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(54) **ELECTROGENERATED CHLORINE OR CHLORIDE COMPOUND LEACHING AND ITS APPARATUS**

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(75) Inventors: **Min-Seuk Kim**, Daejeon-city (KR);  
**Jae-Chun Lee**, Daejeon-city (KR);  
**Jin-Ki Jeong**, Daejeon-city (KR)

Correspondence Address:  
**THE WEBB LAW FIRM, P.C.**  
**700 KOPPERS BUILDING**  
**436 SEVENTH AVENUE**  
**PITTSBURGH, PA 15219 (US)**

(73) Assignee: **Korea Institute of Geoscience and Mineral Resources**, Daejeon-city (KR)

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(57) **ABSTRACT**  
 The present invention relates to a precious metal leaching method by electrogenerated chlorine and its apparatus, more precisely, the electroleaching apparatus is composed of two reaction chambers at both sides (right and left) which is divided by central separation membrane; one of the reaction chamber is leaching chamber equipped with chlorine leaching-stable electrode for the electrogeneration of chlorine and stirrer for solution stirring and the other reaction chamber is reduction chamber equipped with electrode used for electrolytic recovery of some parts or entire compounds of leached precious metal, and the apparatus can additionally include separator/purifier for quick recovery of targeted precious metal, if necessary. The present invention provides a very simple leaching method and an apparatus thereof which has high leaching efficiency and enables the recovery of leached precious metal.

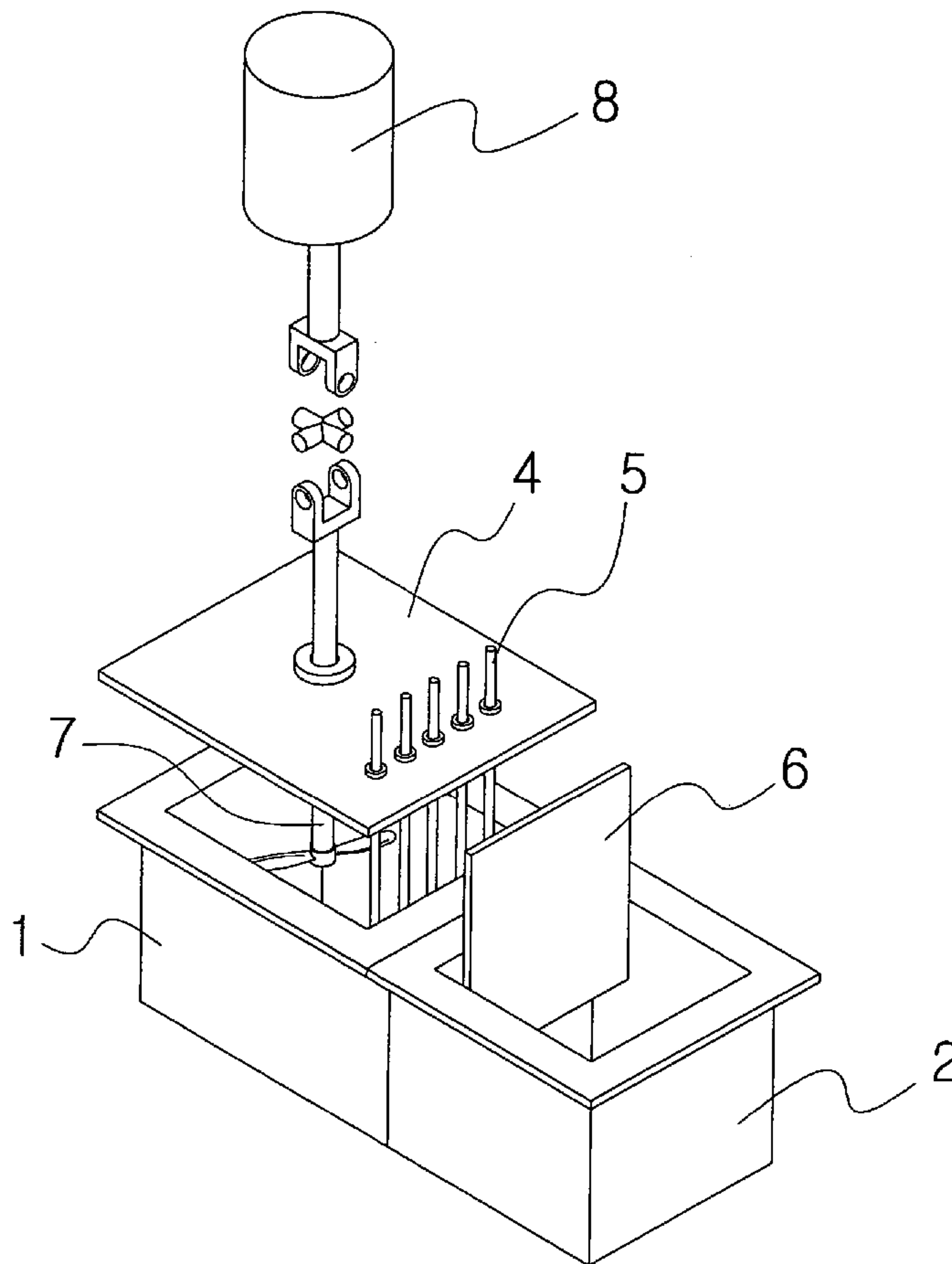


Fig 1.

