

DESCRIPTION

METAL RECOVERING DEVICE

TECHNICAL FIELD

5 [0001] The present invention relates to a metal recovery apparatus for recovering metals from a solution containing metals by an electrolysis method.

BACKGROUND ART

10 [0002] Among waste solutions (e.g. treatment solutions) discharged from industrial plants or the like, there are some which contain metals, for instance, Au, Ag, Cu, platinum-group elements, and the like and these metals are recovered from the waste solutions and reused. As a method for recovering metals from waste solutions has been known an electrolysis
15 method.

[0003] As a metal recovery apparatus using an electrolysis method, for instance, Patent Document 1 proposes a recovery apparatus including a cylindrical inner electrode as a cathode and an outer electrode as an anode installed in the surrounding of the inner electrode and configured in a
20 manner that the cathode is enabled to rotate and a plastic recovery plate is installed in the neighborhood of a surface of the cathode precipitating metals to scrape off metals precipitated on the surface of the cathode in such a condition that the plate contacts with or is adjacent to the surface of the cathode. According to the method of Patent Document 1, it is disclosed that
25 the metals precipitated on the cathode surface are scraped off using the

plastic recovery plate without depositing the metals on the electrode and accumulated under the cathode and thereafter, the metals can be recovered.

[0004] For industrial recovery of metals from waste solutions, it is desired to heighten the recovery efficiency so as to recover the metals within a time as

5 short as possible. However, with the recovery apparatus disclosed in Patent Document 1, the metal recovery efficiency is inferior and it takes a long time to recover metals. Further, since metals are accumulated under the cathode

by scarping the electrodeposited metals on the cathode surface by the plastic recovery plate in Patent Document 1, the recovery apparatus cannot be made

10 compact for saving an installation space. Further, with respect to some kinds of waste solutions, metals accumulated under the cathode are sometimes re-dissolved and metals cannot be recovered sufficiently from waste solutions.

[0005] As a method for increasing the metal recovery efficiency are proposed,

15 for instance, methods using cathode disk plates in Patent Document 2 and Patent Document 3.

[0006] Patent Document 2 discloses that electrolysis is carried out while a disk plate type cathode is rotated to keep good contact between the cathode and an electrolytic solution and thus increase the metal recovery efficiency.

20 Patent Document 3 also discloses a mode of a rotating operation mechanism for rotating one of an anode or a cathode and a mode of installation of stirring blades in the anode or the cathode to improve the metal recovery efficiency by efficiently stirring a solution in an electrolysis bath.

[0007] However, in the case where a cathode disk plate is used just like the
25 case of Patent Document 2, to increase the metal recovery efficiency, it is

required to increase a revolution number of the cathode to an excess extent and thus there is a problem that the equipment load is high.

[0008] On the other hand, although it is not a technique proposed to increase the metal recovery efficiency, Patent Document 4 proposes a metal
5 recovery apparatus including a pipe-like anode and a tubular cathode, wherein a reticulated or lath-like cylinder electrically connected to the cathode is arranged in the inner circumference of the cathode.

[0009] In the recovery apparatus of Patent Document 4, the reticulated or lath-like cylinder arranged in the inner circumference of the cathode is
10 arranged in order to prevent occurrence of short circuit by contact of an electrodeposited metal and the anode when the electrolysis proceeds and the metal electrodeposited on the cathode is separated from the cathode. According to Fig. 1 of Patent Document 4, the reticulated or lath-like cylinder is arranged at a space without being closely attached to the cathode.
15 Further, a portion of the metal electrodeposited on the cathode surface is separated from the cathode and accumulated under the cathode.

[0010] Patent Document 1: Japanese Patent Application Laid-Open No.
61-104096

Patent Document 2: Japanese Patent Application Laid-Open No. 2006-70364

20 Patent Document 3: Japanese Patent Application Laid-Open No.
2005-314742

Patent Document 4: Japanese Patent Application Laid-Open No. 2006-28555

DISCLOSURE OF THE INVENTION

25 PROBLEMS TO BE SOLVED BY THE INVENTION

[0011] An object of the present invention is to provide an apparatus to be used in recovering a metal from a metal-containing solution by electrolysis, which can be installed in a saved space and reduce equipment load and is remarkably excellent in the recovery efficiency for recovering the metal
5 within a short time.

MEANS FOR SOLVING THE PROBLEMS

[0012] A metal recovery apparatus according to the present invention which solves the above-mentioned problems is an apparatus for recovering a metal
10 by electrolyzing a metal-containing solution and is characterized in that the apparatus comprises a columnar or tubular rotary cathode rotating on a shaft, an anode installed opposite to the rotary cathode, and a reticulated or porous conductor and at least a portion of a surface of the rotary cathode arranged opposite to the anode is coated with the conductor.

15 [0013] The metal recovery apparatus of the present invention can recover, for instance, a noble metal from a noble metal-containing aqueous solution.

[0014] As the conductor, for instance, it is preferable to use a metal mesh with an average aperture size of 0.5 to 3 mm or a metal mesh with an average wire diameter of 0.3 to 0.5 mm. More preferably, it is desirable to
20 use a metal mesh with an average aperture size of 0.5 to 3 mm and an average wire diameter of 0.3 to 0.5 mm. It is also preferable to use, as the conductor, a porous body having aperture parts corresponding to the above-mentioned average aperture size and average wire diameter.

[0015] Another metal recovery apparatus of the present invention is
25 characterized in that the apparatus comprises a columnar or tubular rotary

cathode rotating on a shaft and an anode installed opposite to the rotary cathode and at least a portion of a surface of the rotary cathode arranged opposite to the anode is processed so as to be roughened (rugged). Further, at least a portion of the surface of the rotary cathode arranged opposite to
5 the anode is preferably covered with a reticulated or porous conductor.

EFFECTS OF THE INVENTION

[0016] According to the present invention, since at least a portion of the surface of the rotary cathode arranged opposite to the anode is closely
10 adhered and coated with the reticulated or porous conductor or the rotary cathode itself is processed so as to be roughened on the surface, the metal recovery efficiency is improved by employing the rotary cathode and also the following effects are remarkably exhibited.

(1) The surface area of the cathode is increased and the metal recovery
15 efficiency is remarkably increased.

(2) Since the electrodeposition property of a metal in the cathode is improved, separation of the metal once electrodeposited in the cathode can be prevented. Therefore, an additional mechanism for recovering the metal separated from the cathode is no need to be installed separately and thus the
20 installation space of the recovery apparatus can be saved.

(3) If the processed cathode itself is used, as compared with a cathode coated with a conductor, there is no problem of deterioration or separation of a conductor due to repeat use and thus the durability is increased.

25 BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Fig. 1 is a schematic explanatory view showing a cross-section of a metal recovery apparatus of a first embodiment.

Fig. 2 is a graph showing a change of Au concentration (mg/L) of a treatment solution with respect to electrolysis time (hr).

5 Fig. 3 is a graph showing the change of Au concentration (mg/L) of a treatment solution with respect to electrolysis time (hr).

Fig. 4(A) is a perspective view showing a cylindrical rotary cathode employed for a metal recovery apparatus of a second embodiment and Fig. 4(B) is a partially magnified view of the surface cross-section of the
10 cylindrical rotary cathode shown in Fig. 4(A).

DESCRIPTION OF REFERENCE SYMBOLS

[0018]	1	electrolysis bath
	2	anode
15	3	rotary shaft
	4	cylindrical rotary cathode
	5	motor
	6	circulation bath
	7	pump
20	8	conductor (mesh made of titanium)

BEST MODE FOR CARRYING OUT THE INVENTION

[0019] The inventors of the present invention have made various investigations to provide a recovery apparatus capable of saving the
25 installation space of the apparatus, reducing the equipment load, and

excellent in the metal recovery efficiency. As a result, the inventors have found that in order to increase the surface area of a rotary cathode, if at least a portion of a surface of a rotary cathode arranged opposite to an anode is coated with a reticulated or porous conductor or at least a portion of a surface of a rotary cathode arranged opposite to an anode is processed so as to be roughened, the electrodeposition of a metal electrodeposited on the rotary cathode can be improved and separation of the metal once electrodeposited on the rotary cathode can be efficiently prevented and accordingly the metal recovery efficiency is remarkably improved and these findings now leads to completion of the present invention.

