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LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

LARGE SCALE PREPARATION OF HIGH PURITY PLUTONIUM METAL BY ELECTROREFINING
(Preliminary Report)

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LARGE SCALE PREPARATION OF HIGH PURITY PLUTONIUM METAL BY ELECTROREFINING
(Preliminary Report)

by

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ABSTRACT

Plutonium metal produced by the bomb reduction method has been electrorefined successfully on the 100 - 300 g. scale. The purified product was collected continuously from the cathode as a liquid metal of greater than 99.98 percent purity. In addition, plutonium - 10 atomic percent (2.54 weight percent) iron alloy also has been electrorefined to produce a product containing less than 0.02 weight percent iron. The results indicate that plutonium of exceptionally high purity could be produced by using the proper materials of construction for the electrorefining cell. A tungsten cathode has been shown to be superior to tantalum. Using a tungsten cathode, the major metallic impurity detected in electrorefined product was 28 parts aluminum per million parts plutonium, when alumina was used as the ceramic cell construction material.

Collecting the product as a liquid at the cathode provides a means for operating the electrorefining cell continuously. A continuous cell design to be used in future experiments also is discussed.

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INTRODUCTION

The electrochemical preparation of plutonium metal was first reported in 1944 by Kolodney of this Laboratory.(1) Although milligram amounts of metal were produced by electrolysis of plutonium(III) chloride, the method was never applied to large scale operation because of the success of the bomb reduction method.(2) At the present time essentially all plutonium metal is produced by this latter method.

As distinguished from electrolysis of plutonium salts, electrorefining of metal that has been produced by bomb reduction has the following important applications:

a. Production of high-purity plutonium metal for (1) metallurgical studies, and (2) a primary plutonium analytical standard.

b. To provide a pyrometallurgical method for reprocessing plutonium reactor fuel.

c. To provide a pyrometallurgical method for recovering plutonium from alloys (and possibly compounds) generated as scrap from various research programs. At the present time this type of scrap is dissolved and converted to metal by rather expensive methods.

Because of the electropositive nature of plutonium, electrorefining has been limited to molten salt electrolytes. Excellent purification of plutonium-iron alloy that contained macro amounts of typical fission product elements has been reported.(3) The behavior of impurity elements during electrorefining was predictable from thermodynamic considerations. The small scale preparation of very pure plutonium metal also has been reported recently.(4) In this application, solid plutonium was collected from a fused salt electrolyte on a tantalum cathode. A massive rod of plutonium served as the anode. After a suitable amount of cathode deposit had formed, the cathode was withdrawn from the cell and the deposited plutonium was collected by melting in a different molten salt container.

In general it can be assumed that collection of solid plutonium at the cathode will result in a product that is more pure than if liquid plutonium is collected. This is because the liquid product will react with the cell materials to a much greater extent. However, there are several practical advantages to collecting the product as a liquid. For example, the product can be cast directly into the desired shape in the electrorefining cell. Moreover, a liquid cathode deposit can be adapted to continuous cell operation more easily than a solid deposit. The advantages of continuous operation are obvious when cell set-up time and criticality limitations on batch size are considered.

The experiments discussed in this report were directed toward demonstrating the following:

a. The purification of plutonium-iron alloy and collection of plutonium in a molten state.

b. The preparation and collection of molten plutonium of 99.98 percent purity, using production grade metal as the anode.

The procedure and cell design were selected from the viewpoint of being able to convert to a continuous process with a minimum of revision.

These experiments indicated that plutonium metal of greater than 99.98 percent purity can be produced on the hundred gram scale and collected (or cast) as a coalesced product even when plutonium-iron alloy is used as the starting metal.

EXPERIMENTAL

Preparation of Electrolyte: A chloride electrolyte consisting of 10 weight percent plutonium(III) chloride, 50.4 weight percent potassium chloride and 39.6 weight percent sodium chloride was used in all the experiments. A sodium chloride-potassium chloride cylinder was prepared by melting and casting equimolar amounts of A.R. grade materials under vacuum. Plutonium(III) chloride was prepared by the hexachloropropylene reaction(5) followed by vacuum distillation.