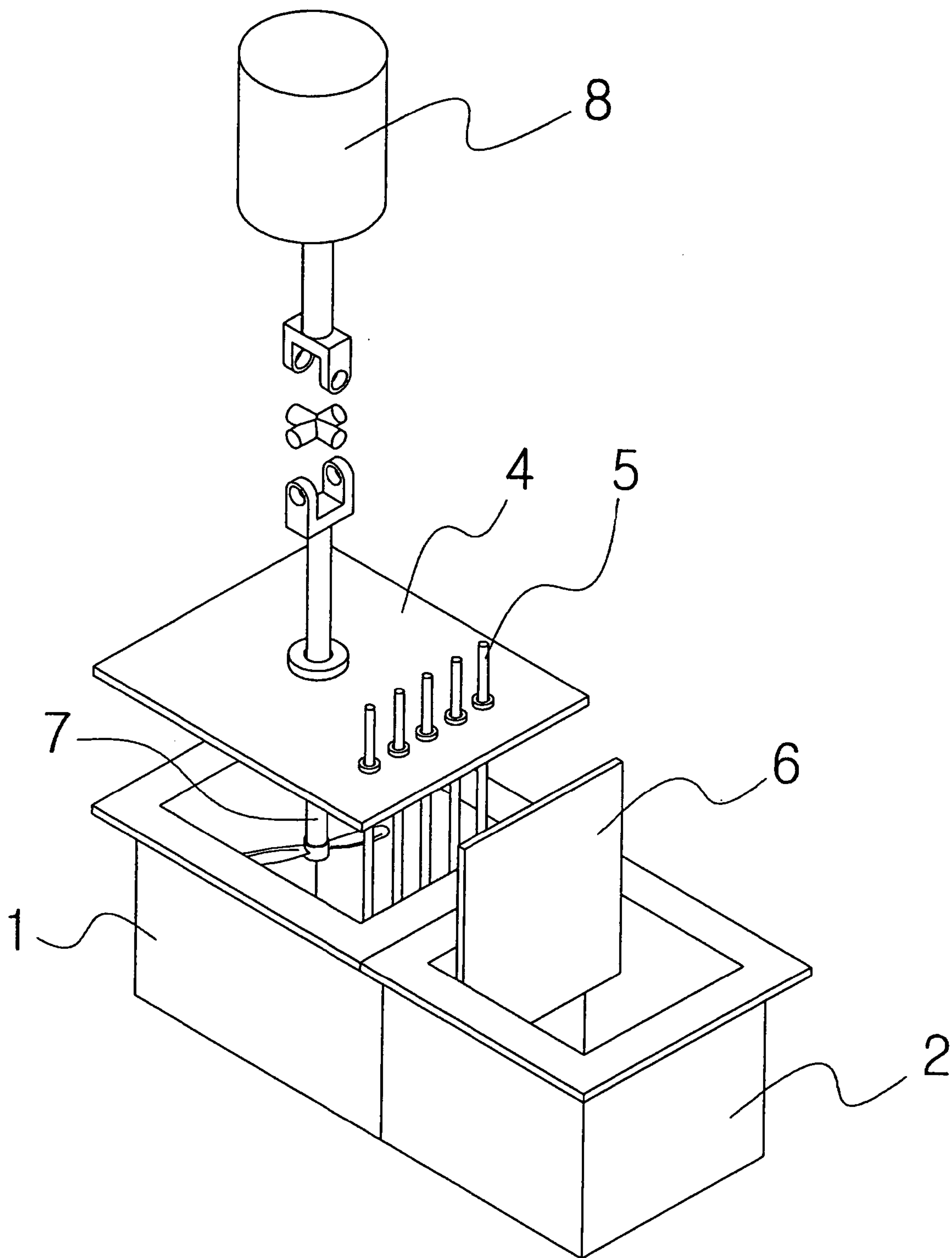


Fig 2.

