained by heating the Cs_2PuCl_6 in a vacuum and detecting the chlorine formed by mass spectroscopy. The chlorine was calculated as 0.48 wt % of the Cs_2PuCl_6 sample. The assumption was made that chlorine has the same sensitivity as argon to make the calculation. Literature values^{6,7} of the molecular cross section and ionization potentials for argon and chlorine atoms (assuming that the chlorine molecule is no more difficult to ionize than the atom) indicate that the chlorine generated was probably less than 0.48%.

Ease of breakout appeared to be a function of feed purity level. The reaction products obtained with site return metal broke out easily, similar to runs with PuCl_3 , which were also made with site return metal. By contrast, the reaction products obtained with highly impure foundry reject metal were difficult to break out, and more metal adhered to the stirrer and thermocouple sheath. Also, after extraction, the highly impure metal presented a rough top surface similar in appearance to an electrolytic anode made from feed high in impurities that form high melting components.

More breakouts with site return metal are needed for more precise characterization.

Salt scrub of salt residues from two large-scale extractions with Cs_2PuCl_6 was completed. These residues yielded 341 grams of salt below the economic discard limit (EDL) containing less than 0.03 grams of plutonium and 80 grams of above-EDL salt with 12 grams of plutonium. Therefore, 81% of the salt scrubbed was discardable. The salts could not be combined to meet the EDL.

CONCLUSIONS

The preparation of Cs_2PuCl_6 was demonstrated on a 200-gram scale utilizing 100 grams of PuO_2 from the aqueous process. Filtrate recycle reduces the waste generation without reducing extraction efficiency.

Extraction data show the feasibility of a single-pass operation yielding plutonium metal that meets foundry specification for americium when americium in the feed metal does not exceed 2900 ppm. Additional experimental work is needed to define in more detail the interaction effects of salt-to-metal ratio and oxidant concentration upon extraction.

Decomposition of Cs_2PuCl_6 does not result in the generation of significant amounts of chlorine unless the compound is heated in air above 300 °C.

The data indicate that cesium contamination of the plutonium product will be less than 50 ppm.

The plutonium investment will not be significantly greater than currently experienced with MgCl_2 , and it may be less.

The feasibility of using the conventional salt-scrub process to obtain salts meeting the economic discard limit has been demonstrated.

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APPENDIX A

**EXPERIMENTAL PROCEDURE FOR THE PREPARATION
OF DICESIUM HEXACHLOROPLUTONATE
[Cs₂ PuCl₆]**

Equipment Needed:

1	Glass-fritted funnel (medium), 600 ml
1	2000-ml beaker
1	400-ml glass beaker
1	Hotplate/stirrer
2 ft	Tygon tubing
2	Rubber stoppers
1	1000-ml filter flash
-
1. Prepare a solution of 12N HNO₃ + 0.1N HF. Pour 280 ml into a 400-ml glass beaker.
 2. Into the beaker, dissolve 98.0 g of PuO₂ calcined below 500 °C. (Assay of oxide used was 84% plutonium)
 3. Stir moderately and heat over a low setting until the mixture is completely dissolved.
 4. Once the oxide is completely dissolved, *very slowly* add 114 ml of concentrated HCl to the mixture.
 5. In a separate beaker (2 l), dissolve 120 g cesium chloride into 1500 ml of concentrated HCl.
 6. While stirring slowly, combine the dissolved plutonium solution into the cesium chloride solution. Cs₂ PuCl₆ will precipitate.
 7. Filter the solution through a medium-porosity, glass-fritted funnel (600 ml). Wash the precipitate cake once with 500 ml of the filtrate. Filter to dryness.
 8. After the filter cake is filtered, transfer to a drying container. Place the container into drying oven at 110 °C for 20 hours.

NOTE: In replacement of Step 5, the used filtrate from the previous batch can be reduced in volume approximately 400 to 500 ml by boiling. To this reduced volume, fresh acid (concentrated HCl) containing the 120 g of dissolved cesium chloride is added to bring the total volume back to 1500 ml. (The acid was recycled seven times with no apparent effect on the quality of the salt produced.) Assays of the product salt are ~0.35 g plutonium/g salt with 1 g/l in solution.