[0020] Hereinafter, for convenience of the explanation, a recovery apparatus using a rotary cathode of which at least a portion of a surface arranged opposite to an anode is coated with a reticulated or porous conductor is sometimes called as "first embodiment" and a recovery apparatus using a rotary cathode of which at least a portion of a surface arranged opposite to an anode is processed so as to be roughened is sometimes called as "second embodiment".

[0021] Both of the first embodiment and the second embodiment are common in a point that the surface area of the cathode is preferably increased at least 3.0 times to heighten the metal recovery efficiency. Further, since the surface of the rotary cathode becomes consequently rough in both embodiments, both are also common in a point that the electrodeposition property of the metal and exfoliation resistance are improved. However, both are different in their concrete means, that is, in the first embodiment, "external means" of coating the rotary cathode with a

conductor is employed, whereas in the second embodiment, "internal means" of forming a roughened (rugged) surface by processing the rotary cathode itself. The recovery apparatus of the present invention is not limited to these embodiments and design modifications can be made without departing
5 from the spirit and scope of the present invention.

[0022] First Embodiment

A metal recovery apparatus according to this embodiment comprises a columnar or tubular rotary cathode rotating on a shaft, an anode arranged opposite to the rotary cathode, and a reticulated or porous conductor, and at
10 least a portion of a surface of the rotary cathode arranged opposite to the anode is coated with the conductor.

[0023] First, the "reticulated or porous conductor" that most characterizes this embodiment will be explained. The form of the conductor to be used in the embodiment is a reticulated (including a lattice-like) or porous
15 (hereinafter, sometimes referred to as "reticulated/porous"). The reticulated or lattice-like form is not particularly limited and may include a form in which wires extended vertically and horizontally are crossed or a form in which wires extended slantingly are crossed with wires extended vertically. The intervals of reticulated or lattice-like aperture parts are not particularly
20 limited and among wires composing the conductor, those in one direction may be arranged densely and the others may be arranged sparsely to form rectangular aperture parts, or the wires may be arranged in a manner that the form of the reticulated or lattice-like aperture parts is a rhombus or square. Further, a porous form just like a punching metal or an expanded
25 metal having a plurality of through holes may be employed.

[0024] Further, the "conductor" is required to have conductivity to some extent that the electrolysis is carried out and insolubility to a metal-containing solution, that is, an electrolytic solution. Practically, for instance, titanium and stainless steel or an object metal to be recovered may
5 be exemplified.

[0025] The above-mentioned "reticulated or porous conductor" is formed as to coat at least a portion of the rotary cathode and the coated rotary cathode is arranged opposite to an anode. Unlike Patent Document 4, there is no gap (space) in the part where the conductor and the rotary cathode are
10 brought into contact with each other. Since a portion of the surface of the rotary cathode arranged opposite to the anode is coated with the reticulated/porous conductor without any gap, the surface of the rotary cathode is made rough and a metal is electrodeposited and collectively agglomerated on the roughened surface and the electrodeposited metal
15 hardly exfoliates from the surface of the rotary cathode and therefore the electrodeposition of the metal is remarkably improved. Further, according to the above-mentioned configuration, the surface area of the rotary cathode is increased and therefore, the electrolysis efficiency is improved and the metal recovery efficiency can be improved.

20 [0026] In addition, the above-mentioned conductor is no need to be formed on the entire surface of the rotary cathode arranged opposite to the anode and may be formed at least partially on the rotary cathode unless electrolysis efficiency is decreased and accordingly leads to interference on the metal recovery efficiency.

25 [0027] In the case where the reticulated or porous conductor is a metal mesh,

it is preferable that the average aperture size is 0.5 to 3 mm or the average wire diameter is 0.3 to 0.5 mm. In this connection, average means the value calculated by measuring aperture sizes or wire diameters at a plurality of points of the metal mesh and averaging these values.

5 [0028] If the average aperture size of the metal mesh is less than 0.5 mm, the mesh is excessively fine. Further, if the average aperture size of the metal mesh exceeds 3 mm, the mesh is too coarse. Therefore, stirring effect for the treatment solution is lowered or the surface area of the rotary cathode cannot be increased and accordingly it becomes difficult to develop the effect
10 of improving the metal recovery efficiency by improving the electrolysis efficiency.

[0029] If the average wire diameter of the metal mesh is less than 0.3 mm, the wire diameter is too small. Further, if the average wire diameter of the metal mesh exceeds 0.5 mm, the wire diameter is too large. Therefore,
15 stirring effect for the treatment solution is lowered or the surface area of the rotary cathode cannot be increased and accordingly it becomes difficult to develop the effect of improving the metal recovery efficiency by improving the electrolysis efficiency.

[0030] The metal mesh particularly preferably has an average aperture size
20 of 0.5 to 3 mm and an average wire diameter of 0.3 to 0.5 mm.

[0031] Additionally, in the case where the reticulated or porous conductor is a porous one, it is preferable to use a porous one having aperture parts corresponding to the average aperture size and the average wire diameter in the above-mentioned ranges.

25 [0032] The metal mesh is preferably attached doubly to quadruply to the

surface of the rotary cathode. The area of the rotary cathode can be sufficiently increased by adjustment of the number of the metal mesh coats to be double or more and thus the metal recovery efficiency can further be improved. However, even if the metal mesh is wound (wrapped) over
5 quadruply, the effect of attachment of the metal mesh is saturated and the metal recovery efficiency is scarcely changed and therefore, it is preferable to adjust the number of the metal mesh coats to be quadruple or less.

[0033] A method for coating the surface of the rotary cathode with the reticulated/porous conductor is not particularly limited, for instance, the
10 metal mesh may be spot welded on the surface of the rotary cathode at regular intervals and fixed without a gap between the surface of the rotary cathode and the metal mesh.

[0034] Second Embodiment

The metal recovery apparatus of this embodiment is characterized in
15 that the apparatus comprises a columnar or tubular rotary cathode rotating on a shaft and an anode arranged opposite to the rotary cathode and at least a portion of a surface of the rotary cathode arranged opposite to the anode is processed so as to be roughened. The surface of the rotary cathode itself is processed so as to be roughened to increase the surface area of the rotary
20 cathode, so that the metal recovery efficiency can be increased and also the rotary cathode can be made repeatedly usable for a long time. That is, as the first embodiment described above, the configuration of coating the surface of the rotary cathode with the conductor, the conductor coat on the surface is possibly separated from the surface of the rotary cathode by long
25 time use of the rotary cathode. It is because long time use sometimes

makes the wire diameter of the conductor thin to loosen the meshes or the welded parts come off. On the other hand, in the second embodiment, since the surface area is increased by processing the rotary cathode itself without using a conductor, the above-mentioned problems attributed to the conductor do not occur. Therefore, long time stable operation is made possible.

[0035] The above-mentioned roughness may be formed on at least a portion of the surface of the rotary cathode and is not necessarily have to be formed on the entire surface. As described above, in this embodiment, it is sufficient to form the roughness so as to make the surface area after the processing for the roughness be at least 3.0 times as large as that before the processing. Further, the form of the roughness to be formed on the surface may be changed by processing means, which will be described later, and for instance, fine roughness (fine unevenness) can be formed by shot blast and recessed parts such as grooves and holes can be formed by a cutting process.

Alternatively, sharkskin patterns may be formed by special processing. Further, preferable ranges of the average intervals of roughness and the average height of roughness (difference of the projections and recesses) may be about 0.5 mm or more, respectively, although they differ in accordance with the shape and size of the rotary cathode to be used. A preferable form of the recesses will be described in detail with reference to an apparatus illustrated in Fig. 4.