Preparation of Anode Feeds: The plutonium metal was prepared by the bomb reduction of plutonium(IV) fluoride.(2) The metal was then vacuum cast into a cylindrical shape. In the case of the plutonium-iron alloy the plutonium was alloyed with iron prior to casting.(6)

Procedure: The electrorefining equipment is shown schematically in Fig. 1. The cell consisted of an outside compartment (2-5/8 in. O.D. by 4 in. high) which contained the molten salt electrolyte and a concentric inner anode compartment (1-1/2 in. O.D. by 1-3/4 in. high). Both compartments were made of highly vitrified alumina, and were cemented together. A 2-1/2 in. O.D. by 2 in. long by 0.010 in. metal tube was immersed in the electrolyte above the anode compartment to act as the cathode. A tantalum stirrer served as the conductor to the impure plutonium in the anode compartment and provided agitation to the molten plutonium and to the electrolyte. The entire assembly was contained in a 3 in. O.D. stainless steel tube mounted in a commercial tube furnace. During operation, plutonium was oxidized at the anode, entered the molten salt electrolyte, and was reduced back to metal at the cathode surface. Because the cell was operated above the melting point of plutonium, the dense cathode deposit drained continuously down into the annular space around the inner anode compartment during operation.

Prior to each experiment the cell was outgassed at 700°C for 2 hr. under vacuum. The general procedure for an experiment consisted of loading the plutonium anode, the sodium chloride-potassium chloride cylinder and the plutonium(III) chloride into the electrorefining cell, heating the mixture to slightly above the melting point of plutonium(III) chloride (767°C) and electrolyzing the mixture at a potential of 2 volts at 700°C in a helium atmosphere. The molten anode and salt were stirred continuously. At the conclusion of the electrorefining period, the contents of the cell were permitted to freeze after withdrawing the anode stirrer from the melt. The cell was broken apart and the plutonium product was recovered as an annular metal casting. This casting was sampled by cutting wedges from the ring. The samples were pickled in water and nitric acid prior to analysis. Samples for iron determinations were also pickled in hydrochloric acid. Although the electrorefining cell was operated under a dry helium atmosphere, all salts and metals were handled at room temperature in the glove box filled with room air while loading and unloading the cell. The results indicate that an inert atmosphere within the glove box is not necessary, even when the experiments were conducted on humid days, provided that exposure of materials to the moist air was not excessive.

The conditions for each experiment are summarized in Table 1. All runs were made in alumina cells containing 0.1 percent magnesia by weight. In Run IV, the helium was purified by passing the gas through a Drierite tower and a uranium chip furnace at 600°C. In Runs I, II and III the chip furnace was not used. Tantalum cathodes were used in Runs I and II and tungsten cathodes were used in Runs III and IV.

Analyses of the anode feed material and the plutonium products are given in Tables 2 and 3. Iron, tungsten, and tantalum were determined colorimetrically; carbon and oxygen were determined by combustion analysis. All remaining elements were done spectrochemically. The wide variations in tantalum analyses on duplicate samples necessitates the recording of both values in Table 3. These variations are caused by segregation of tantalum metal upon cooling and freezing of the casting.

DISCUSSION OF RESULTS

It is apparent from the results of Run IV that plutonium metal of excellent purity can be produced from bomb reduction metal by this electrorefining procedure. A comparison of the plutonium produced using

Table 1

SUMMARY OF EXPERIMENTAL CONDITIONS FOR PLUTONIUM ELECTROREFINING EXPERIMENTS

Run	Anode	Cathode Material	Voltage	Avg. Current amps	Time, hr	Product wt. g.	Cathode Effic. %	Temp., °C
I	302 g. Pu-Fe alloy	Ta	2.0	3.88	26.9	222	71.4	700
II	304 g. Pu	Ta	2.0	2.87	36.7	278	89.4	700
III	287 g. Pu	W	2.0	--	20*	128	--	700
IV	298 g. Pu	W	2.0	2.44	27.0	169.8	83	690

