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ELECTROREFINING METALS

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2 Sheets-Sheet 1

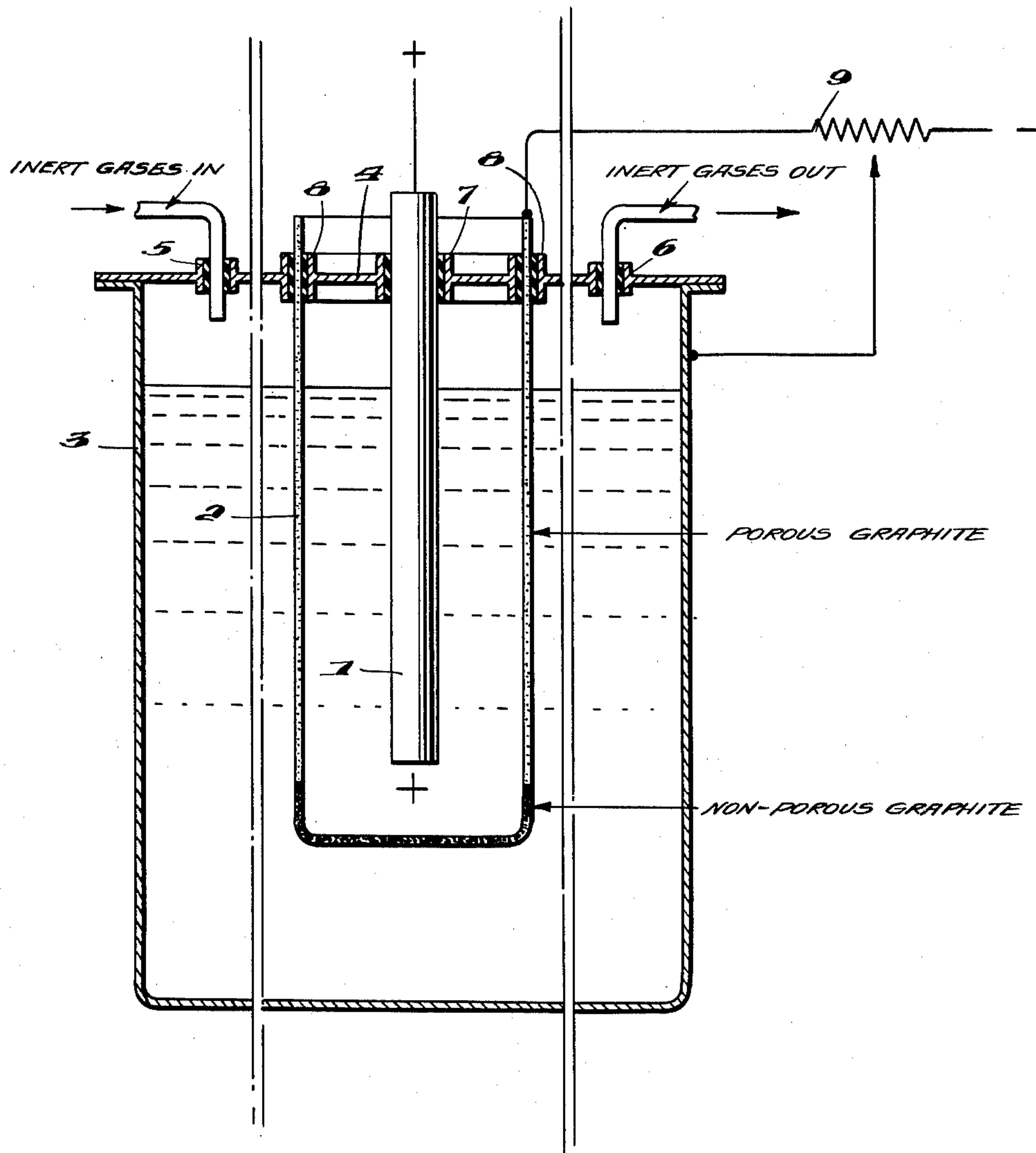


Fig. 1.