[0036] The form of the roughness formed on the surface of the rotary cathode is not particularly limited. For instance, the recesses may be shallow recesses formed intermittently (hereinafter, sometimes referred to as holes) and also grooves formed continuously along the cathode surface.

Alternatively, holes and grooves may be properly combined to form the roughened surface of the rotary cathode.

[0037] The cross-sectional shape of the roughened part is not particularly limited and may be, for example, a rectangular, polygonal, U-shape, V-shape, W-shape, wavy, and the like as the shape in the case of observing the cross-section vertical to the cathode surface.

[0038] The appearance of the roughened part is also not particularly limited and for example, may show linear, curved, rectangular, polygonal, circular, or sharkskin patterns. Further, these patterns may be properly combined to form the roughened surface of the rotary cathode.

[0039] A processing method of the roughness is not particularly limited and a conventional surface-roughening treatment may be carried out on the surface of the rotary cathode to form the roughness. The surface-roughening treatment may be, for example, a cutting process, a blasting process, an electric discharge process, a laser process, an etching process, and the like. Further, a plate to be a material of the rotary cathode may be pressed to form a cross-sectional shape into a V-shape, W-shape, wavy, or the like and then the obtained plate may be rolled to be cylindrical and form a rotary cathode. A metal to be a material for the rotary cathode may be, for example, a sintered sponge-like Ti having high porosity produced by powder metallurgy.

[0040] In the second embodiment, the surface of the rotary cathode having the roughness may be coated with the above reticulated or porous conductor. Coating with the conductor can further increase the surface area of the rotary cathode. For example, Experiment Example 23, which will be

described later, is an example of wrapping a titanium mesh one turn on the surface of a rotary cathode having grooves as shown in Fig. 4, and as compared with Experiment Example 9 in which a titanium mesh is wound once on the surface of a rotary cathode having no groove as shown in Fig. 1,

5 the surface area is increased and a metal can be recovered in a short time.

In an embodiment of coating the surface of a grooved rotary cathode with a conductor, in combination with the effect of increasing the surface area by forming the roughened surface of a rotary cathode, the surface area of the rotary cathode can be further increased by winding a conductor only one turn

10 on the rotary cathode. As a result, a metal can be recovered in a short time.

[0041] The surface area of the rotary cathode to be used for the first embodiment and the second embodiment is preferably at least about 3.0 times as large as the surface area of the rotary cathode before coating with the conductor or processing to form the roughness. It is more preferably at

15 least 3.3 times and even more preferably at least 3.5 times. The surface area of the rotary cathode is more preferable as it is larger, however if the reticulated/porous conductor is wound to an excess extent, the rotary cathode becomes too heavy and too much load is burdened for rotation and the increase of the surface area by roughness formation means is limited and therefore, at the most, the upper limit may be about 10 times. It is more preferably 8 times or less and even more preferably 6 times or less.

[0042] The rotary cathode to be used for the first embodiment and the second embodiment is a columnar or tubular rotary cathode rotating on a shaft. Use of such a rotary cathode further improves the electrolysis efficiency and the metal recovery efficiency. In the present invention, as

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compared with the case of using a disk-like rotary cathode just like those described in Patent Document 2 and Patent Document 3, an electrolytic solution can sufficiently be stirred at a small number of revolutions and therefore, the equipment load can be lowered.

5 [0043] Herein, "columnar" means a solid body or a shape having a hollow space in the inside that is not opened to the outside and "tubular " means a hollow body having a hollow space in the inside opened to the outside. In the present invention, both embodiments are preferably employed. The rotary cathode to be used in the present invention is typically approximately
10 round-columnar or approximately cylindrical. The cross-sectional shape of the rotary cathode is not limited to a circle and for instance, it may be "polygonal" rather much close to circular. However, if the cross-sectional shape of the rotary cathode is rectangular (e.g. tetragon), when the cathode is rotated, the resistance which the cathode receives from the solution is
15 increased and therefore, the load on motive power, e.g. a motor, installed for rotating the cathode becomes too high and an electrolytic solution is sometimes scattered and therefore, the shape should be properly selected in consideration of the equipment load and the like.

[0044] A material for the rotary cathode may have conductivity to an extent
20 that the electrolysis is carried out and insolubility sufficient not to be dissolved in the metal-containing solution (that is, the electrolytic solution) and not to be eluted even at the time of electrolysis. Practically, for instance, titanium and stainless steel or an object metal to be recovered itself may be exemplified.

25 [0045] The rotary cathode and an anode may be arranged as follows.

[0046] First, in the case of using a columnar rotary cathode, an anode is arranged in the outside (outer circumference) of the columnar rotary cathode. The shape of the anode to be arranged in the surrounding of the columnar rotary cathode is not particularly limited and those commonly used for metal recovery apparatuses may be employed. Accordingly, either plate-like or tubular anode can be used. Practically, a plate-like or tubular anode may be arranged in a manner that the anode surrounds the circumference (outer circumference) of the columnar rotary cathode. In the case where a plate-like anode is used, the plate-like anode is arranged in a manner that the anode is opposite to the surface of the columnar rotary cathode coated with a reticulated/porous conductor or to the surface of the columnar rotary cathode having roughness. Such a plate-like anode may be arranged in a plurality of sheets so as to surround the columnar rotary cathode.

[0047] On the other hand, in the case of using a tubular rotary cathode, an anode may be arranged in the outside of the tubular rotary cathode or may be arranged in the inside of the tubular rotary cathode.

[0048] The shape and the arrangement method of the anode to be arranged in the surrounding (outside and inside) of the tubular rotary cathode may be substantially same as those in the case of using the columnar rotary cathode.

[0049] In the case where the anode is arranged in the inside of the tubular cathode, in the first embodiment, the reticulated/porous conductor may be formed on at least the inner surface, if necessary, the outer surface of the tubular rotary cathode. On the other hand, in the case of the second embodiment, the roughness may be formed on at least the inner surface, if necessary, the outer surface of the tubular rotary cathode. Further, the

anode may be arranged near, or apart a little from, the center shaft of the tubular rotary cathode.

[0050] The present invention uses a rotary cathode configured in a manner that a columnar or tubular cathode can be rotated on a shaft of the cathode.

5 When electrolysis is carried out while the cathode is rotated, a solution (an electrolytic solution) in an electrolysis bath can be stirred and therefore the solution and the cathode are effectively brought into contact with each other to improve the metal recovery efficiency and recover the metal within a short time.

10 [0051] The rotary cathode is connected to motive power of a motor, installed in the apparatus, to be rotated. The circumferential velocity (rotation speed) of the rotary cathode is changed in accordance with the size of an electrolysis bath to be used, the solution amount to be supplied to the electrolysis bath, or the type of an object metal to be recovered and therefore
15 it is difficult to define it. However, for instance in the case where a noble metal is recovered the circumferential velocity is preferably controlled in a range of approximately 0.5 to 1.8 m/sec.

[0052] It is because if the circumferential velocity of the cathode is less than 0.5 m/sec, the treatment solution in the electrolysis bath is not stirred and
20 the treatment solution is stagnated in the periphery of the surface of the rotary cathode and it becomes difficult to improve the electrolysis efficiency. Accordingly, the circumferential velocity of the cathode is preferably 0.5 m/sec or more, and more preferably 0.7 m/sec or more.

[0053] However, if the circumferential velocity of the cathode exceeds 1.8
25 m/sec, the treatment solution starts foaming and the electrolysis reaction on

the rotary cathode is inhibited to rather lower the electrolysis efficiency. Further, if the circumferential velocity of the cathode is too increased, the treatment solution starts waving and the treatment solution overflows the electrolysis bath to cause unsafe condition. Consequently, the circumferential velocity of the cathode is preferably adjusted at 1.8 m/sec or less. It is more preferably 1.6 m/sec or less and even more preferably 1.5 m/sec or less.

[0054] A metal element to be recovered by employing the apparatus of the present invention may be, for example, noble metals, Cu, Ni, and the like.