*Run III had to be terminated after 20 hr. because of a tantalum thermowell failure (see Discussion of Results)

Table 2

ANALYSES OF PLUTONIUM FEED MATERIAL

Element	Concentration of Element, parts per million parts plutonium		
	Run I	Run II	Runs III, IV
Li	< 0.2	< 0.2	< 0.2
Be	< 0.2	< 0.2	< 0.2
Na	< 10	< 10	< 10
Mg	30	15	80
Ca	< 5	20	25
Al	20	90	25
La	< 10	< 10	< 10
Si	< 100	20	35
Pb	< 20	< 1	< 1
Cu	20	7	2
Ni	< 100	50	35
Cr	< 100	10	10
B	< 10	< 0.5	< 0.5
Mn	< 20	15	5
Sn	< 20	< 1	< 1
Bi	< 20	< 1	< 1
Co	< 5	< 5	< 5
Zn	< 200	10	< 10
Ag	--	--	< 1
Fe	2.54×10^4	60	80
W	--	--	< 20
Ta	< 50	280;490	< 50
C	80	140	-
O_2	90	135	-

Table 3

ANALYSES OF PLUTONIUM PRODUCTS

Element	Concentration of Element, parts per million parts plutonium			
	Run I	Run II	Run III	Run IV
Li	< 0.2	< 0.2	< 0.2	< 0.2
Be	< 0.2	< 0.2	< 0.2	< 0.2
Na	< 10	< 10	< 10	< 10
Mg	30	< 5	< 5	< 5
Ca	< 5	< 5	10	15
Al	35	20	250	28
La	< 10	< 10	< 10	< 10
Si	< 10	< 10	< 10	< 10
Pb	< 1	< 1	< 1	< 2
Cu	1	< 1	2	< 2
Ni	< 10	< 10	< 10	< 10
Cr	< 10	< 5	5	< 5
B	0.5	< 0.5	< 0.5	< 0.5
Mn	< 1	< 1	< 1	< 2
Sn	< 1	< 1	< 1	< 1
Bi	< 1	< 1	< 1	< 1
Co	< 5	< 5	< 5	< 5
Zn	< 10	< 10	< 10	< 10
Ag	--	--	< 1	--
Fe	178	20	40	< 20
W	--	--	< 20	12
Ta	270	600;220	275;400*	< 35
C	60	35	--	32
O_2	--	25	--	25

*High tantalum concentration was caused by tantalum thermowell failure (see Discussion of Results) a tungsten cathode (Runs III, IV) with that produced using a tantalum cathode (Runs I, II) shows that tungsten is a superior cathode material. The only detectable impurities in the product from Run IV were 15 ppm Ca, 28 ppm Al, 12 ppm W, 32 ppm C and 25 ppm O_2. The high concentration of tantalum in Run III was caused by failure of a tantalum thermocouple sheath which resulted in the loss of the end of the sheath and the leakage of air into the cell. Potentiometric determinations of the plutonium concentration of the product from Runs I, II, III and IV gave results of 99.98, 100.02, 100.00 and 100.02 percent, respectively. It is interesting to note that remelting of the product from Run II in an alumina crucible and holding the melt at 800°C for 2 hr. resulted in an increase in aluminum contamination from 20 to 150 ppm. In an effort to reduce the aluminum contamination in the product, calcia coated alumina crucibles will be tested in future experiments. The greater thermodynamic stability of calcia should make it a superior container material for plutonium metal.

Batch electrorefining will produce superior metal more economically than the method now used to meet pure metal requirements. However, present and forecast requirements indicate that sufficient high purity plutonium will be required to justify development of continuous operation. Therefore, the effort on this project is now being devoted to developing a continuous method for electrorefining bomb reduction metal.

