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(54) Titre : PROCEDE ELECTROLYTIQUE D'EXTRACTION DE PLATINE D'UNE GRANDE PURETE A PARTIR
D'ALLIAGES DE PLATINE
(54) Title: ELECTROLYTIC PROCESS FOR EXTRACTING PLATINUM OF HIGH PURITY FROM PLATINUM ALLOYS

(57) **Abrégé/Abstract:**

Disclosed is electrolytic process for obtaining platinum of a high purity from concentrated hydrochloric acid solutions containing a platinum alloy, the process comprising the steps of a) providing an electrolysis cell having an anode and a cathode and a cation exchanger membrane subdividing the electrolysis cell, b) placing in the electrolysis cell a concentrated hydrochloric acid solution containing metal impurities and a platinum alloy selected from the group consisting of Platinum-Rhodium alloys, Platinum-Iridium alloys and Platinum-Palladium alloys, c) applying a potential across the anode and the cathode of 8 V to 16 V to perform an electrolysis under voltage-controlled conditions at a current density of 12.5 to 37.5 A/dm² so as to form a purified platinum-containing solution and at least one platinum alloy metal deposit, d) recovering the at least one platinum alloy metal deposit, and e) obtaining the platinum of high purity from the purified platinum-containing solution.



ABSTRACT

Disclosed is electrolytic process for obtaining platinum of a high purity from concentrated hydrochloric acid solutions containing a platinum alloy, the process comprising the steps of a) providing an electrolysis cell having an anode and a cathode and a cation exchanger membrane subdividing the electrolysis cell, b) placing in the electrolysis cell a concentrated hydrochloric acid solution containing metal impurities and a platinum alloy selected from the group consisting of Platinum-Rhodium alloys, Platinum-Iridium alloys and Platinum-Palladium alloys, c) applying a potential across the anode and the cathode of 8 V to 16 V to perform an electrolysis under voltage-controlled conditions at a current density of 12.5 to 37.5 A/dm² so as to form a purified platinum-containing solution and at least one platinum alloy metal deposit, d) recovering the at least one platinum alloy metal deposit, and e) obtaining the platinum of high purity from the purified platinum-containing solution.

ELECTROLYTIC PROCESS FOR EXTRACTING PLATINUM OF HIGH PURITY FROM PLATINUM ALLOYS

BACKGROUND OF THE INVENTION

The present invention concerns an electrolytical process for extracting platinum of high purity from concentrated hydrochloric solutions of alloys of platinum and Rh, Ir and/or Pd under simultaneous depletion of other noble and base metal impurities.

Platinum alloys find a variety of applications in industry as instrument platinum, for thermocouple elements, as catalyzers for ammonia oxidation, in organic chemistry, for automobile exhaust catalyzers, in dental technology and many other areas. Depending on the chemical and other production processes concerned, these alloys are passed to noble metal processing plants after a certain period of time in the form of scrap platinum alloy and are chemically separated and refined in those plants.

The classical separation of platinum from Rh, Ir and/or Pd occurs by means of precipitation in the form of $(\text{NH}_4)_2[\text{PtCl}_6]$. Due to the chemically very similar properties of the platinum metals, however, this process is very labour- and time-consuming.

The separation of the platinum from the iridium is particularly complicated, since both metals are present in the same stable valency (IV) and, during precipitation with NH_4Cl , form salts with almost identical properties.

A rough separation is only possible if the IV-valent iridium is converted into the III-valent oxidation stage. During subsequent precipitation of the platinum with NH_4Cl , co-precipitation of the iridium occurs nonetheless. Similar conditions are observable during separation of the platinum from the rhodium and palladium. The precipitated $(\text{NH}_4)_2(\text{PtCl}_6)$ contains large amounts of Rh and Pd. Re-precipitation or re-crystallization steps are therefore required for further purification.

From the DE-PS 272 6558 a process for separating the platinum from the iridium by means of ion exchangers is known. This process merely results in platinum containing iridium.

A large number of extraction processes are further known for precipitation of platinum alloys, which, however, also require subsequent precipitation of the platinum metals.

All processes require elaborate apparatus and technology and are therefore very cost-intensive.

Electrolytical processes for refining gold have been known for a long time Gmelins Handbuch der Anorganischen Chemie, Gold, System-Nr. 62, E.H. Erich Pietsch (Editor), Carl Winter's Universitätsbuchhandlung Heidelberg (Germany), 1949, and have been continuously developed (EP 0 253 783).