Examples of the noble metals include Au, Ag and platinum-group elements (Pd, Pt, Ir, Ru, and Rh). Particularly, if the recovery apparatus of the present invention is used, precious noble metals such as Au can be recovered at a low cost within a short time as compared with a case of conventional recovery and therefore, the recovery apparatus of the present invention is extremely useful as a noble metal recovery apparatus from a solution.

[0055] Any metal-containing solution which contains the above metal can be applied for the present invention and it may be typically a plating waste solution, a photographic development waste solution, a waste solution of washing water for plated products, a waste solution of exfoliation reagents and the like.

[0056] The electrolysis conditions for a metal-containing solution using the above recovery apparatus are not particularly limited and for example, electrolysis may be carried out at a voltage of about 1 to 10 V and an electric current of about 10 to 25 A.

[0057] After a metal is electrodeposited on the cathode surface from a

metal-containing solution by electrolysis, the cathode is taken out of the recovery apparatus and the cathode is immersed in a solution in which the object metal to be recovered is dissolved to elute and recover the metal.

[0058] Next, the metal recovery apparatus of the present invention will be explained in more details with reference to drawings.

[0059] Fig. 1 is a cross-sectional view of a metal recovery apparatus of a first embodiment according to the present invention. It is a cross-sectional view of a recovery apparatus using a cylindrical rotary cathode 4 coated with a reticulated or porous conductor 8 in a firmly adhesion state on the surface and an anode 2 installed as to surround the outside of the rotary cathode 4. In Fig. 1, a reference numeral 1 shows an electrolysis bath; a reference numeral 3 a rotary shaft; a reference numeral 5 a motor; a reference numeral 6 a circulation bath; and a reference numeral 7 a pump. In addition, the metal recovery apparatus shown in Fig. 1 is an embodiment of one example of the present invention and it is not intended that the present invention may be limited to the illustrated embodiment.

[0060] The metal recovery apparatus shown in Fig. 1 comprises a cylindrical rotary cathode 4 rotating on the shaft, four plate-like anodes 2 arranged opposite to the cylindrical rotary cathode 4, and a reticulated or porous conductor (titanium mesh) 8. At least a portion of the surface of the rotary cathode 4 facing the plate-like anodes 2 is coated with the titanium mesh 8. In Experiment Examples 1 to 20 described below, this recovery apparatus is used for experiments.

[0061] Fig. 4(A) is a perspective view showing a cylindrical rotary cathode 4a employed in the second embodiment among metal recovery apparatuses

according to the present invention. Fig. 4(B) is a magnified view of the part of the cylindrical rotary cathode 4a shown in Fig. 4(A) circumscribed with a square. Recesses (grooves) with a constant shape are regularly formed on the entire surface of the cylindrical rotary cathode 4a shown in Fig. 4(A).

5 As shown in Fig. 4(B), these grooves have a width x , an interval y between neighboring grooves, and a depth z .

[0062] With respect to the grooves, grooves may be formed in the horizontal direction along the circumference of the rotary cathode or may be formed in the vertical direction in parallel to the shaft of the rotary cathode.

10 Alternatively, the grooves may be formed in a lattice-like form by forming them in both vertical and horizontal directions or in a rhombic lattice-like form by forming them in a slanting direction to the vertical direction.

[0063] The size x of the recesses is preferably 0.5 mm or more, more preferably 1 mm or more, and even more preferably 1.5 mm or more. The

15 size of the recesses means the width of the grooves in the case where the recesses are grooves and the diameter of a corresponding circle of the aperture parts in the case where the recesses are holes. The width of the grooves may be measured as the maximum value of the distance between wall faces in the horizontal direction, concerning to a cross-section vertical to
20 the cathode surface.

[0064] The interval y of the recesses is preferably 0.5 mm or more, more preferably 1 mm or more, and even more preferably 1.5 mm or more. In this connection, the interval of the recesses means the interval between neighboring grooves, the interval between neighboring holes, or the interval

25 between neighboring grooves and holes.

[0065] The depth z of the recesses is preferably 0.5 mm or more, more preferably 1 mm or more, and even more preferably 1.5 mm or more. In this connection, the depth of the recesses means the maximum value of the distance in the vertical direction from the aperture parts, concerning to a cross-section vertical to the cathode surface.

[0066] In the Experiment Examples 21 to 24 described below, a metal recovery apparatus in which the cylindrical rotary cathode 4a shown in Fig. 4 is attached was employed to carry out the experiments. Additionally, in Experiment Example 23 described below, a cylindrical rotary cathode (not illustrated) obtained by further coating the surface of a cylindrical rotary cathode 4a in which grooves are formed with a titanium mesh was employed to carry out the experiment.

EXAMPLES

[0067] Hereinafter, the present invention will be described more in detail along with Experiment Examples; however, the following Experiment Examples are described, purely by way of non-limiting the invention and it will be appreciated that many modifications and variants can be made without departing from the spirit and scope of the present invention described hereinbefore and after, all of which come within the scope of the inventive context.

[0068] (Experiment Example 1)

Experiment Example 1 and Experiment Examples 2 to 10, which will be described later, were carried out to investigate the recovery efficiency when Au was recovered from washing water of Au-containing cyanide type

plating-coated products.

[0069] In Experiment Example 1, Au was recovered as follows, using the metal recovery apparatus shown in Fig. 1.

[0070] A cylindrical rotary cathode 4 was attached to a rotary shaft 3
5 arranged in the center of an electrolysis bath 1 (capacity 10 L) and the cylindrical rotary cathode 4 was rotated in the circumferential direction on the rotary shaft 3 by operating the motor 5.

[0071] The cylindrical rotary cathode 4 was made of titanium and cylindrical with a diameter of 160 mm and a length of 200 mm and as a
10 conductor 8, a titanium mesh having an average aperture size of 1 mm and an average wire diameter of 0.3 mm (20 meshes) was wound doubly around the outer surface. The titanium mesh was welded by spot welding to closely attach to the surface of the cylindrical rotary cathode 4.

[0072] When the surface area was calculated without taking into
15 consideration the parts where the cylindrical rotary cathode 4 and the titanium mesh were brought into contact with each other, the surface area in the case where the above-mentioned titanium mesh was attached to the surface of the cylindrical rotary cathode 4 was increased about 3.9 times as much as the surface area of the cylindrical rotary cathode 4 to which no
20 titanium mesh was attached.

[0073] In inner wall faces of the electrolysis bath 1, plate-like insoluble anodes (100 mm × 250 mm) were installed one by one in total four plates in the respective wall faces.

[0074] The electrolysis bath 1 was filled with 30 L of water used for washing
25 Au-containing cyanide type plating-coated products and having a Au

concentration of 97 mg/L as a treatment solution and the treatment solution overflowing the electrolysis bath 1 was stored in a circulation bath 6 and thereafter, supplied to near the bottom of the electrolysis bath 1 from the circulation bath 6 by a pump 7 to circulate the treatment solution in the electrolysis bath 1.

[0075] The solution amount circulated in the electrolysis bath 1 was 10 L/min and electrolysis was carried out at a voltage of 4 to 6 V, an electric current of 12 A and a circumferential velocity of the cylindrical rotary cathode 4 of 1.0 m/sec (revolution number 120 rpm).

[0076] The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 1. Further, the change of the Au concentration (mg/L) to the electrolysis time (hr) is shown with ■ in Fig. 2.

[0077] As clear from the following Table 1, at the moment when electrolysis was carried out for 3 hours, the Au concentration of the treatment solution was lowered to 1 mg/L and Au in the treatment solution was electrodeposited on the surface of the cylindrical rotary cathode 4.

[0078] (Experiment Example 2)

In Experiment Example 2, the effect of a titanium mesh on the recovery efficiency of Au was investigated. Practically, electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 1, except that a cylindrical rotary cathode 4 with a diameter of 160 mm and a length of 200 mm and having no titanium mesh on the surface was used as the cylindrical rotary cathode 4 in Experiment

Example 1. The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 1. Further, the change of the Au concentration (mg/L) to the electrolysis time (hr) is shown with ♦ in Fig. 2.

[0079] As clear from the following Table 1, it took 15 hours to lower the Au concentration of the treatment solution to 1 mg/L.

