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ANL-FGF-318

To be submitted to the
Journal of Inorganic
and Nuclear Chemistry.

30 November 1961

ELECTRODEPOSITION OF PLUTONIUM FROM MOLTEN SALT SOLUTIONS OF Cs_2PuCl_6*

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Facsimile Price $ 1.60
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ABSTRACT

The usefulness of molten salt solutions of Cs_2PuCl_6 for plutonium electrolyses has been investigated. Plutonium metal has been recovered from solutions without the use of Pu anodes. Up to 66% of the Pu dissolved in salt solutions has been recovered with Ta cathodes. No net Pu was recovered from solution when Pu cathodes were used because of the reoxidation of the deposit by dissolved chlorine. The potential of the Pu(IV)-Pu(III) couple was measured and found to be - 0.28 volts.

INTRODUCTION

Studies of the electrolysis of plutonium in molten salt solutions have

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* Work performed under the auspices of the United States Atomic Energy Commission.

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Electrodeposition of Pu from molten salt been concerned, thus far, with the electrorefining of impure metal.(1,2,3,4) In those experiments, impure Pu anodes were electrolytically dissolved in the salt and purified metal was deposited on the cathodes. Solutions of PuF_4(1,2) and $PuCl_3$(3,4) in LiCl-KCl eutectic have been used as electrolytes. PuF_4 was used at this Laboratory because it is not hygroscopic and was available from Los Alamos. The presence of fluorine in solution with Pu, however, leads to a potential radiation hazard from the $F^{19}(\alpha,n)Na^{22}$ reaction. A flux of 20 fast neutrons/cm^2-sec, which is the maximum permissible limit for a 40 hour week, has been measured one foot from a cell which contained 100 g PuF_4.(1) Although there is no neutron hazard associated with $PuCl_3$-LiCl-KCl solutions, the hygroscopic nature of $PuCl_3$(5) makes it difficult to handle and store the salt without it picking up moisture. Any moisture in the salt would have a detrimental effect on the cell operations.(2)

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(1) B. Blumenthal, private communication (1958).

(2) B. Blumenthal and M. B. Brodsky, "Plutonium 1960." Ed. E. Grison, W. B. H. Lord and R. D. Fowler, pp. 171-186. Proc. 2nd Int. Conf. on Plutonium Metallurgy, Grenoble, France. Cleaver-Hume Press, London (1961).

(3) J. A. Leary, R. Benz, D. F. Bowersox, C. W. Bjorklund, K. W. R. Johnson, W. J. Maraman, L. J. Mullins and J. G. Reavis. Proc. 2nd U. N. Int. Conf. on Peaceful Uses of Atomic Energy, Vol. 17, pp. 376-382 (1958).

(4) L. J. Mullins, J. A. Leary and C. W. Bjorklund, LAMS-2441 (1960).

(5) B. M. Abraham, B. B. Brody, N. R. Davidson, F. Hageman, I. Karle, J. J. Katz and M. J. Wolf, "The Transuranium Elements." Ed. G. T. Seaborg, J. J. Katz and W. M. Manning, NNES, Plutonium Project Record, Vol. 14B., pp. 740-758. McGraw-Hill, New York (1949).

It has been shown(6) that the double chloride, Cs_2PuCl_6, is non-hygroscopic and can be crystallized in high yields from aqueous solution. Solutions of Cs_2PuCl_6 in LiCl-KCl show the presence of Pu(IV) ions and will decompose to Pu(III) ions above 650°C.(7) It was suggested(6) that Cs_2PuCl_6 might be superior to either PuF_4 or $PuCl_3$ in plutonium electrolyses because it combines the best features of each. The double salt is non-hygroscopic, easily prepared and causes no neutron problems.

This study was undertaken to determine the behavior of Cs_2PuCl_6 in electrolytic cells. The work reported here was based on electrodeposition experiments which attempted to recover the Pu which was present as Cs_2PuCl_6 in solution. This type of electrolysis differs from those described above(1,2,3,4) in that no soluble Pu anodes were used in the cells. A series of preliminary experiments were carried out with solutions of Cs_2UCl_6. This salt is also precipitated from aqueous solution without water of hydration(6) and was useful as a stand-in for the Pu salt.