From British Patent 157 785 and German Patent 594 408 electrolytical platinum refining processes are known, which partly operate with combinations of chemical and electrolytical processes.

These processes are all very time-intensive and cannot be reproduced in technically acceptable form

in all aspects.

The US-PS 4,382,845 describes a partial electrolytical separation of palladium from solutions containing an excess of palladium. Precipitation, however, is only possible up to the threshold at which platinum and palladium are present in equal quantities. The precipitation of remaining base and noble metals is not mentioned in this process.

In the known process for precipitating platinum and palladium the electrolysis cell comprises a cation exchanger membrane whose advantages are, however, not apparent, since platinum and palladium can also be precipitated without a cation exchanger membrane in the described concentration ratio and voltage range. Moreover, this process displays the same disadvantage as all other known processes in that it can only be operated with a maximum concentration of $\leq 100\text{g/l}$.

The invention therefore proceeds from the problem of providing a process for extracting platinum of high purity, whereby platinum can be separated from its alloy elements and impurities in a purity of 99.95 % with simple machinery, in a short period of time, with minimal losses, low expenditure of labour and without addition of expensive chemical substances.

It was surprisingly found that platinum of high purity can be extracted from platinum metal - solutions contaminated with alloys of the platinum by electrolytical means under simultaneous depletion of other noble and base metal impurities.

The subject of the invention is therefore an electrolytical process for extracting platinum of high purity from concentrated hydrochloric solutions of alloys of the platinum with Rh, Ir and/or Pd under simultaneous depletion of other noble and base metal impurities. The process according to the invention is characterized in that the purification process occurs in an electrolysis cell subdivided by a cation exchanger membrane, under potentiostatic or voltage-controlled conditions in the range of 8 V to 16 V and a current density of 12.5 to 37.5 A/dm² and that the precipitated platinum alloy metals are recovered.

According to the invention, the hydrochloric solutions of the platinum have a platinum alloy content of 50 to 700 g/l and total impurities of $\leq$ 5000 ppm.

In the process according to the invention solutions of the alloy having a content of 500 to 700 g/l are preferably used.

The concentrated solutions of the alloys of the platinum used for the process according to the invention display contaminations with the elements Au and/or Ag, Cu, Fe, Co, Ni, Sb, As, Pb, Cd, Al, Mn, Mo, Si, Zn, Sn, Zr, W, Ti, and Cr.

Hydrochloric platinum metal solutions, preferably hexachlorine platinum acid, are used as the anolyte, and 6 to 8 N hydrochloric acid, preferably 6 N hydrochloric acid, is used as the catholyte.

The anode consists of platinum metal, whilst the cathode is made of platinum metal, titanium or

graphite.

A teflone membrane (Nafion[®]-Membrane) is used as the preferred cation exchanger membrane loaded with sulfonic acid groups. The process according to the invention preferably operates under potentiostatic or voltage-controlled conditions in the range of 11.5 V to 12 V and a current density of 22.5 to 35 A/dm².

The base and noble metal impurities precipitate at the cathode with minimal platinum metal contents. It was surprisingly found that the alloy components Ir, Rh and/or Pd precipitate at the anode together with small quantities of the platinum.

The surprising precipitation of the alloy components at the anode was achieved as a result of the higher concentration of the platinum alloy solution and the higher voltage range used in the process according to the invention.

The precipitation at the cathode is mechanically removed from the latter and separately recovered.

The Ir, Rh and/or Pd is refined by further electrolysis after conversion into the solution.

The chlorine gas developing during the process according to the invention is abstracted by known methods.

The metallic platinum can be recovered from the solutions of the platinum metal alloys purified by the process according to the invention by electrolytical or chemical means.

The process according to the invention possesses the following advantages:

- it requires minimal expenditure in terms of machinery and safety technology;
- it causes minimal environmental stress;
- it is far more time- and cost-efficient than conventional processes.

EXAMPLES

The invention is now described by reference to several examples.