[0080] In comparison of the results of Experiment Example 2 and the results of Experiment Example 1, the results of Experiment Example 2 showed that the time taken to lower the Au concentration of the treatment solution to 1 mg/L was about 5 times as long as that of Experiment Example 1. Accordingly, it could be understood that the recovery efficiency of Au could be improved about 5 times by increasing the surface area only about 3.9 times by forming the titanium mesh on the surface of the cylindrical rotary cathode.

[0081] (Experiment Example 3)

In Experiment Example 3, the effect of the circumferential velocity of the rotary cathode on the recovery efficiency of Au was investigated.

[0082] Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 2, except that the circumferential velocity of the cylindrical rotary cathode 4 was increased to 2.0 m/sec (revolution number 240 rpm) which is twice that in Experiment Example 2. The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 1. Further, the change of

the Au concentration (mg/L) to the electrolysis time (hr) is shown with ▲ in Fig. 2.

[0083] As clear from the following Table 1, it took 12 hours to lower the Au concentration of the treatment solution to 1 mg/L.

5 [0084] In comparison of the results of Experiment Example 3 and the results of Experiment Example 2, even if the circumferential velocity of the cylindrical rotary cathode 4 was increased two times, the electrolysis time was shortened only by 3 hours and the recovery ratio of Au was improved no more than about 20%.

10 [0085] The circumferential velocity of the cylindrical rotary cathode 4 was about 2.0 m/sec (revolution number 240 rpm) at most and if the circumferential velocity was increased further, the wave of the treatment solution became too significant to carry out stable operation.

[0086] As clear from Fig. 2, the electrolysis time was remarkably shortened and the recovery efficiency of Au was rather much improved by forming the titanium mesh on the surface of the cylindrical rotary cathode 4 (■ in Fig. 2) as compared with those in the case where no titanium mesh was attached to the surface of the cylindrical rotary cathode 4 (♦ and ▲ in Fig. 2).

[0087] (Experiment Example 4)

20 Experiment Example 4 and Experiment Example 5, which will be described later, were other experiments carried out to investigate the effect of the circumferential velocity of the rotary cathode on the recovery efficiency of Au.

[0088] Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 1, except that the

circumferential velocity of the cylindrical rotary cathode 4 was decreased to 0.3 m/sec (revolution number 40 rpm), which is 1/3 times as low as that in Experiment Example 1. The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 1.

[0089] As clear from the following Table 1, it took 6 hours to lower the Au concentration of the treatment solution to 1 mg/L.

[0090] In comparison of the results of Experiment Example 4 and the results of Experiment Example 1, it was understood that if the circumferential velocity of the cylindrical rotary cathode 4 was decreased too slow, the electrolysis time became long and the recovery ratio of Au was not so improved. The reason for that the recovery efficiency was not improved was supposedly because of insufficient stirring of the treatment solution and thus the progress of the electrolysis reaction became difficult.

[0091] (Experiment Example 5)

Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 1, except that the circumferential velocity of the cylindrical rotary cathode 4 was increased to 2.0 m/sec (revolution number 240 rpm), which is two times as high as that in Experiment Example 2. The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 1.

[0092] As clear from the following Table 1, it took 5 hours to lower the Au concentration of the treatment solution to 1 mg/L.

[0093] In comparison of the results of Experiment Example 5 and the

results of Experiment Example 1, it was understood that as a result of Experiment Example 5, the period became about 1.7 times to lower the Au concentration of the treatment solution to 1 mg/L and accordingly, in the case where the circumferential velocity of the rotary cathode 4 was too high, the recovery efficiency of Au was rather worsened. The reason for the worsening of the recovery efficiency of Au was supposedly because the circumference velocity was so high as to cause foaming of the treatment solution and consequently, the contact surface area of the cylindrical rotary cathode 4 and the treatment solution was decreased due to the generated foams and it made the electrolysis reaction difficult to proceed.

[0094] As clear from the following Table 1, it was found that when the circumferential velocity of the cylindrical rotary cathode 4 was decreased too low or increased too high, it took longer time to recover Au than that in Experiment Example 1 and thus the recovery efficiency of Au was not so much improved.

[0095] (Experiment Example 6)

Experiment Example 6 and Experiment Examples 7 and 8, which will be described later, were experiments carried out to investigate the effect of the aperture size and wire diameter of the titanium mesh on the recovery efficiency of Au.

[0096] Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 1, except that as the titanium mesh, a mesh with an average aperture size of 5 mm and an average wire diameter of 1 mm (4 meshes) was employed. In this connection, when the surface area was calculated without taking into consideration the parts

where the cylindrical rotary cathode 4 and the titanium mesh were brought into contact with each other, the surface area was increased about 3.1 times in the case of the above-mentioned titanium mesh was attached to the surface of the cylindrical rotary cathode 4 as compared with the surface area of the cylindrical rotary cathode 4 to which no titanium mesh was attached.

[0097] The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 1.

[0098] As clear from the following Table 1, it took 6 hours to lower the Au concentration of the treatment solution to 1 mg/L.

[0099] In comparison of the results of Experiment Example 6 and the results of Experiment Example 1, it was found that if a so much coarse mesh was used as the titanium mesh, it took so long time to recover Au and the recovery efficiency of Au could not be improved so much.

[0100] (Experiment Example 7)

Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 1, except that as the titanium mesh, a mesh with an average aperture size of 2 mm and an average wire diameter of 0.5 mm (10 meshes) was employed. In this connection, when the surface area was calculated without taking into consideration the parts where the cylindrical rotary cathode 4 and the titanium mesh were brought into contact with each other, the surface area was increased about 3.5 times in the case of the above-mentioned titanium mesh was attached to the surface of the cylindrical rotary cathode 4 as compared with the surface area of the cylindrical rotary cathode 4 to which no titanium mesh was attached.

[0101] The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 1.

[0102] As clear from the following Table 1, when the electrolysis was carried out for 4 hours, the Au concentration of the treatment solution was decreased to less than 1 mg/L.

[0103] In comparison of the results of Experiment Example 7 and the results of Experiment Example 1, it was found that the time taken to lower the Au concentration of the treatment solution to about 1mg/L was almost same in the case of using the titanium mesh with 10 meshes and with 20 meshes and the recovery efficiency of Au was approximately same.

[0104] (Experiment Example 8)

Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 1, except that as the titanium mesh, a mesh with an average aperture size of 0.3 mm and an average wire diameter of 0.1 mm (60 meshes) was employed. In this connection, when the surface area was calculated without taking into consideration the parts where the cylindrical rotary cathode 4 and the titanium mesh were brought into contact with each other, the surface area was increased about 4.1 times in the case of the above-mentioned titanium mesh was attached to the surface of the cylindrical rotary cathode 4 as compared with the surface area of the cylindrical rotary cathode 4 to which no titanium mesh was attached.

[0105] The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 1.

[0106] As clear from the following Table 1, when the electrolysis was carried out for 5 hours, the Au concentration of the treatment solution was decreased to 1 mg/L.

[0107] In comparison of the results of Experiment Example 8 and the results of Experiment Example 1, it was found that even if a mesh having too fine meshes as the titanium mesh, the electrolysis time could not be shortened so much and the recovery efficiency of Au could not be improved so much.

[0108] As clear from the following Table 1, it was found that even if the meshes of the titanium mesh were made too much coarse or too much fine, it took a longer time to recover Au than the results of Experiment Examples 1 and 7 and thus the recovery efficiency of Au was not improved.

[0109] (Experiment Example 9)

Experiment Example 9 and Experiment Example 10, which will be described later, were experiments carried out to investigate the effect of the number of turns of the titanium mesh on the recovery efficiency of Au.

[0110] Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 1, except that the number of turns of the titanium mesh wound on the surface of the cylindrical rotary cathode 4 was changed to be single. In this connection, when the surface area was calculated without taking into consideration the parts where the cylindrical rotary cathode 4 and the titanium mesh were brought into contact with each other, the surface area was increased about 2.4 times in the case of the above-mentioned titanium mesh was attached to the surface of the cylindrical rotary cathode 4 as compared with the surface area of the

cylindrical rotary cathode to which no titanium mesh was attached.