EXPERIMENTAL

Electrolytic Cells. Figure 1 shows the cells used in this work. The arrangement in Fig. 1a was used for electrolyses with molten metal cathodes above the melting point of Pu, 640°C. The electrodes shown in Fig. 1b were used to deposit solid Pu. The Vycor cells had standard-tapered, ground-glass tops which fitted a water cooled brass cap. Holes were drilled in a tight fitting rubber stopper for electrode and gas leads.

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(6) J. Kooi, E. Weisskopf and D. M. Gruen, J. Inorg. Nucl. Chem. 13, 310 (1960).

(7) D. M. Gruen, R. L. McBeth, J. Kooi and W. T. Carnall, Ann. N. Y. Acad. Sci. 79, 941 (1960).

Cells were heated in a water cooled, resistance furnace inside a Pu glovebox.(8) The glovebox atmosphere was He containing a total of 0.1 w/o water, oxygen and nitrogen. Tank He (20 ppm O_2) was passed directly through the cell.

Electrodes. Spectroscopically pure graphite rods, 1/8" in diameter, were used as anodes. Close fitting silica tubes insulated the anodes and helped prevent them from being broken.

Solid metal cathodes were made of 1/8" Ta rod and 1/4" Pu rod. Molten metal cathodes of Pu and Pb were used. A silica insulated Ta wire was used to supply current to the molten metal. The molten Pb cathode was used in the uranium electrolyses and permitted the depostion of uranium onto a molten cathode at the same temperature of the molten Pu electrolyses, viz. 700°C.

Materials. Chemically pure CsCl, obtained from the American Potash and Chemical Corp., was filtered through a quartz frit at 700°C to remove the insoluble impurities. LiCl-KCl eutectic was prepared from J. T. Baker and Co. C.P. salts. The eutectic mixture was dried by bubbling HCl through the molten salt. The dried eutectic mixture was then filtered through a Pyrex frit.

Cs_2PuCl_6 was prepared by coprecipitation as described by Anderson.(9) The Pu(III) solution was obtained by dissolving Pu metal in HCl. Batches of 11, 18, 25 and 36 grams of Cs_2PuCl_6 were made with yields of 69, 80, 91

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(8) L. R. Kelman, "Gloveboxes and Shielded Cells," Ed. G. N. Walton, Academic Press, New York (1958).

(9) H. H. Anderson, "The Transuranium Elements," op. cit. pp. 793-5.

and 81%, respectively. The highest yield was obtained by using minimum amounts of solvents. Analyses of the second batch showed 32.9% Pu and 29.3% Cl. These results compare favorably with theoretical values of 33.3% Pu and 29.6% Cl, and represent a Cl:Pu ratio of 6.01.

Ferraro(10) has described the Cs_2UCl_6 preparation. Yields of 85 and 92% were obtained on 100 g batches. The salts analyzed at 37.3 and 37.0% Cs; 33.5 and 33.6% U; and 29.3 and 29.1% Cl. The theoretical values are 37.04% Cs, 33.30% U and 29.66% Cl.

Experimental Procedures. Cells were preheated at the electrolysis temperature overnight with the tank He being passed through the cell. Enough alkali halide was put into the cell to give a 1-1/2" level. After the solvent had melted, approximately 5 m/o Cs_2PuCl_6 or Cs_2UCl_6 was added to the bath. The electrodes were pushed below the surface of the solution after the electrolyte had dissolved.

A six volt storage battery, in series with a suitable group of resistors, was used to furnish the cell potential. E.m.f.'s were measured with a Leeds and Northrup millivolt potentiometer through an L. and N. voltbox. The number of coulombs passed through the cell was estimated from the cell current and time of electrolysis. Potential-current curves were obtained for cells having Pu cathodes.

After the electrolysis, the deposit was melted under 50-50 m/o NaCl-KCl in Vycor and Pu beads were recovered by physical separation from the salt. This method of recovery has been used before to recover deposits(1,2) and

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(10) J. Ferraro, J. Inorg. Nucl. Chem. 4, 283 (1957).

is probably accurate to 0.01 g. The uranium content of the Pb cathode was determined after electrolysis by analyzing the Pb-U alloy for total U.