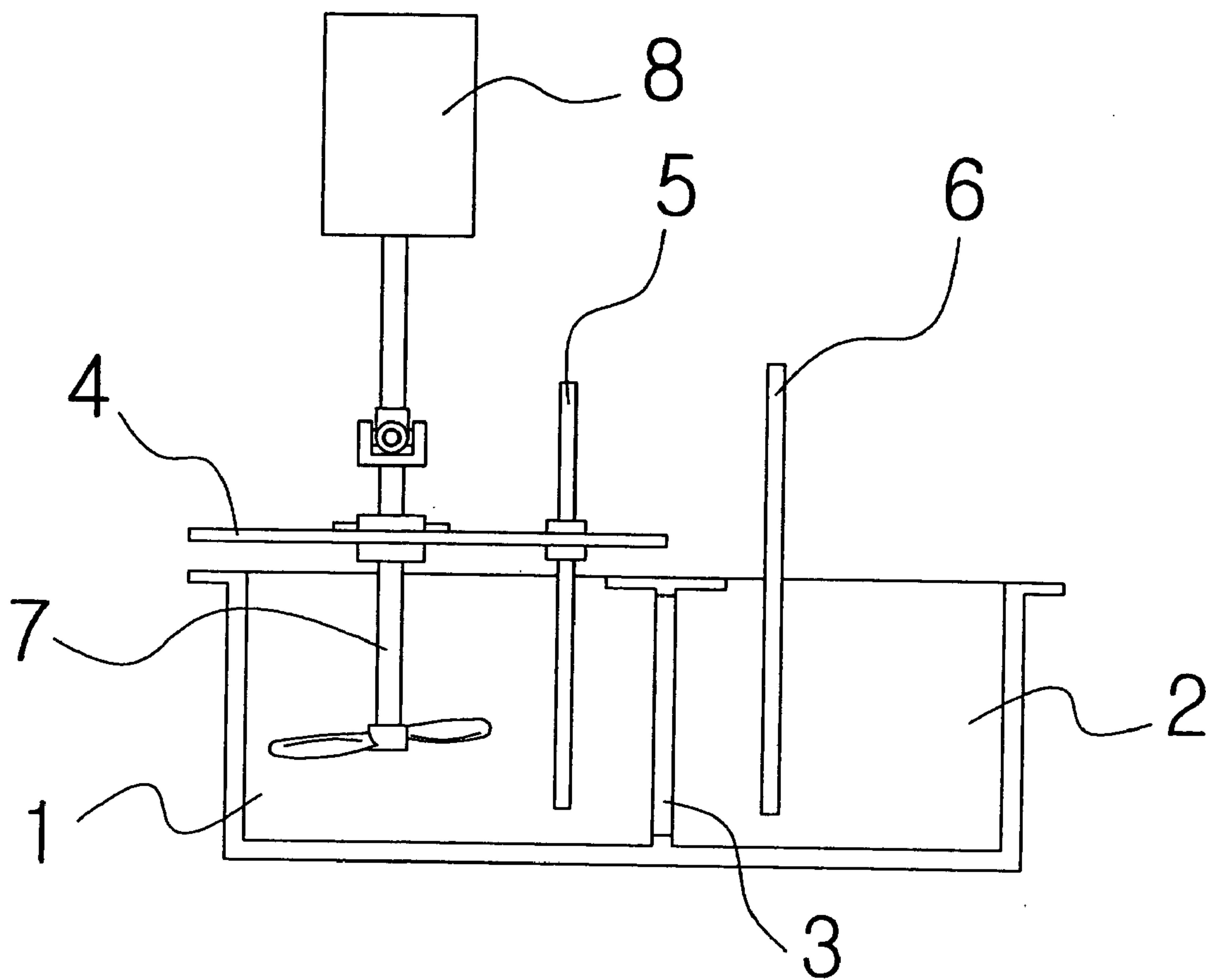
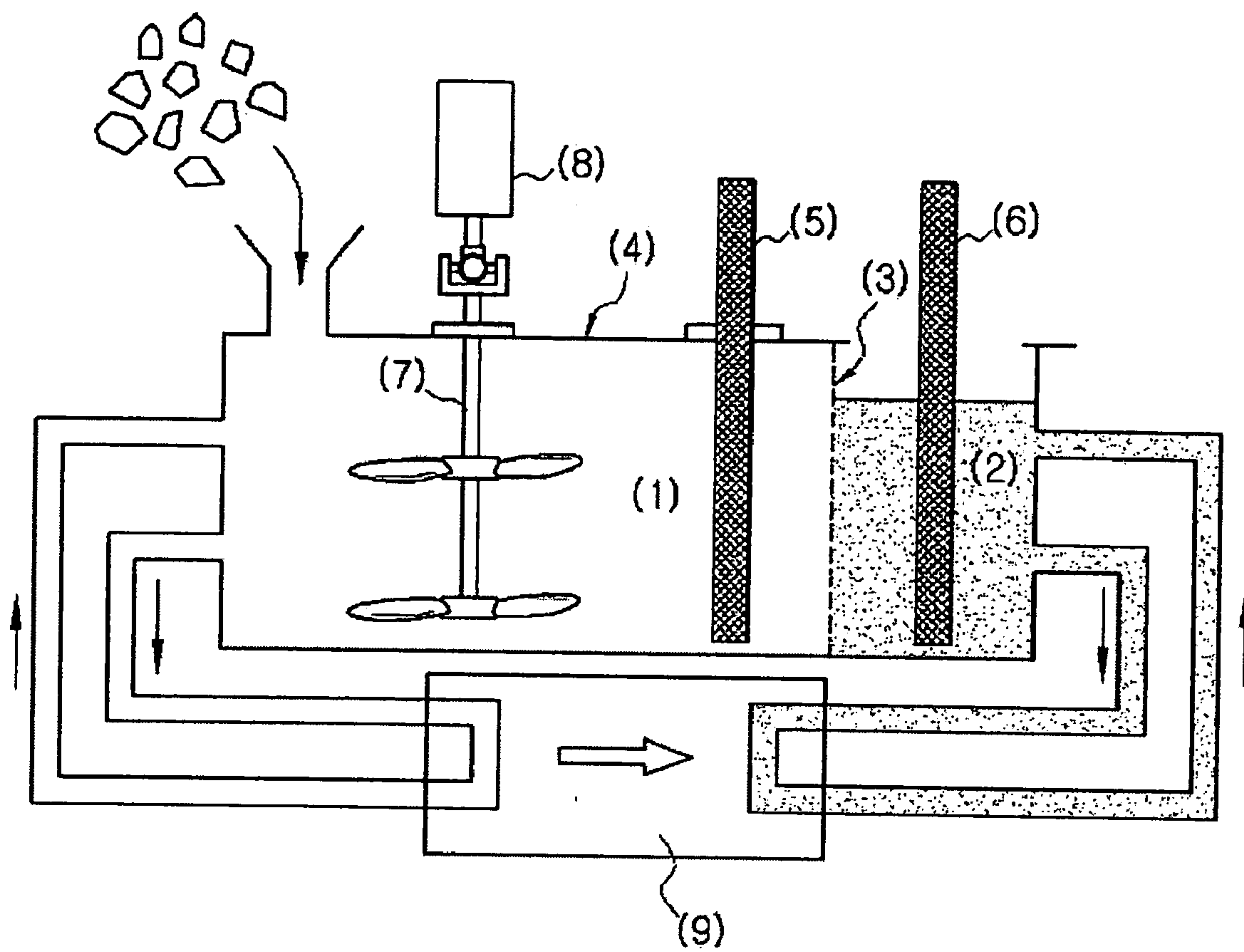