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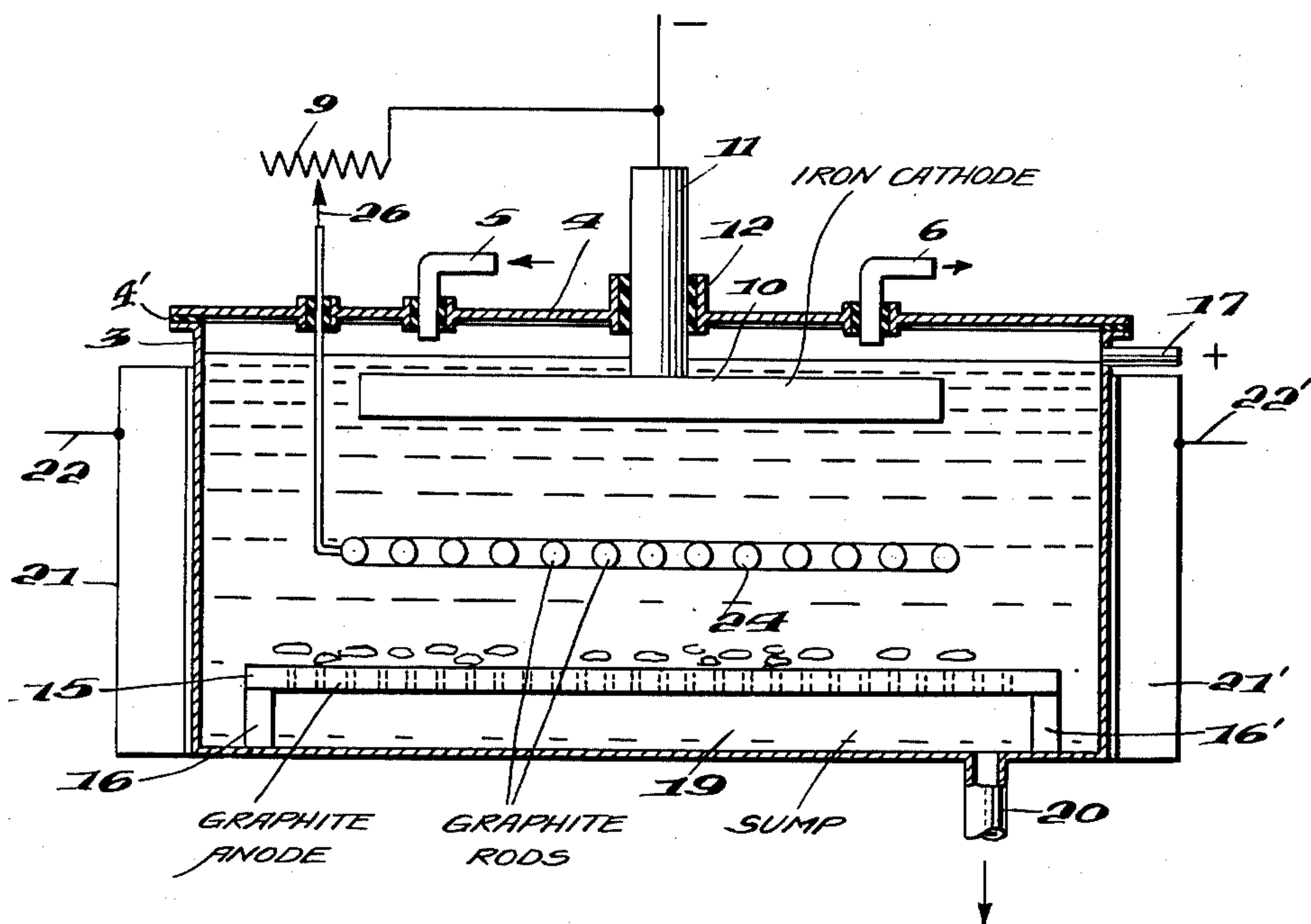
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*Fig. 2.*

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## ELECTROREFINING METALS

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5 Claims. (Cl. 204—1.5)

This invention relates to the refining of metals by molten electrolysis. It relates especially to the electrorefining of metals the chlorides and bromides of which conduct electricity poorly in the molten state. Such metals are, for example, beryllium, vanadium, tantalum, hafnium, thorium, molybdenum, columbium, zirconium, titanium, and uranium.