The continuous cell design is shown schematically in Fig. 2. It is essentially the same as the batch cell, except that the molten plutonium product will be removed continuously by overflowing in the center bottom of the cell. This lower portion of the cell also is tapered to minimize liquid metal residence time and holdup. Impure plutonium can be added periodically to the anode through an inert atmosphere air lock in the top of the cell lid.

Electrorefining of the plutonium iron alloy, Run I, reduced the iron concentration from 2.54 weight percent to 0.018 weight percent. Therefore plutonium-rich iron alloy scrap probably can be recovered directly by electrorefining. No additional experiments on the electrorefining of irradiated plutonium reactor fuels have been conducted. Previous experiments(3) have indicated that very good purification can be achieved if large scale cell operation is successful. Cells designed to electrorefine bomb reduction metal should also be applicable to reprocessing plutonium alloy scrap and irradiated fuel.

ACKNOWLEDGEMENTS

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CORRECTION TO LAMS-2441

Figures 1 and 2 of the above report were transposed in the original printing. The correct arrangement is shown below. It is requested that this sheet be stapled in all copies of this report.

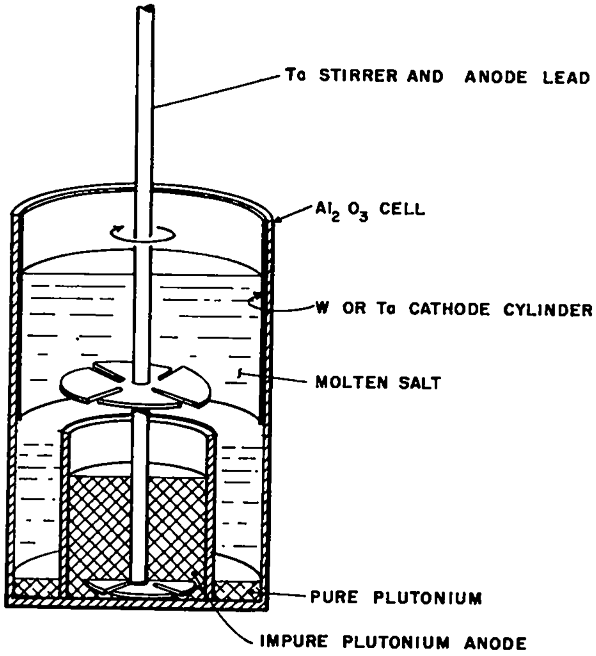


Fig. 1 Batch Electrorefining Cell.