Fig 3.





**ELECTROGENERATED CHLORINE OR  
CHLORIDE COMPOUND LEACHING AND ITS  
APPARATUS**

TECHNICAL FIELD

[0001] The present invention relates to a leaching method of precious metal including copper by electrogenerated chlorine and its apparatus.

BACKGROUND ART

[0002] For leaching of precious metals including copper with high oxidation-reduction potential or poorly soluble metals, they are reacted with oxidizing acid at high concentration at high temperature. At this time, huge amount of acid is required owing to the continuous acid consumption, causing environmental problem by the post-treatment of resultant waste solution. To recover leached precious metals including copper, a special apparatus is needed, for which extra energy is required.

[0003] The conventional chlorine leaching method is to inject chlorine gas stored in a compressed gas cylinder into a reaction vessel (Hydrometallurgy, 29(1992) 205-215) or to produce chlorine chemically by adding chemicals. However, the conventional leaching method has safety problems and complications in handling chlorine gas outside the leaching vessel. In addition, a separate leached metal recovery step is necessary upon completion of leaching, like the acid leaching method.

[0004] To recycle precious metals including copper with high oxidation-reduction potential or poorly soluble metals, a safe and low-energy pro-environmental leaching and recovery method and an apparatus thereof are required.

DISCLOSURE OF THE INVENTION

[0005] It is an object of the present invention to provide a precious metal leaching method by electrogenerated chlorine or chloride compound and its apparatus, which requires minimum amount of acid at lower concentration than that used for conventional leaching, simple equipment and simultaneous leaching and precious metal recovery to have high energy efficiency, and thereby improves energy efficiency of whole process by separation/purification of recovered metal ions.

[0006] It is another object of the present invention to provide a precious metal and poorly soluble metal leaching using the electroleaching apparatus above and a recovery method for the leached precious metals.

[0007] Hereinafter, the present invention is described in detail.

[0008] The present invention relates to electrogenerated chlorine leaching from solid substance containing precious metals including copper, which have not been leached by the conventional chemical leaching and its apparatus, precisely the leaching method composed of the steps of electrogeneration stage of chlorine which oxidizes chloride ions contained in solution at anode, leaching reaction stage of electrogenerated chlorine with leaching target and recovery stage of leached precious metals including copper occurring at cathode simultaneously and an apparatus for realizing the leaching.

[0009] The method of the present invention is characterized by that electrogeneration of chlorine or chloride compound occurs simultaneously with leaching reaction using the same in a same reactor.

[0010] The present invention relates to a leaching method using chlorine or chloride compound electrogenerated at anode in leaching solution containing chloride ions and an electroleaching apparatus for recovering leached precious metals including copper at cathode simultaneously with the leaching.

[0011] The present invention provides another apparatus that additionally includes separator/purifier in which leached precious metals including copper in oxidation chamber is separated, purified and transferred in order to selectively recover a target metal. The separator/purifier is equipped on the pathway between reaction chamber at anode and recovery chamber, so precious metal ions generated in leaching chamber can be selectively transferred into recovery chamber where reduction occurs. Then, the precious metal ions are converted at cathode in recovery chamber, leading to the recovery of targeted metals. That is, the supplementary apparatus enables efficient recovery of leached precious metals including copper and shortens recovery time by additional separator/purifier equipped for the purpose of recovering and transferring target metal ions only, among leached various metals, into reduction chamber.