In the electrorefining of these metals it is necessary to add a chloride or bromide of an alkali or alkaline earth metal to conduct the current. The refining operation is therefore one of anodic solution and chemical precipitation by the alkali or alkaline earth metal formed at the cathode. Since the alkali and alkaline earth metals are soluble in their molten chlorides and bromides, precipitation may not take place on the cathode unless special conditions are maintained, and to maintain such conditions requires a low current density. If the current density is increased so as to produce a substantial open circuit voltage of the cell then conditions for electrorefining are no longer present. Impurities more noble than the metal to be refined will dissolve at the anode and be deposited by chemical reaction at or near the cathode.

My invention provides a simple method of segregating the more noble metals from the electrolyte before their ions reach the cathodic area in which they would be precipitated thereby contaminating the metal being refined. Under these conditions higher current densities may be used and the capacity of the cell accordingly increased.

To accomplish the purpose of my invention I provide between the anode and the cathode an inert, conducting, foraminous partition. This partition, which is conveniently located nearer the anode, is electrically connected to the cathode through a resistance so that it forms a voltage divider. In certain instances the resistance may be very large, even infinite, and the necessary voltage between the anode and the partition is obtained by its position in the bath. The more noble ions formed at the anode will be discharged at the partition and such metals will not pass to the zone of precipitation for the metal being refined.

The voltage of the divider with respect to the anode must be cathodic to nearly the extent of the excess voltage applied to the anode. This is slightly less than the open circuit voltage of the cell from anode to cathode. Under these conditions the metal to be refined will not deposit at the divider but the more noble impurities will.

The selection of material for the divider is a matter of engineering knowledge. Carbon or graphite is an excellent porous separator when it is not attacked by the contents of the electrolyte. This is true in an electrolyte of magnesium chloride or bromide but in other alkali or alkaline earth chlorides carbides may be formed. I have found that certain commercial alloys are substantially inert as separators, particularly Nichrome V and Alnico V. In general, however, it will be most satisfactory to use a metal more noble than the one being refined from which slight contamination will be least objectionable. In refining zirconium, for example, the slightly more noble metal titanium may be used.

The apparatus aspects of the invention are illustrated in the accompanying drawing, in which:

FIG. 1 is a diagrammatic representation of one form of electrolytic cell in accordance with the invention, in which

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the anode is vertically disposed and a foraminous conducting separator in the form of a cylinder surrounds the anode; and

FIG. 2 is a diagrammatic representation of a modification of the form of electrolytic cell shown in FIG. 1, in which a horizontal cathode is disposed above and spaced from a horizontal anode and a conducting separator in the form of an array of graphite rods is horizontally disposed between cathode and anode.

Having now described my invention in general I will illustrate it by several examples.

### Example I

I make an electrolytic cell as shown in FIG. 1. In this figure, 1 is a crude titanium anode containing 1.2% Fe and 3.0% Ni as the significant impurities, 2 is a porous graphite cup, and 3 is an iron pot which also serves as the cathode. 4 is a cover for the pot provided with openings 5 and 6 for argon or helium entrance and exit, and insulated connections 7 and 8 for the anode and the graphite cup or separator. The pot is electrically connected to the graphite separator through the variable resistance 9.