[0111] The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 1.

5 [0112] As clear from the following Table 1, it took 5 hours to lower the Au concentration of the treatment solution to 1 mg/L.

[0113] In comparison of the results of Experiment Example 9 and the results of Experiment Example 1, it was found that if the number of turns of the titanium mesh wound on the surface of the cylindrical rotary cathode 4
10 was decreased so much, it became difficult to sufficiently achieve the effect of winding the titanium mesh.

[0114] (Experiment Example 10)

Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 1, except that the number of
15 turns of the titanium mesh wound on the surface of the cylindrical rotary cathode 4 was changed to be quadruple. In this connection, when the surface area was calculated without taking into consideration the parts where the cylindrical rotary cathode 4 and the titanium mesh were brought into contact with each other, the surface area was increased about 6.8 times
20 in the case of the above-mentioned titanium mesh was attached to the surface of the cylindrical rotary cathode 4 as compared with the surface area of the cylindrical rotary cathode to which no titanium mesh was attached.

[0115] The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the
25 measurement are shown in the following Table 1.

[0116] As clear from the following Table 1, it took 3 hours to lower the Au concentration of the treatment solution to 1 mg/L.

[0117] In comparison of the results of Experiment Example 10 and the results of Experiment Example 1, it was found that if the number of turns of the titanium mesh wound on the surface of the cylindrical rotary cathode 4 was increased so much, the effect of winding the titanium mesh was saturated.

[0118] As clear from the following Table 1, if the number of turns of the titanium mesh was decreased so much, it took a longer time for electrolysis than the results of Experiment Examples 1 and 10 and thus it was difficult to improve the recovery efficiency of Au.

[0119] [Table 1]

	Experiment Example 1	Experiment Example 2	Experiment Example 3	Experiment Example 4	Experiment Example 5	Experiment Example 6	Experiment Example 7	Experiment Example 8	Experiment Example 9	Experiment Example 10
Mesh	20	-	-	20	20	4	10	60	20	20
Average aperture size (mm)	1	-	-	1	1	5	2	0.3	1	1
Average wire diameter (mm)	0.3	-	-	0.3	0.3	1	0.5	0.1	0.3	0.3
Number of turns	Double	None	None	Double	Double	Double	Double	Double	Single	Quadruple
Circumferential velocity (m/sec)	1.0	1.0	2.0	0.3	2.0	1.0	1.0	1.0	1.0	1.0
Electrolysis time (hr)	Au concentration (mg/L)	Au concentration (mg/L)	Au concentration (mg/L)	Au concentration (mg/L)	Au concentration (mg/L)	Au concentration (mg/L)	Au concentration (mg/L)	Au concentration (mg/L)	Au concentration (mg/L)	Au concentration (mg/L)
0	97	97	97	97	97	97	97	97	97	97
1	19			37	28	49	23	52	33	18
2	4			15	10	21	6	22	9	3
3	1	55	42	7	3	10	2	7	3	1
4				4	2	5	Less than 1	3	2	
5				2	1	2		1	1	
6		24	13	1						
8		10	4							
12		4	1							
15		1								

[0120] (Experiment Example 11)

Experiment Example 11 and Experiment Examples 12 and 13, which will be described later, were carried out to investigate the effect of the titanium mesh when the Au recovery process was carried out repeatedly.

5 [0121] In Experiment Example 1, as a treatment solution, 30 L of washing water of Au-containing cyanide type plating-coated products was loaded to a metal recovery apparatus shown in Fig. 1. A process, in which, after electrolysis was carried out until the Au concentration of the waste solution became 1 mg/L, further 30 L of washing water of Au-containing cyanide type
10 plating-coated products was loaded without recovering Au electrodeposited in the cylindrical rotary cathode 4, was repeated 30 times. The Au concentration of the washing water of Au-containing cyanide type plating-coated products was 97 mg/L. The Au amount deposited on the bottom of the electrolysis bath 1 due to separation of Au electrodeposited on
15 the cylindrical rotary cathode 4 was measured. The measurement results are shown in the following Table 2.

[0122] The washing water of Au-containing cyanide type plating-coated products was used in total 900 L. The total Au amount contained in the waste solution was 87.3 g.

20 [0123] As being clear from the following Table 2, after the electrolysis was carried out repeatedly 30 times, the Au amount electrodeposited on the cylindrical rotary cathode 4 was 86.1 g and the Au amount deposited on the bottom of the electrolysis bath was 0.3 g. Accordingly, the ratio of Au separated from the cylindrical rotary cathode 4 was 0.3%.

25 [0124] (Experiment Example 12)

Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 11, except that a cylindrical rotary cathode 4 with a diameter of 160 mm and a length of 200 mm and having no titanium mesh on the surface was used as the cylindrical rotary
5 cathode 4 in Experiment Example 11.

[0125] As clear from the following Table 2, after electrolysis was carried out repeatedly 30 times, the Au amount electrodeposited on the cylindrical rotary cathode 4 was 81.3 g and the Au amount deposited on the bottom of the electrolysis bath was 5.1 g. Accordingly, the ratio of Au separated from
10 the cylindrical rotary cathode 4 was 5.8%.

[0126] (Experiment Example 13)

Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 11, except that the cylindrical rotary cathode 4 used here was prepared by connecting a plurality of points
15 in upper parts of the titanium mesh and the cylindrical rotary cathode 4 with a conductive wire at the time of winding a titanium mesh on the surface of the cylindrical rotary cathode 4 and winding the titanium mesh doubly while inserting a spacer to keep a gap about 1 mm so as not to closely attach the titanium mesh to the surface of the cylindrical rotary cathode 4.

20 [0127] As clear from the following Table 2, after electrolysis was carried out repeatedly 30 times, the Au amount electrodeposited on the cylindrical rotary cathode 4 was 85.0 g and the Au amount deposited on the bottom of the electrolysis bath was 1.4 g. Accordingly, the ratio of Au separated from the cylindrical rotary cathode 4 was 1.6%.

25 [0128] In comparison of the results of above-mentioned Experiment

Examples 11 to 13 with one another, it was understood the electrodeposition property on the cylindrical rotary cathode 4 could be improved by attaching the titanium mesh to the surface of the cylindrical rotary cathode 4 and Au could be recovered from the surface of the cylindrical rotary cathode 4 without being separated. Therefore, it was no need to separately install additional mechanism for recovery a metal separated from the surface of the cylindrical rotary cathode 4 and thus the installation space for the recovery apparatus could be saved.

[0129] [Table 2]

	Experiment Example 11	Experiment Example 12	Experiment Example 13
Mesh	20	-	20
Average aperture size (mm)	1	-	1
Average wire diameter (mm)	0.3	-	0.3
Number of turns	Double	None	Double, kept at gap
Circumferential velocity (m/sec)	1.0	1.0	1.0
Total Au amount (g)	87.3	87.3	87.3
Au amount electrodeposited on cathode (g)	86.1	81.3	85.0
Separated Au amount (g)	0.3	5.1	1.4
Separated Au ratio (%)	0.3	5.8	1.6

[0130] (Experiment Example 14)

Experiment Example 14 and Experiment Examples 15 and 16, which will be described later, were experiments carried out to investigate the recovery efficiency when Au was recovered from a waste solution of a Au-containing aqua regia separation solution.

[0131] Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 1, except that the waste solution of a Au-containing aqua regia separation solution was used as the treatment solution and the electrolysis was carried out at a voltage of 1.0 to 2.0 V and an electric current of 20 A in Experiment Example 1. The Au concentration in the waste solution of the Au-containing aqua regia separation solution was 80 mg/L. The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 3. Further, the change of the Au concentration (mg/L) of the treatment solution to the electrolysis time (hr) is shown with ■ in Fig. 3.