[0012] The electroleaching method using electrogenerated chlorine or chloride compound of the present invention electrogenerates highly oxidizing chlorine or chloride compound directly in reaction solution at comparatively low temperature. Thus, the leaching method is always possible when low concentration of chloride ions is supplied. Theoretically, no chlorine is lost in the reaction solution, and thus surplus chlorine or chloride compound supply is not necessary for leaching. Besides, as a counter-action to electrogeneration of chlorine or chloride compound, electro-recovery of leached precious metals including copper is simultaneously carried out, making the method of the invention energy-efficient. In particular, chlorine, which might cause an environmental problem when it leaks, is only generated and consumed inside the restricted device in reactor according to the method of the invention. Therefore, the electroleaching method provided by the present invention is very safe and equipped simply, compared with the conventional chlorine leaching method.

[0013] The separator/purifier equipped in the apparatus of the present invention has functions of separation/purification and transfer of leached precious metal ions, leached using chlorine or chloride compound generated in leaching chamber, according to solvent extraction or ion exchange technique to reduction chamber. The techniques involved in separation and purification by separator/purifier of the invention are based on the conventional method using solvent extraction or ion exchange technique which is well-known to those in the art. Thus, any informed techniques can be used. For example, solvent extraction method described in J. of the Korea Inst. of Met. & Mater. pp 486-490, Vol. 34, No 4 (1996) or the same description of pp 399-403, Vol. 43, No 5 (2005) can be applied to the apparatus. Ion exchange technique described in J. of the Korea Inst. of Met. & Mater. pp 600-607, Vol. 30, No 5 (1992) can be applied to the separator/purifier, which will be connected to the electroleaching apparatus of the present invention.



[0014] Salts or acids can be added to the leaching solution of the present invention. Salts can be added for the purpose of endowing ionic conductivity to electrolyte and available salts are exemplified by chlorine ion containing salts such as ammonium chloride ( $\text{NH}_4\text{Cl}$ ), potassium chloride ( $\text{KCl}$ ) and sodium chloride ( $\text{NaCl}$ ), sulfate and nitrate, etc. Acid is not limited in a specific kind, but general acid compounds including organic acid or inorganic acid can be used as long as it can increase ionic conductivity.

[0015] When anodic current is applied to anode in leaching solution containing chloride ions according to the present invention, chlorine generation reaction is carried out by the following formula (1).



[0016] Chlorine generated at anode is spread in leaching solution by efficient stirring and then reacted with solid substance included in the leaching solution by the following formula (2) and (3), resulting in leaching. At this time, chlorine which has been used for leaching of metal (M) turns into chloride ions, so the loss of chlorine source in leaching solution is minimum and additional chlorine supply is not necessary.

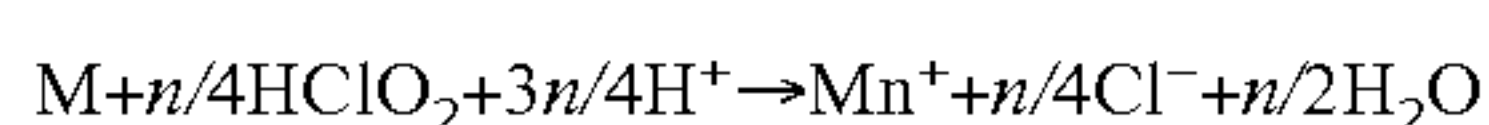
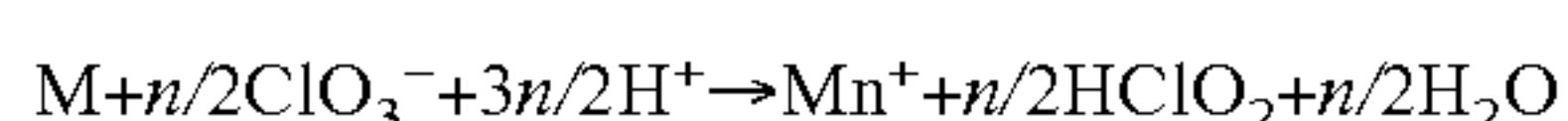
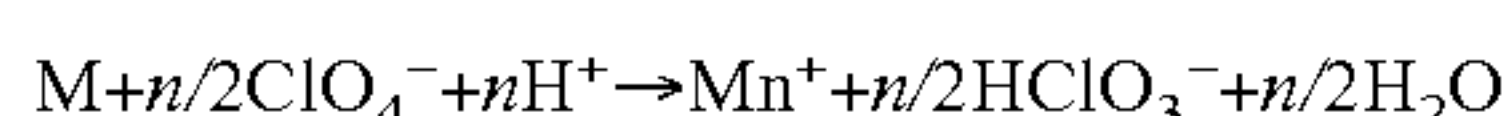
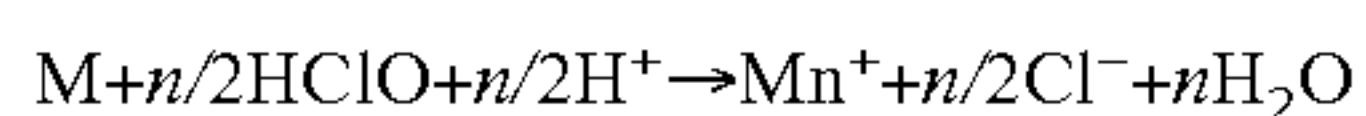


[0017] The entire reaction formula is represented by formula (4).