In use the cell is heated to 850° C. and partially filled with pure anhydrous magnesium chloride. To carry out my experiment I disconnect the variable resistance 9 and pass a current of 250 amperes through the cell. The voltage drop is 4.2 volts. The open circuit voltage is 0.50 volt corresponding to some magnesium at the cathode, thereby forming an appreciable concentration of lower chloride of titanium in solution in the molten magnesium chloride. I now connect the variable resistance 9 and again pass current at 250 amperes. I adjust the resistance so that the voltage between the anode and the graphite cup is slightly less than 0.50 volt. It will be evident that under these conditions the graphite cup is at the voltage for pure titanium dissolution and that any metals more noble than titanium which have been dissolved at the anode will be separated in the graphite cup. The following analyses show the extent of refining for the crude titanium used:

Anode	Deposit in Cup	Deposit at Cathode
1.2% Fe 3.0% Ni	57.7% Ni 23.3% Fe	0.001% Fe 0.0005% Ni

In this example the deposit at the cathode is a titanium product which, excepting for the above stated amounts of iron and nickel is substantially pure titanium.

The nature of the cathodic deposit will depend on a number of factors and the separation of this deposit from the electrolyte may be accomplished in various ways which are, however, beyond the scope of this invention which is concerned only with the removal of more noble impurities of the anode from the melt as the salt of the metal to be refined moves into the cathode zone.

### Example II

I proceed as in Example I except that I substitute for the porous graphite cup a perforated cylinder of Nichrome V, a commercial alloy containing about 80% nickel and 20% chromium. In this experiment I use an electrolyte of lithium chloride and potassium chloride of eutectic composition. The experiment is carried on at 400° C. and has for its object the separation of tantalum and columbium (niobium). An alloy of the two metals is used as an anode and the procedure is exactly as in Example I. With the use of the lithium chloride-potassium chloride electrolyte the open circuit voltage is 1.24 volts



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at 250 amperes. The nichrome separator is therefore adjusted to about 1.20 volts against the anode. Under these circumstances the columbium is separated on the nichrome separator and the tantalum separates as a powder in the vicinity of the cathode. The separation of the tantalum was restricted to the cathode by the addition of chlorine in the cathode area. The tantalum prepared in this way analyzed less than 0.1% columbium.

Addition of chlorine in the cathode area may be effected in the manner disclosed in my copending application Serial No. 470,609, filed November 23, 1954 (Patent 2,838,393); or such addition may be, and preferably is, effected by the procedure disclosed in my copending application Serial No. 408,310, filed February 4, 1954, entitled "Methods of Producing Titanium and Zirconium" (Patent 2,817,630). In accordance therewith, chlorine gas is introduced, at a controlled rate, into the electrolyte surrounding the cathode by forcing the gas through a hollow porous cathode of graphite, titanium, zirconium or the like.

#### Example III

In this example I proceed exactly as in Example II except that I use a perforated columbium separator which prevents any possibility of contamination of the retained columbium.

#### Example IV

In this experiment I separate hafnium from zirconium. I use as anode an alloy of the two metals. The cell is constructed as in Example I. The electrolyte is lithium chloride maintained at 700° C., and the separator is a cylinder of screen fabricated from zirconium wire. The screen cylinder is longer than the anode and terminates in a separate compartment of the pot from which, however, it is insulated. In the experiment I pass 100 amperes and the open circuit voltage is maintained at 0.50 by adding chlorine to the cathode area. The screen is maintained at 0.49 volt against the anode. As electrolysis proceeds zirconium powder is formed at the separator and falls to the separate compartment at the bottom of the cell. Hafnium is deposited on the cathode.

#### Example V

In this experiment I purify vanadium. I use a cell as in Example I and an electrolyte of magnesium bromide. The crude vanadium used as anode is a material containing appreciable amounts of iron, nickel, aluminum and insoluble compounds as contaminants of the vanadium. A current of 100 amperes is passed from the anode to the pot. The open circuit voltage is 0.5 but is reduced to 0.15 by adding chlorine. The separator is given a potential of .14 with respect to the anode. The impurities of iron, nickel, aluminum, and insoluble compounds remain in the carbon cup, and pure vanadium is deposited on the cathode.