Example 1

Electrolytical precipitation of platinum-iridium-1

A hydrochloric platinum-iridium-1 solution with a content of 300 g/l and the impurities (in relation to the platinum metal content)

Au	20 ppm
Fe	136 ppm
Ni	534 ppm
Cu	960 ppm
Pb	24 ppm
Cd	12 ppm
Zn	16 ppm

is electrolyzed in an electrolysis cell, in which cathode and anode are separated by a cation exchanger membrane, under a voltage of 12 V and a

current density of 27.5 A/dm^2 . After an electrolysis period of 20 hours, the base metals and the gold are depleted to a final concentration of $\leq 20 \text{ ppm}$, the rhodium is depleted to a concentration of 150 ppm and the iridium to a concentration of 0.5% . The palladium precipitation occurs in a highly acidic medium in smaller concentrations.

After a further electrolysis period of 20 hours the iridium content $\leq 200 \text{ ppm}$, the rhodium content $\leq 20 \text{ ppm}$ and the palladium content $\leq 100 \text{ ppm}$.

Example 2

Electrolytical precipitation of platinum-rhodium 5

A hydrochloric solution of platinum-rhodium-5 with a platinum metal content of 250 g/l and the impurities (in relation to the platinum metal content)

Ir	250 ppm
Pd	500 ppm
Au	150 ppm
Fe	210 ppm
Ni	453 ppm
Cu	760 ppm
Pb	55 ppm
Cd	22 ppm
Zn	40 ppm

is electrolyzed in an electrolysis cell, in which the cathode and the anode are separated by a cation exchanger membrane, under a voltage of 15 V and a current density of 32.5 to 35 A/dm^2 . After 20 hours the base metal impurities and the gold are depleted

to a concentration of ≤ 20 ppm, the palladium is depleted to a concentration of 400 ppm and the rhodium to a concentration of 1.2 %. After a further electrolysis period of 25 hours a depletion of the rhodium to a concentration of ≤ 200 ppm and of the palladium to ≤ 100 ppm is observed.

Example 3

Electrolytic precipitation of platinum-palladium-5

A hydrochloric solution of platinum-palladium-5 with a metal content of 100 g/l and the impurities (in relation to the platinum metal content)

Ir	400 ppm
Rh	450 ppm
Au	80 ppm
Fe	160 ppm
Ni	500 ppm
Cu	810 ppm
Pb	76 ppm
Cd	15 ppm
Zn	43 ppm

was electrolyzed in an electrolysis cell, in which cathode and anode are separated by a cation exchanger membrane, under a voltage of 11.5 V and a current density of 22.5 A/dm². The base metals and the gold are depleted within 10 hours to contents of ≤ 20 ppm, the iridium and the rhodium are depleted to concentrations of ≤ 100 ppm and the palladium to 2.3 %. After a further electrolysis period of 15 hours depletion of the palladium to values of ≤ 500 ppm is achieved.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Electrolytic process for obtaining platinum of a high purity from concentrated hydrochloric acid solutions containing a platinum alloy, said process comprising the steps of:

a) providing an electrolysis cell having an anode and a cathode and a cation exchanger membrane subdividing said electrolysis cell;

b) placing in said electrolysis cell a concentrated hydrochloric acid solution containing metal impurities and a platinum alloy selected from the group consisting of Platinum-Rhodium alloys, Platinum-Iridium alloys and Platinum-Palladium alloys;

c) applying a potential across said anode and said cathode of 8 V to 16 V to perform an electrolysis under voltage-controlled conditions at a current density of 12.5 to 37.5 A/dm² so as to form a purified platinum-containing solution and at least one platinum alloy metal deposit;

d) recovering said at least one platinum alloy metal deposit; and

e) obtaining the platinum of high purity from said purified platinum-containing solution.

2. Process according to claim 1, wherein said concentrated hydrochloric acid solution of said platinum alloy has a platinum alloy content of 50 to 700 g/l and a content of said metal impurities of not greater than 5000 ppm in relation to a platinum metal content of said concentrated hydrochloric acid solution.
3. Process according to claim 2, wherein said platinum alloy content of said concentrated hydrochloric acid solution is between 500 to 700 g/l.
4. Process according to claim 1, 2 or 3, wherein said metal impurities in said concentrated hydrochloric acid solution contain at least one element selected from the group consisting of Au, Ag, Cu, Fe, Co, Ni, Sb, As, Pb, Cd, Al, Mn, Mo, Si, Zn, Sn, Zr, W, Ti and Cr.
5. Process according to any one of claims 1 to 4, wherein said concentrated hydrochloric acid solution surrounds said anode so as to form an anolyte and is 6 to 8 N in HCl, and further comprising placing a 6 to 8 N concentrated hydrochloric acid solution around said cathode to provide a catholyte around said cathode.
6. Process according to claim 5, wherein said anolyte comprises hexachloric platinum acid.