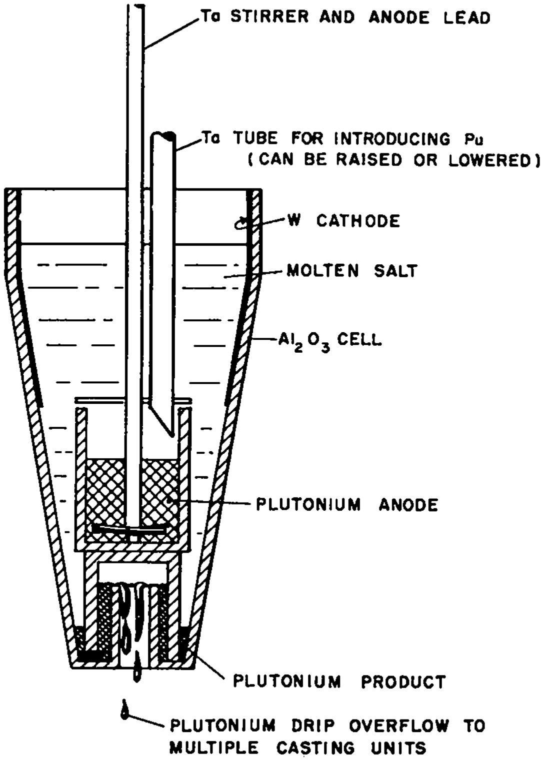
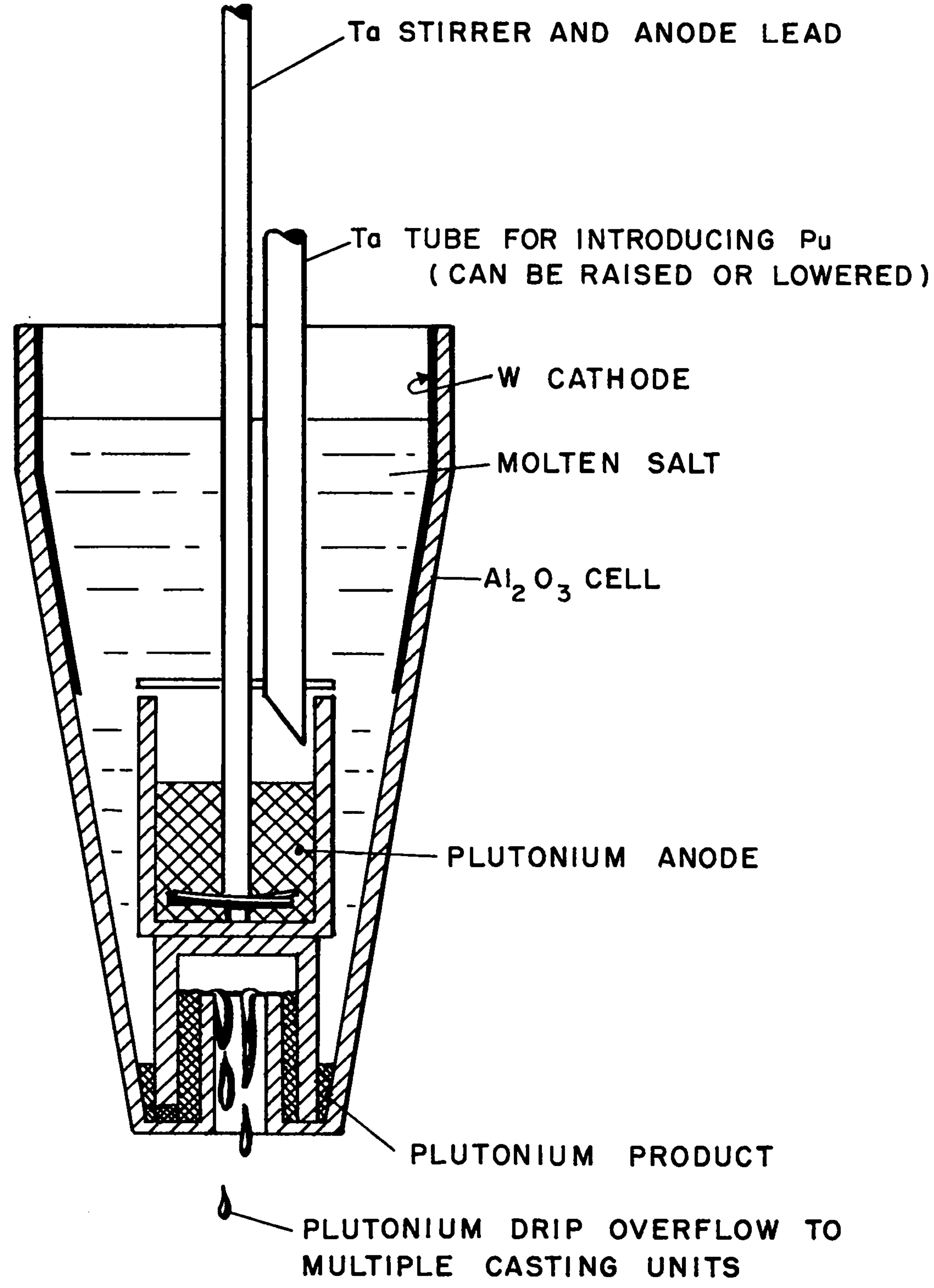


Fig. 2 Tentative Continuous Electrorefining Cell.