[0132] As clear from the following Table 3, at the moment when electrolysis was carried out for 6 hours, the Au concentration of the treatment solution was lowered to 3 mg/L. During the 6 hours, separation of Au electrodeposited on the cylindrical rotary cathode 4 was not seen.

[0133] (Experiment Example 15)

Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 14, except that a cylindrical rotary cathode 4 with a diameter of 160 mm and a length of 200 mm and having no titanium mesh on the surface was used as the cylindrical rotary cathode 4 in Experiment Example 14. The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 3. Further, the change of the Au concentration (mg/L) of the treatment solution to the electrolysis time (hr) is shown with ♦ in Fig. 3.

[0134] As clear from the following Table 3, the Au concentration of the treatment solution was lowered to 10 mg/L when the electrolysis was carried out for 12 hours, and thereafter, the Au electrodeposited on the cylindrical rotary cathode 4 was separated and dissolved again and therefore, the Au concentration increase was observed.

[0135] Additionally, since the Au separated from the cylindrical rotary cathode 4 was dissolved in the aqua regia after a short time, the separated Au amount could not be measured.

[0136] (Experiment Example 16)

Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 14, except that the cylindrical rotary cathode 4 used here was prepared by connecting a plurality of points in upper parts of the titanium mesh and the cylindrical rotary cathode 4 with a conductive wire at the time of winding a titanium mesh on the surface of the cylindrical rotary cathode 4 and winding the titanium mesh doubly while inserting a spacer to keep a gap about 1 mm so as not to closely attach the titanium mesh to the surface of the cylindrical rotary cathode 4. The Au concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 3. Further, the change of the Au concentration (mg/L) of the treatment solution to the electrolysis time (hr) is shown with ▲ in Fig. 3.

[0137] As clear from the following Table 3, at the moment when the electrolysis was carried out for 3 hours, the Au electrodeposited on the cylindrical rotary cathode 4 was separated and dissolved again. The Au

concentration of the treatment solution was fluctuated around 20 mg/L and the Au concentration was not lowered furthermore.

[0138] Additionally, since the Au separated from the cylindrical rotary cathode 4 was dissolved in the aqua regia after a short time, the separated
5 Au amount could not be measured.

[0139] As clear from Fig. 3 in which the results of Experiment Examples 14 to 16 are plotted, it could be understood that the electrolysis time could be shortened and the Au recovery efficiency was increased by using the cylindrical rotary cathode 4 to which the titanium mesh was closely attached
10 (■ in Fig. 3) even in the case of using the waste solution of a Au-containing aqua regia separation solution as the treatment solution. Further, the Au concentration of the treatment solution could be lowered to 3 mg/L by using the cylindrical rotary cathode 4 to which the titanium mesh was closely attached (■ in Fig. 3).

[0140] [Table 3]

	Experiment Example 14	Experiment Example 15	Experiment Example 16
Mesh	20	-	20
Average aperture size (mm)	1	-	1
Average wire diameter (mm)	0.3	-	0.3
Number of turns	Double	None	Double, kept at gap
Circumferential velocity (m/sec)	1.0	1.0	1.0
Electrolysis time (hr)	Au concentration (mg/L)	Au concentration (mg/L)	Au concentration (mg/L)
0	80	80	80
1	45		44
2	29		23
3	18	50	22
4	11		14
5	6		23
6	3	32	20
9		19	
12		10	
15		19	

[0141] (Experiment Example 17)

In Experiment Example 17 and Experiment Example 18, which will
5 be described later, the recovery efficiency was investigated when Pd was
recovered from a Pd-containing waste solution.

[0142] Electrolysis of the treatment solution was carried out in the same
conditions as those in Experiment Example 1, except that a Pd-containing
waste solution (Pd concentration was 113 mg/L and pH = 8) was used as the
10 treatment solution and the electrolysis was carried out at a voltage of 7 to 8
V in Experiment Example 1. The Pd concentration of the treatment
solution was measured at every several hours from starting the electrolysis

and the results of the measurement are shown in the following Table 4.

[0143] As clear from the following Table 4, at the moment when electrolysis was carried out for 6 hours, the Pd concentration of the treatment solution was lowered to 1 mg/L.

5 [0144] (Experiment Example 18)

Electrolysis of the treatment solution was carried out in the same conditions as those in Experiment Example 17, except that a cylindrical rotary cathode 4 with a diameter of 160 mm and a length of 200 mm and having no titanium mesh on the surface was used as the cylindrical rotary
10 cathode 4 in Experiment Example 17. The Pd concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 4.

[0145] As clear from the following Table 4, it took 27 hours to lower the Pd
15 concentration of the treatment solution to 1 mg/L.

[0146] In comparison of the results of Experiment Example 18 and the results of Experiment Example 17, the electrolysis time in Experiment Example 18 was about 4.5 times as long as that in Experiment Example 17 and thus it was understood that according to the present invention the Pd
20 recovery efficiency was improved about 4.5 times only by installing the titanium mesh on the surface of the cylindrical rotary cathode 4 and increasing the surface area about 3.9 times.

[0147] As clear from the following Table 4, even in the case of recovering Pd from the Pd-containing waste solution, it could be understood that the
25 electrolysis time was remarkably shortened and the Pd recovery efficiency

was improved by installing the titanium mesh on the surface of the cylindrical rotary cathode 4 as compared with the case of installing no titanium mesh on the surface of the cylindrical rotary cathode 4.

[0148] [Table 4]

	Experiment Example 17	Experiment Example 18
Mesh	20	-
Average aperture size (mm)	1	-
Average wire diameter (mm)	0.3	-
Number of turns	Double	None
Circumferential velocity (m/sec)	1.0	1.0
Electrolysis time (hr)	Pd concentration (mg/L)	Pd concentration (mg/L)
0	113	113
1	46	
2	24	
3	10	65
4	6	
5	3	
6	1	35
9		20
12		12
15		8
18		5
21		3
24		2
27		1

5

[0149] (Experiment Example 19)

In Experiment Example 19 and Experiment Example 20, which will be described later, the recovery efficiency was investigated when Cu was recovered from a Cu-containing sulfuric acid waste solution.

10 [0150] Electrolysis of the treatment solution was carried out in the same

conditions as those in Experiment Example 1, except that a Cu-containing sulfuric acid waste solution (Cu concentration was 166 mg/L and acid concentration was 1 mol/L) was used as the treatment solution and the electrolysis was carried out at a voltage of 3 to 4 V in Experiment Example 1.

5 The Cu concentration of the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 5.

[0151] As clear from the following Table 5, at the moment when electrolysis was carried out for 3 hours, the Cu concentration of the treatment solution
10 was lowered to 5 mg/L and at the moment when electrolysis was carried out for 6 hours, the Cu concentration of the treatment solution was lowered to less than 1 mg/L.

[0152] (Experiment Example 20)

Electrolysis of the treatment solution was carried out in the same
15 conditions as those in Experiment Example 19, except that a cylindrical rotary cathode 4 with a diameter of 160 mm and a length of 200 mm and having no titanium mesh on the surface was used as the cylindrical rotary cathode 4 in Experiment Example 19. The Cu concentration of the treatment solution was measured at every several hours from starting the
20 electrolysis and the results of the measurement are shown in the following Table 5.

[0153] As clear from the following Table 5, it took 24 hours to lower the Cu concentration of the treatment solution to less than 1 mg/L.

[0154] In comparison of the results of Experiment Example 20 and the
25 results of Experiment Example 19, the electrolysis time in Experiment

Example 20 was about 4 times as long as that in Experiment Example 19 and accordingly it was understood that the Cu recovery efficiency was improved about 4 times only by installing the titanium mesh on the surface of the cylindrical rotary cathode 4 and increasing the surface area about 3.9 times.

[0155] As clear from the following Table 5, it could be understood that the electrolysis time was remarkably shortened and the Cu recovery efficiency was improved by installing the titanium mesh on the surface of the cylindrical rotary cathode 4 as compared with the case of installing no titanium mesh on the surface of the cylindrical rotary cathode 4.