RESULTS AND DISCUSSION

Results of Cell Runs. Nine preliminary cell runs were made with solutions of Cs_2UCl_6 in CsCl and with molten Pb cathodes. These cells were operated between 685° and 715°C and yields of 25 to 73% were obtained.

Table I summarizes the results of the Pu electrolyses. CsCl was used as the solvent in runs 1, 2, 3a and 3b, while LiCl-KCl eutectic was used in all other runs. It is evident that little or no Pu was recovered from the salt when Pu cathodes were used but up to 66% of the dissolved Pu was electrodeposited onto Ta cathodes. At the end of runs with solid Pu cathodes, a blue reaction product was always found on the upper part of the cathode. This material, undoubtedly $PuCl_3$, was not found on Ta cathodes.

The dark brown color of the Cs_2PuCl_6 solutions changed to light tan after the electrolyses. The color change generally occurred when enough current had passed through the cell to reduce twice as much Cs_2PuCl_6 as had been put into the cell. If the tan solution was kept at temperature overnight, the color disappeared or changed to a very faint blue. During further electrolysis of the clear bath, Cl_2 gas evolved at the anode darkened the salt solution. When the current was then interrupted, the color would fade after 10-15 minutes. When current to a cell was interrupted immediately after the solution had turned from dark brown to tan, a dark blue product was seen to come off the submerged Pu cathode.

It is apparent that the solubility of chlorine in the salt was high enough to reoxidize Pu metal to Pu(III) or to Pu(IV). It seems likely that the liberated chlorine reacted with the Pu deposit or cathode to reverse the direction of the electrolytic reaction and to reduce the Pu yield. Naturally, it is to be expected that the reverse reaction would be more important with Pu cathodes because of the larger surface available for reaction. The redissolution of the deposit did not occur in the uranium electrolyses because the uranium formed UPb_3 compound which had a protective layer of Pb.(11)

Decomposition Potential of Pu. Although it was not the purpose of this study to investigate the thermodynamics of the Pu(IV)-Pu(III)-Pu(0) reactions, current-potential curves were obtained. When a Pu cathode was used, one had the cell:

$$Cl_{2(g)} \mid Cs_2PuCl_6\text{-}LiCl\text{-}KCl_{(l)} \mid Pu_{(l,s)}$$

for which the reaction was the decomposition of Pu(IV). Several representative curves obtained in this study are shown in Figure 2. Breaks were consistently obtained in the curves at - 2.70 ± .08 and - 2.98 ± .03 volts.

If one assumes that the activity coefficient for $PuCl_3$ in LiCl-KCl solutions is the same as in KCl(12) and NaCl(13) solutions, and that the solutions obey Henry's Law below 50 m/o $PuCl_3$, the expected potential for Pu(III)-Pu(0) would be - 2.59 to - 2.67 volts in these experiments. This agreement with the measured value of - 2.70 is excellent when one considers the assumptions made and the accuracy of these measurements.

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(11) R. J. Teitel, Trans. AIME 194, 397 (1952).

(12) R. Benz, J. Phys. Chem. 65, 81 (1961).

(13) R. Benz and J. A. Leary, J. Phys. Chem. 65, 1056 (1961).

It seems likely that the potential at - 2.98 volts is due to the Pu(IV)-Pu(0) reaction, which gives a net potential of - 0.28 volts for the reaction Pu(IV)-Pu(III). This result is in agreement with the prediction that the potential for Pu(IV)-Pu(III) should be more positive than it is for U(IV)-U(III), which is - 0.56 volts.(7) The calculation of this potential has assumed that the activities of the Pu(III) and Pu(IV) species were equal in these studies and that the temperature variations of the two potential breaks were similar. The scatter of the data made it difficult to determine the effect of temperature on the observed potentials, but the variation of the difference in the two potentials with temperatures was not worse than the limits given above.

The results are in agreement with the observation that Pu(IV) decomposes thermally to Pu(III) at higher temperatures, e.g., 700°C.(7) It is seen from Fig. 2 that the reaction Pu(III)-Pu(0) contributed a greater fraction of the cell current at 700° (run 8) than at 450-500° (runs 4 and 6). This was because there were more Pu(III) ions present at the higher temperature due to the thermal decomposition.