#### Example VI

In this example I refine titanium scrap. Since the scrap occurs in fragments, turnings, clippings, bar ends, etc., it is necessary to provide a means of utilizing such material as an anode. For this purpose I provide a metal basket. The basket is made of an alloy of 80% nickel, 20% chromium which is anodically dissolved to only a small extent. This basket is placed centrally of the cell in the position of the anode, 1, in the figure. It is provided with a non-foraminous sump at the bottom end to collect anode slime. The foraminous diaphragm, 2, of the figure is replaced with an iron screen of 16 meshes per linear inch. I then place another screen basket within the cell at a distance of 12" from the diaphragm screen. This basket I make the cathode. The electrolyte is fused sodium chloride at 850° C. An argon atmosphere is provided. I pass a unidirectional current through the cell until the cathode basket is filled to a depth of several inches with titanium deposit. I use a current density at

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the cathode of 500 amps./sq. ft. When the indicated amount of titanium has collected on the basket, I discontinue the electrolysis and add enough chlorine to react with dissolved sodium. I then add enough magnesium to react with the titanium chloride in the melt. I skim any excess magnesium from the surface of the melt. The molten salt is then removed through the cathode basket by draining it from the bottom of cell 3 of the figure through a suitable opening. After cooling in the argon atmosphere the basket and contents are washed with hot water to provide pure particulate titanium.

According to the apparatus modification illustrated in FIG. 2, a horizontally disposed iron cathode 10 is suspended in the upper part of cell 3 by means of conductive shaft 11 which is electrically insulated as at 12 from the material of cell cover 4. Cell 3 is formed of graphite. Adjacent the bottom of the cell there is arranged a foraminous graphite plate 15 functioning as the anode of the cell and supported above the bottom of the cell by means of graphite supporting blocks 16, 16'. As indicated at 17, the cell 3 is provided with a connector, to connect the positive pole of the cell. The space 19 between member 15 and the bottom of the cell 3 functions as a sump. At 20 is indicated a draw-off conduit for withdrawing fluid from the bottom of the cell. For the purpose of maintaining the cell and its contents above the melting point of the molten electrolyte therein, there are provided on cell 3 a pair of conductive lugs 21, 21' connected as indicated at 22, 22' to a source (not shown) of alternating current.

Intermediate cathode 10 and anode 15 is a series of horizontally disposed, electrically communicating rods 24, which series of graphite rods functions as a foraminous electrically conductive, separator member. The latter is in operative communication with variable resistance 9 through conductive supporting rod 26. Resistance 9 is electrically connected to shaft 11.

In using this modified apparatus, the impure metal to be refined, in comminuted form or in the form of scraps, is placed on the graphite plate anode 15, unidirectional current is passed from anode to cathode through the electrolytic bath of fused alkaline metal chloride or bromide, and variable resistance 9 is adjusted so that separator member 24 is maintained at a cathodic potential with respect to the anode, which is slightly less than the open-circuit voltage of the cell.

I claim:

1. Process for electrorefining a metal selected from the group consisting of beryllium, tantalum, hafnium, columbium, zirconium, uranium, titanium, vanadium, thorium, and molybdenum which comprises passing a unidirectional current between an anode composed of the metal to be refined and a more noble impurity and a conducting cathode in a fused electrolyte containing at least one salt selected from the group consisting of alkali and alkaline earth metal chlorides and bromides to form a salt of the metal to be refined selected from the group consisting of chlorides and bromides dissolved in the electrolyte, inserting between the anode and the cathode a foraminous, chemically and electrochemically inert separator and maintaining the separator at a slightly lower potential than is the open-circuit voltage of the cell thereby depositing at the separator any more noble impurity from the anode which may be dissolved and depositing the metal to be refined at the cathode.

2. The process of claim 1, in which the separator is carbon and the electrolyte is a magnesium salt selected from the group consisting of chloride and bromide.

3. The process of claim 1, in which the anode is composed of the metal to be refined and a more noble metal, and in which the separator is composed of the more noble of the metals being separated by the electrorefining operation.

4. The process of claim 1 further characterized by the step of chlorinating the electrolyte in the cathode area



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to reduce the open-circuit voltage to a lower but significant voltage.

5. The process of claim 1, further characterized in that the metal to be separated in the cathode area is restricted to the cathode by the chlorination of electrolyte in the cathode area. **5**

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