[0018] The metals having lower redox potential than that of chlorine can be leached by the above reaction. When anodic current is applied, voltage increases, resulting in the generation of chloride compound 'oxychloride', which is also an oxidizing compound useful for leaching.

[0019] According to the present invention, chloride compound is exemplified by  $\text{HClO}$ ,  $\text{HClO}_2$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{ClO}_2$ ,  $\text{ClO}^-$  and  $\text{ClO}_2^-$ . The following formulas are examples of leaching reactions by those compounds. That is, precious metals including copper are leached by the following leaching reactions in acids.



[0020] Unlike water-soluble chlorine, reaction with the above compounds consumes hydrogen, so a system mostly generating chlorine is preferred in the aspect of efficiency.

[0021] Electroleaching apparatus of the present invention is described in more detail hereinafter with reference to the attached figures.

[0022] First, the apparatus without separator/purifier of FIG. 1 and FIG. 2 is described and next the apparatus equipped with separator/purifier of FIG. 3 is described.

[0023] FIG. 1 is a schematic diagram illustrating the electroleaching apparatus according to the present invention, and FIG. 2 is a cross section illustrating the electroleaching apparatus according to the present invention. Precisely, these Figures illustrate the apparatus of the invention which is composed of leaching chamber (1) and leached metal recovery chamber (2), which are divided by central separation

membrane (3); cover of leaching chamber (4); stirring rod (7) and stirring motor (8), electrolyte stirring device of leaching chamber; anode (5) for electrogeneration of chlorine in leaching chamber; and cathode (6) of leached metal recovery chamber.

[0024] The separation membrane (3) is one of simple separation membrane, through which leached metal ions are passed but leachate or electrogenerated chlorine or chloride compound cannot be passed, ion exchange membrane or combination of the two. Leaching chamber (1) and recovery chamber (2) are both made of corrosion resistant substance against oxidation of chlorine or chloride compound and the vessel can be modified in various forms. The cover of leaching chamber (4) plays a role in preventing the leakage of electrogenerated chlorine or chloride compound, that is the cover is to seal the leaching chamber, and at the same time, to support stirring rod (7) and anode (5). Stirring rod (7) plays a key role in increasing efficiency in leaching by mixing electrogenerated chlorine into electrolyte, and stirring blade can be designed in various forms to maximize the effect. Anode (5) plays a role in electrogenerating chlorine or chloride compound as anodic current is applied, and can be produced in various forms of physicochemically stable graphite or other conductors, which are stable during electrogeneration of chlorine or chloride compound. Stirring rod (7) and anode (5) can be designed in different forms and locations. Stirring motor (8) can be attached on the cover (4) of leaching chamber or installed separately.

[0025] Cathode (6) of leached metal recovery chamber is the place where leached metal ions are electrolytic reduced and recovered, which can be prepared with most conductive material that is stable in chloride ion containing electrolyte. In general, stainless steel plate is built as a cathode for convenience.

[0026] The electroleaching method and the operation mechanism of apparatus, according to the present invention, are described hereinafter. The electroleaching apparatus of the invention is stable in leaching solution containing electrogenerated chlorine and can be built with various materials having enough mechanical strength for keeping the functions of the apparatus. In the apparatus, during leaching, anodic current is applied to anode (5), by which chloride ions included in leaching solution are oxidized into chlorine or chloride compound, and then followed by stirring by stirring rod (7). As a result, electrogenerated chlorine or chloride compound is reacted with metal compound in leachate and dissolve the compound into metal ions. During the dissolution, chlorine or chloride compound is re-reduced into chloride ions, indicating that chloride ions in leaching solution are not consumed. The amount of electrogenerated chlorine per unit time is determined by the amount of anodic current and anode, which is closely related to the leaching amount. The leached metal remains in leaching solution as metal ions. If a simple separation membrane is equipped, the metal ions move to reduction chamber through the separation membrane (3) and then are reduced electrochemically as metal at cathode where cathodic current is flowing. The electro-reduction is replaced with hydrogen generation when anion exchange membrane is used as a separation membrane.

[0027] A separate solution heating device can be used to regulate electrolyte for electroleaching. In addition, it is



possible to install a separate device for sample loading and residue recovery without breaking airtight leaching apparatus.

[0028] FIG. 3 illustrates the electroleaching apparatus equipped with separator/purifier. The functions of the apparatus, except that of separator/purifier, are same as the apparatus of FIG. 1, so illustration on the functions is not given here again. Separator/purifier takes charge of separating target metal ions which were separated by solvent extraction or ion exchange technique, a method for concentrating a specific metal dissolved in leaching chamber, and then sending the metal ions to reduction chamber, a recovery chamber. The separator/purifier might be equipped with solid/liquid separation filter or a specific organic adsorption filter according to a purpose.