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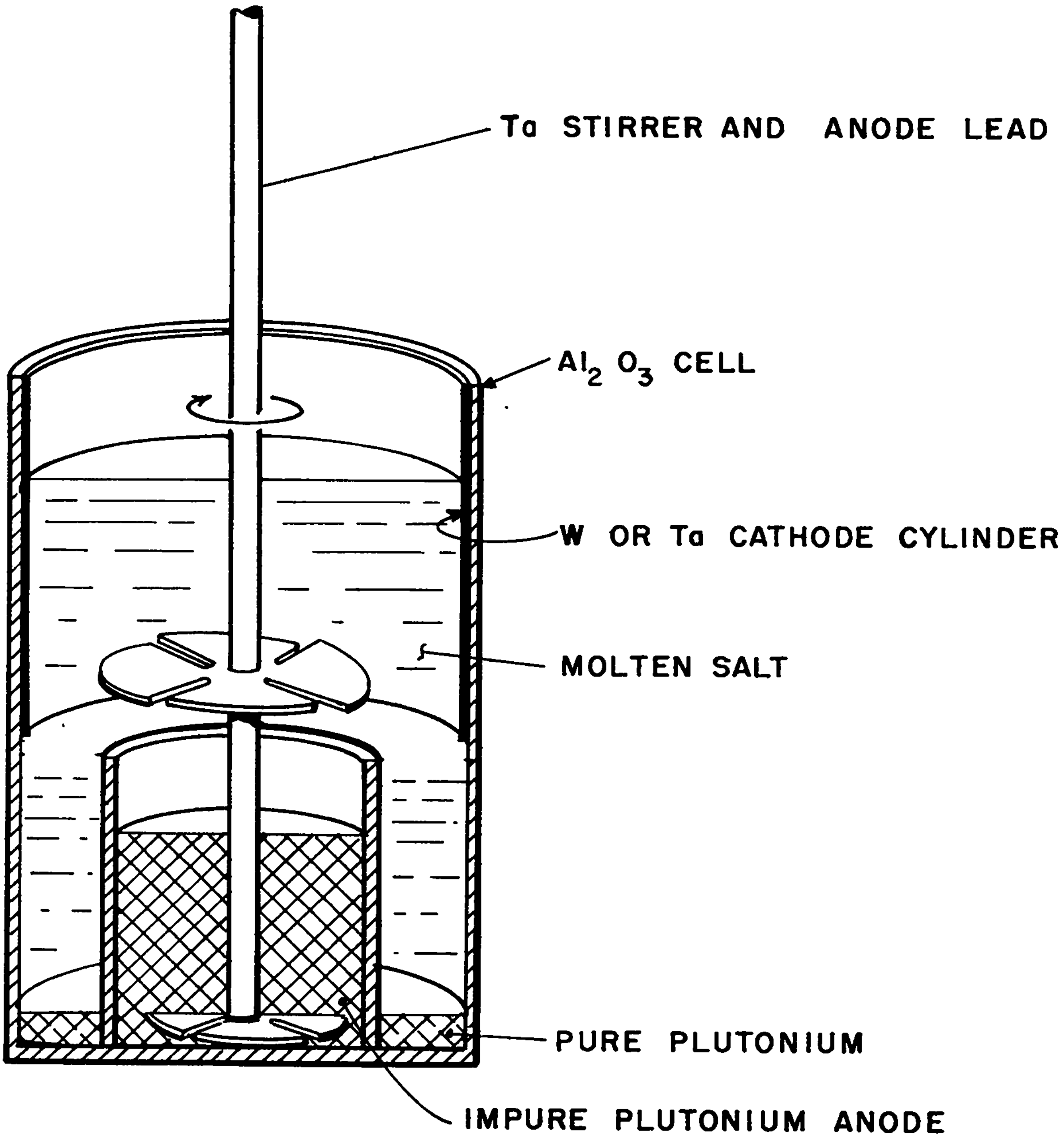

Fig. 2 Tentative Continuous Electrorefining Cell.

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