Purity of Deposited Metal. The small amount of metal recovered in these studies made it difficult to obtain good samples for chemical analysis. Results from the analysis of run 3a are given, however, in Table II. The surface cleanliness of the sample is seen from the low K and Na concentrations. Comparison of the data with the impurity content of the Pu used to make the Cs_2PuCl_6 shows improvement only for Ca, Mo and Ni. The high Zn content may be due to contamination of the salt bath by reaction between Cl_2 and the brass cap. The Cs impurity may have been due to codeposition of some Cs metal in run 3a.

Since the starting material for the salt used in run 3a was fairly pure, it is unknown if greater purification could have been obtained if less pure Pu had been used to make the Cs_2PuCl_6. Less pure Pu was used for the electrolytes of runs 4-10, but the very small recoveries did not permit adequate cleaning of the samples. Therefore, analytical results such as 200-1000 ppm K and 150-500 ppm Na were obtained. The other impurities were also high, e.g. Al - 350 ppm, Cr - 500 ppm, Fe - 1000 ppm, Ni - 150 ppm, etc., and were probably due to surface contamination.

CONCLUSIONS

This work has shown that Pu metal can be electrodeposited from solutions of Cs_2PuCl_6. Since the efficiency of the process is severely limited by reactions between the generated chlorine and Pu metal, it would be necessary to reduce the amount of the reverse reaction before the process could have wide usage. It might be possible to prevent the chlorination of the metal by the use of anolyte or catholyte compartments; by removing the Cl_2 quickly with fast flushing or evacuation; by a process which removes the deposit frequently; etc. Greater recoveries of Pu would be obtained if a non-reactive molten metal cathode were used. Such an approach would be most useful if alloys of Pu with suitable cathode metals were desired.

It was seen that Pu metal of fairly high purity could be obtained by the electrolysis of Cs_2PuCl_6 solutions. The removal of impurities from Pu by the crystallization of Cs_2PuCl_6 has been observed.(14) It would seem, therefore, that purification of starting materials, e.g. irradiated fuels, could be obtained by their conversion to Cs_2PuCl_6 followed by fused salt electrodeposition.

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(14) J. A. Long, private communication (1961).

Since molten salt solutions of Cs_2PuCl_6 are suitable for Pu electrolyses, it would be desireable to demonstrate the electrorefining of impure Pu anodes in cells having the dihalide electrolyte. Such studies are in progress.

ACKNOWLEDGEMENTS

The authors wish to thank D. M. Gruen and L. T. Lloyd for their useful discussions and interest in this work. The assistance of J. D. Bader in carrying out the experiments and E. A. Huff for the analyses is gratefully acknowledged.

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Table I. Summary of Cell Runs

Run No.	Temp. °C	Cathode(a)	Grams Pu Put(b) Into Cell	Grams Pu Recovered	Current Efficiency %
1	700	Pu	6.00	0.00	0
2	700	Pu	6.00	0.00	0
3a	700	Ta	3.50	0.42	4.7
3b	740	Ta	(c)	0.00	0
4	500	Pu	0.53	- 0.09	0
5	500	Pu	0.55	- 0.01	0
6	450	Pu	0.53	0.01	0.1
7	504	Pu	0.53	- 0.04	0
8	706	Pu	1.07	- 0.17	0
9	445	Ta	0.53	0.23	20.6
10a	600	Ta	0.53	0.10	18.0
10b	591	Ta	(c)	0.14	25.1
10c	443	Ta	(c)	0.06	10.8
10d	442	Ta	(c)	0.05	9.0
10e	441	Ta	(c)	0.00	0

(a) Graphite anodes used in all runs

(b) Charged to cell as Cs_2PuCl_6

(c) Electrolysis continued on solution from previous run

Table II. Impurity Content of Deposited Pu

Element(a)	Concentration in PPM	
	Pu Used to Make Cs_2PuCl_6	Deposited Pu
Al	29	40
Ca	13	L5
Cr	L0.01(b)	4
Fe	40	30
K	N.D.(c)	30
Li	0.02	0.02
Cs	N.D.	G500(d)
Mg	8	2
Mn	1	3
Mo	46	1
Na	13	15
Ni	10	L2
Rb	N.D.	20
Pb	L2	10
Zn	0	2000

(a) Elements not detected: Ag, B, Ba, Be, Bi, Co, Cu, Cd, Ga, La, Sb, Sn, Sr, Ti, V, W and Zr.