[0029] A separate storage vessel can be installed in between separator/purifier and recovery chamber to store remaining solution.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0030] FIG. 1 is a schematic diagram of the electroleaching apparatus of the present invention.

[0031] FIG. 2 is a cross section of the electroleaching apparatus of the present invention.

[0032] FIG. 3 is a schematic diagram of the electroleaching apparatus of the present invention equipped with separator/purifier.

[0033]

Description of the Drawings Code	
1: leaching chamber	2: recovery chamber
3: separation membrane	4: cover
5: anode	6: cathode
7: stirring rod	8: stirring motor
9: separator/purifier	

#### BEST MODE FOR CARRYING OUT THE INVENTION

[0034] Practical and presently preferred embodiments of the present invention are illustrative as shown in the following Examples and Comparative Examples.

[0035] However, it will be appreciated that those skilled in the art, on consideration of this disclosure, may make modifications and improvements within the spirit and scope of the present invention.

#### EXAMPLE 1

[0036] Electronic scrap containing approximately 45.7% metal (a target for leaching) and Cu as a major metal compound is used as a leaching sample. Electrogenerated chlorine leaching was performed using 400 mL of 1 M HCl solution. The average particle size of crushed scrap was 0.6 mm ~1.2 mm, and 10 g of the scrap was used for experiment. Graphite having 50 cm<sup>2</sup> of surface area was used as an anode and titanium was used as a cathode. Applied current was 20 mA/cm<sup>2</sup>, stirring speed was 400 rpm, and solution tempera-

ture was 50° C. 180 minutes later, leaching efficiency of metal component was 97.4%.

#### EXAMPLE 2

[0037] Electronic scrap containing approximately 45.7% metal (a target for leaching) and Cu as a major metal compound is used as a leaching sample. Electrogenerated chlorine leaching was performed using 400 mL of 1 M HCl solution. The average particle size of crushed scrap was 0.6 mm ~1.2 mm, and 10 g of the scrap was used for experiment. Graphite having 50 cm<sup>2</sup> of surface area was used as an anode and titanium was used as a cathode. Applied voltage was 4 V, stirring speed was 400 rpm, and solution temperature was 50° C. 180 minutes later, leaching efficiency of metal component was 95.2%.

#### EXAMPLE 3

[0038] Electronic scrap containing approximately 45.7% metal (a target for leaching) and Cu as a major metal compound is used as a leaching sample. Electrogenerated chlorine leaching was performed using 400 mL of 0.5 M HCl solution. The average particle size of crushed scrap was 0.6 mm ~1.2 mm, and 10 g of the scrap was used for experiment. Graphite having 50 cm<sup>2</sup> of surface area was used as an anode and titanium was used as a cathode. Applied current was 10 mA/cm<sup>2</sup>, stirring speed was 800 rpm, and solution temperature was 50° C. 180 minutes later, leaching efficiency of metal component was 93.5%.

#### EXAMPLE 4

[0039] Electronic scrap containing approximately 45.7% metal (a target for leaching) and Cu as a major metal compound is used as a leaching sample. Electrogenerated chlorine leaching was performed using 400 mL of 1 M HCl solution. The average particle size of crushed scrap was 0.6 mm ~1.2 mm, and 10 g of the scrap was used for experiment. Graphite having 50 cm<sup>2</sup> of surface area was used as an anode and titanium was used as a cathode. Applied current was 10 mA/cm<sup>2</sup>, stirring speed was 800 rpm, and solution temperature was 30° C. 180 minutes later, leaching efficiency of metal component was 91.5%.

#### EXAMPLE 5

[0040] Electronic scrap containing approximately 45.7% metal (a target for leaching) and Cu as a major metal compound is used as a leaching sample. Electrogenerated chlorine leaching was performed using 400 mL of 1 M HCl solution. The average particle size of crushed scrap was 0.6 mm ~1.2 mm, and 10 g of the scrap was used for experiment. Graphite having 50 cm<sup>2</sup> of surface area was used as an anode and titanium was used as a cathode. As a separation membrane, Neosepta CMX cation exchange membrane (Tokuyama, Japan) was used. Applied current was 10 mA/cm<sup>2</sup>, stirring speed was 800 rpm, and solution temperature was 30° C. 180 minutes later, leaching efficiency of metal component was 91.5%.

[0041] Leaching solution was circulated through separator/purifier which was three layered acryl mixer-settler (10 cm×15 cm×30 cm). For solvent extraction of Cu, kerosene was used as organic phase, LIX 84 (2-hydroxy-5-nonylacetophenon oxime) was used as extractant, and aqueous phase was replaced with sulfuric acid solution for stripping.



Considering the efficiency of reduction recovery process, the sulfuric acid solution used herein kept its Cu content at least 30 g/L, was primarily stored in a reservoir and then being circulated from reservoir through reduction chamber at the speed of 200 mL/min. The Cu obtained in reduction chamber was 1.68 g (current efficiency was 99.5%). The Cu purity was more than 3 N.