7. Process according to claim 5 or 6, wherein said catholyte comprises said 6 N concentrated hydrochloric acid solution.

8. Process according to any one of claims 1 to 7, wherein said potential applied across said anode and cathode is from 11.5 to 12 V and said current density is from 22.5 to 35 A/dm².

9. Process according to any one of claims 1 to 8, further comprising controlling said potential so that chlorine gas is generated during said electrolysis and removing said chlorine gas from said electrolysis cell.

10. Process according to any one of claims 1 to 9, wherein said anode is made of platinum metal and said cathode is made of a member selected from the group consisting of platinum, titanium and graphite.

11. Process according to any one of claims 1 to 10, wherein said cation exchanger membrane is a TeflonTM membrane.

12. Process according to any one of claims 1 to 11, wherein said at least one platinum alloy metal deposit is formed on said anode and at least one other platinum alloy

metal deposit containing at least one of said metal impurities is deposited on said cathode.

13. Process according to claim 12, wherein said at least one other platinum alloy metal deposit is mechanically removed from said cathode.

14. Process according to claim 12, wherein said at least one platinum alloy metal deposit is mechanically removed from said anode, dissolved to form an anode deposit-containing solution, and further comprising purifying said anode deposit-containing solution by electrolysis.

15. Process according to any one of claims 1 to 14, wherein said obtaining of said platinum of said high purity from said purified platinum-containing solution occurs by an electrolytic method.

16. Process according to any one of claims 1 to 14, wherein said obtaining of said platinum of said high purity from said purified platinum-containing solution occurs by chemical means.

17. Process according to any one of claims 1 to 16, wherein said potential is applied across said anode and

said cathode during said electrolysis under potentiostatic conditions.

18. Electrolytic process for obtaining a purified platinum-containing solution from a concentrated hydrochloric acid solution containing at least one platinum alloy and metal impurities, said process comprising the steps of:

a) providing an electrolysis cell having an anode and a cathode and a cation exchanger membrane subdividing said electrolysis cell;

b) placing in said electrolysis cell a concentrated hydrochloric acid solution containing not greater than 5000 ppm of the metal impurities in relation to a platinum metal content of said concentrated hydrochloric acid solution and 50 to 700 g/l of a platinum alloy selected from the group consisting of Platinum-Rhodium alloys, Platinum-Iridium alloys and Platinum-Palladium alloys, said metal impurities containing at least one element selected from the group consisting of Au, Ag, Cu, Fe, Co, Ni, Sb, As, Pb, Cd, Al, Mn, Mo, Si, Zn, Sn, Zr, W, Ti and Cr;

c) applying a potential across said anode and said cathode of 8 V to 16 V to perform an electrolysis under voltage-controlled conditions at a current density of

12.5 to 37.5 A/dm² so as to form the purified platinum-containing solution and at least one platinum alloy metal deposit; and

d) recovering said at least one platinum alloy metal deposit.

19. Process according to claim 18, wherein said concentrated hydrochloric acid solution surrounds said anode so as to form an anolyte and is 6 to 8 N in HCl, and further comprising placing a 6 to 8 N concentrated hydrochloric acid solution around said cathode to provide a catholyte around said cathode.

20. Process according to claim 18 or 19, wherein said potential applied across said anode and cathode is from 11.5 to 12 V and said current density is from 22.5 to 35 A/dm².

21. Process according to claim 18, 19 or 20, wherein said potential is applied across said anode and said cathode during said electrolysis under potentiostatic conditions.

22. Process according to any one of claims 18 to 21, further comprising controlling said potential so that chlorine gas is generated during said electrolysis and removing said chlorine gas from said electrolysis cell.

23. Process according to any one of claims 18 to 22, wherein said anode is made of platinum metal and said cathode is made of a member selected from the group consisting of platinum, titanium and graphite.

24. Process according to any one of claims 18 to 23, wherein said cation exchanger membrane is a Teflon™ membrane.

25. Process according to any one of claims 18 to 24, further comprising the step of obtaining a platinum of high purity from said purified platinum-containing solution formed during said electrolysis.

26. Process according to claim 25, wherein said obtaining of said platinum of said high purity from said purified platinum-containing solution occurs by an electrolytic method.

27. Process according to claim 25, wherein said obtaining of said platinum of said high purity from said purified platinum-containing solution occurs by chemical means.