(b) Less than

(c) Not determined for this sample

(d) Greater than

Figure 1. Electrolytic cells, (a) cell arrangement for molten metal cathode, (b) electrode assembly with solid Pu cathode.

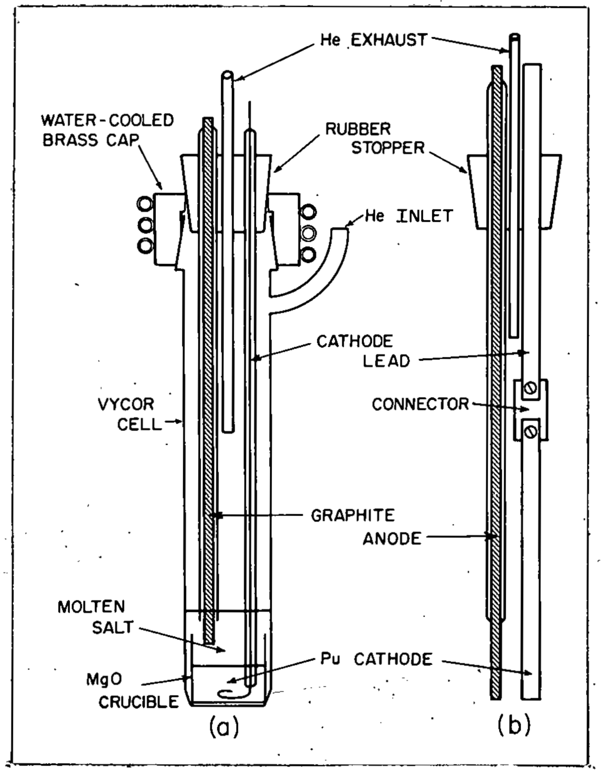

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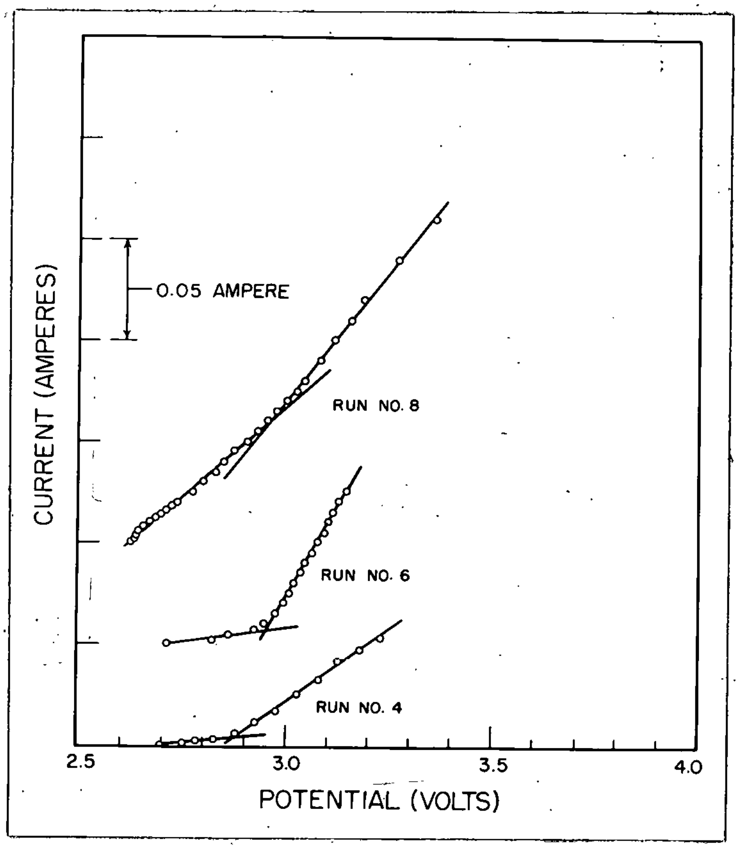
Figure 2. Potential-current curves. Ordinate shifted (current = 0 at lowest potential for each curve).



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