#### INDUSTRIAL APPLICABILITY

[0042] The electrogenerated chlorine leaching method of the present invention has advantages of using lower concentration of acid as electrolyte, no use of additional chlorine supply during leaching, high production efficiency and least possibility of chlorine leakage, suggesting that it is very stable and efficient method, compared with the conventional chlorine leaching methods. The electroleaching apparatus of the present invention is constructed to enable simultaneous leaching by using electrogenerated chlorine and electro-reduction of leached metal ion, showing high energy efficiency. The additional use of separator/purifier increases the purity of a recovered target metal, and thereby increases energy efficiency of whole process.

[0043] Those skilled in the art will appreciate that the conceptions and specific embodiments disclosed in the foregoing description may be readily utilized as a basis for modifying or designing other embodiments for carrying out the same purposes of the present invention. Those skilled in the art will also appreciate that such equivalent embodiments do not depart from the spirit and scope of the invention as set forth in the appended claims.

1-11. (canceled)

12. An airtight electroleaching apparatus for precious metals using electrogenerated chlorine or a chloride compound, comprising a leaching chamber and a leached metal recovery chamber divided by a separation membrane, an anode for electrogeneration of the chlorine or chloride compound in the leaching chamber and a cathode in the leached metal recovery chamber.

13. The airtight electroleaching apparatus for precious metals using electrogenerated chlorine or a chloride compound as set forth in claim 12, further comprising a separator/purifier for separating and sending leached metal in the leaching chamber to the leached metal recovery chamber.

14. The airtight electroleaching apparatus for precious metals using electrogenerated chlorine or a chloride compound as set forth in claim 12, wherein the leaching chamber additionally includes a stirring rod, a stirring motor operating stirring rod, and an airtight cover.

15. The airtight electroleaching apparatus for precious metals using electrogenerated chlorine or a chloride compound as set forth in claim 13, wherein the leaching chamber additionally includes a stirring rod, a stirring motor operating stirring rod, and an airtight cover.

16. The airtight electroleaching apparatus for precious metals using electrogenerated chlorine or a chloride compound as set forth in claim 12, wherein the separation membrane is selected from the group consisting of a porous separation membrane through which leached metal ions or solvent is passed, an ion exchange membrane through which only specific ions are passed, or a combination of the two.

17. The airtight electroleaching apparatus for precious metals using electrogenerated chlorine or a chloride compound as set forth in claim 13, wherein the separation

membrane is selected from the group consisting of a porous separation membrane through which leached metal ions or solvent is passed, an ion exchange membrane through which only specific ions are passed, or a combination of the two.

18. The airtight electroleaching apparatus for precious metals using electrogenerated chlorine or a chloride compound as set forth in claim 12, wherein the anode is made by a material that is electrochemically stable under the application of anodic current or voltage for electrogeneration of chlorine or a chloride compound and that is chemically stable under oxidation according to the electrogenerated chlorine or the chloride compound.

19. The airtight electroleaching apparatus for precious metals using electrogenerated chlorine or a chloride compound as set forth in claim 13, wherein the anode is made by a material that is electrochemically stable under the application of anodic current or voltage for electrogeneration of chlorine or a chloride compound and that is chemically stable under oxidation according to the electrogenerated chlorine or the chloride compound.

20. The airtight electroleaching apparatus for precious metals using electrogenerated chlorine or a chloride compound as set forth in claim 13, wherein the separator/purifier takes charge of separating target metal ions which were separated by solvent extraction or by an ion exchange resin and then sending the metal ions to the leached metal recovery chamber.

21. An electroleaching method for precious metals using electrogenerated chlorine comprising the following steps:

adding a leaching sample containing a metal component into an airtight leaching chamber containing chloride ions;

applying current or voltage to an anode in a leaching chamber to electrogenerate chlorine or a chloride compound; and

electrogenrating chlorine and reacting the leaching sample with the chlorine simultaneously.

22. The electroleaching method for precious metals using electrogenerated chlorine as set forth in claim 21, further comprising the step of recovering leached metal from a cathode.

23. The electroleaching method for precious metals using electrogenerated chlorine as set forth in claim 21, wherein the anode and cathode are separated by a separation membrane.

24. The electroleaching method for precious metals using electrogenerated chlorine as set forth in claim 21, further including the step of stirring the leaching sample with a stirring rod at the anode to promote leaching.

25. The electroleaching method for precious metals using electrogenerated chlorine as set forth in claim 22, further including the step of stirring the leaching sample with a stirring rod at the anode to promote leaching.

26. The electroleaching method for precious metals using electrogenerated chlorine as set forth in claim 23, further including the step of stirring the leaching sample with a stirring rod at the anode to promote leaching.

27. The electroleaching method for precious metals using electrogenerated chlorine as set forth in claim 24, wherein



the stirring rod is installed in the leaching chamber and then sealed by an airtight cover.

**28.** The electroleaching method for precious metals using electrogenerated chlorine as set forth in claim 25, wherein the stirring rod is installed in the leaching chamber and then sealed by an airtight cover.

**29.** The electroleaching method for precious metals using electrogenerated chlorine as set forth in claim 26, wherein the stirring rod is installed in the leaching chamber and then sealed by an airtight cover.

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