[0156] [Table 5]

	Experiment Example 19	Experiment Example 20
Mesh	20	-
Average aperture size (mm)	1	-
Average wire diameter (mm)	0.3	-
Number of turns	Double	None
Circumferential velocity (m/sec)	1.0	1.0
Electrolysis time (hr)	Cu concentration (mg/L)	Cu concentration (mg/L)
0	166	166
3	5	98
6	Less than 1	40
9		15
12		7
15		4
18		2
21		1
24		Less than 1

[0157] (Experiment Example 21)

Experiment Example 21 and Experiment Examples 22 to 24, which will be described later, were carried out to investigate the recovery efficiency when Au was recovered from washing water of Au-containing cyanide type plating-coated products using a recovery apparatus including the cylindrical rotary cathode 4a shown in Fig. 4 in the above-mentioned metal recovery apparatus shown in Fig. 1. On the surface of the cylindrical rotary cathode 4a, grooves were formed on the entire surface by a cutting process. The shape of the grooves was regularly processed and the width x of the grooves was 1 mm; the interval y of neighboring grooves was 1 mm; and the depth z of the grooves was 3 mm. The cross-sectional shape of the grooves formed on the surface of the rotary cathode was rectangular and with respect to the appearance of the grooves, as shown in Fig. 4, grooves formed in the vertical direction were arranged at equal intervals in the circumferential direction.

[0158] The experiment conditions were same as the conditions of Experiment Example 1. The surface area of the cylindrical rotary cathode 4a made so as to be roughened was increased 4.0 times as large as the surface area in the case where no roughness was formed. The surface area increase ratio was same as that in Experiment Example 1.

[0159] The Au concentration in the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 6.

[0160] As clear from the following Table 6, at the moment when electrolysis was carried out for 3 hours, the Au concentration of the treatment solution was lowered to 1 mg/L. The Au in the treatment solution was electrodeposited on the surface of the cylindrical rotary cathode 4a.

[0161] As clear from Experiment Example 21 and Experiment Example 1, the recovery efficiency of Au was not changed and equal in the case of using the cylindrical rotary cathode 4a having the grooves with a depth of 3 mm on the surface and in the case of using the cylindrical rotary cathode 4 coated doubly with the titanium mesh on the surface.

[0162] (Experiment Example 22)

In Experiment Example 22, the effect of the depth of the grooves on the recovery efficiency of Au was investigated. Practically, electrolysis of the treatment solution was carried out in the same conditions as those of Experiment Example 21, except that a cylindrical rotary cathode 4a with a depth z of the grooves formed to be as shallow as 1.5 mm was used in the Experiment Example 21. The surface area of the cylindrical rotary cathode 4a made to have the roughness was only 2.5 times as large as the surface area in the case where no roughness was formed.

[0163] The Au concentration in the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 6. As clear from the following Table 6, it took 5 hours to lower the Au concentration in the treatment solution to 1 mg/L.

[0164] As clear from Experiment Example 22 and Experiment Example 21, the recovery efficiency of Au could be improved by making the grooves deep and increasing the surface area of the rotary cathode.

[0165] (Experiment Example 23)

In Experiment Example 23, the effect of a conductor coating the surface of the cylindrical rotary cathode 4a on the recovery efficiency of Au

was investigated by combining the first embodiment and the second embodiment. Practically, electrolysis of the treatment solution was carried out in the same conditions as those of Experiment Example 21, except that a titanium mesh with an average aperture size of 1 mm and an average wire
5 diameter of 0.3 mm (20 meshes) as a conductor was wound singly on the surface of the cylindrical rotary cathode 4a (groove depth z was 1.5 mm) used in Experiment Example 22. The titanium mesh was welded to the surface of the cylindrical rotary cathode 4a by spot welding to closely attach the titanium mesh to the surface. Additionally, the surface area of the
10 cylindrical rotary cathode 4a used in this Experiment Example (roughness + conductor coating) was increased 3.9 times as large as the surface area in the case where neither roughness nor conductor coating was formed.

[0166] The Au concentration in the treatment solution was measured at every several hours from starting the electrolysis and the results of the
15 measurement are shown in the following Table 6. As clear from the following Table 6, it took 3 hours to lower the Au concentration of the treatment solution to 1 mg/L.

[0167] As clear from Experiment Example 23 and Experiment Example 22, it was understood that even in the case where the depth of the recessed parts
20 formed on the surface of the cylindrical rotary cathode was relatively shallow and was 1.5 mm, if the surface was coated further with the conductor, the surface area was increased and thus an effect to improve the recovery efficiency of Au could be achieved almost same as that in the case of the above Experiment Example 21 using the cylindrical rotary cathode having
25 recessed parts with a depth as deep as 3.0 mm on the surface to increase the

surface area.

[0168] (Experiment Example 24)

In Experiment Example 24, electrolysis of the treatment solution was carried out in the same conditions as those of Experiment Example 21, except that the roughened surface of the cylindrical rotary cathode 4a was formed by carrying out blast treatment in Experiment Example 21. The blast treatment was carried out using alumina particles with a particle diameter of about 120 μm . The maximum height difference of the projections and recesses of the cylindrical rotary cathode 4a after the blast treatment was about 0.01 mm and the intervals of the projections (convex portions) and recesses (concave portions) were about 0.05 to 0.06 mm. The surface area of the cylindrical rotary cathode 4a subjected to the blast treatment was increased only about 1.1 to 1.2 times as large as that in the case where no blast treatment was carried out.

[0169] The Au concentration in the treatment solution was measured at every several hours from starting the electrolysis and the results of the measurement are shown in the following Table 6. As clear from the following Table 6, it took 15 hours to lower the Au concentration of the treatment solution to 1 mg/L.

[0170] As clear from Experiment Example 24 and Experiment Example 21, it was understood that since the surface area increased by blast treatment in Experiment Example 24 did not reach a desired level, time taken to lower the Au concentration of the treatment solution to 1 mg/L was 5 times as long as that of Experiment Example 21 in which the surface area was increased about 4.0 times.

[0171] [Table 6]

	Experiment Example 21	Experiment Example 22	Experiment Example 23	Experiment Example 24
Groove (depth)	3mm	1.5mm	1.5mm	—
Mesh coating (number of turns)	—	—	Single	—
Blast treatment	—	—	—	Processed
Electrolysis time (hr)	Au concentration (mg/L)	Au concentration (mg/L)	Au concentration (mg/L)	Au concentration (mg/L)
0	97	97	97	97
1	17	30	19	
2	4	8	4	
3	1	3	1	50
4		2		
5		1		
6				22
9				9
12				4
15				1

[0172] (Experiment Example 25)

Experiment Example 25 and Experiment Example 26, which will be
5 described later, were carried out to evaluate the durability of the cylindrical
rotary cathode.

[0173] In Experiment Example 25, the cylindrical rotary cathode 4a on
which Au was electrodeposited in Experiment Example 21 was disassembled
from the apparatus and immersed in 10 L of heated aqua regia for 600 hours.

10 The aqua regia was heated to be at 70 to 90°C. Further, with lapse of time a
portion of the solvent was evaporated to decrease the liquid quantity of the
aqua regia, new aqua regia was properly added.

[0174] After 600 hours passed, the cylindrical rotary cathode 4a was taken
out of the aqua regia, washed with water, dried and thereafter, observed with

eyes to evaluate the shape change of the surface of the cylindrical rotary cathode 4a before and after immersion. After 600 hours passed, any change of the surface shape of the cylindrical rotary cathode 4a was scarcely observed.

5 [0175] (Experiment Example 26)

In Experiment Example 26, the cylindrical rotary cathode 4 on which Au was electrodeposited in Experiment Example 1 was disassembled from the apparatus and the cylindrical rotary cathode 4 was immersed in aqua regia under the same conditions as those of Experiment Example 25 to
10 evaluate the shape change. After 600 hours passed, when the shape change of the surface of the cylindrical rotary cathode 4 was observed with eyes, a portion of the titanium mesh coating the surface of the cylindrical rotary cathode 4 was separated from the surface of the cylindrical rotary cathode 4.
[0176] In comparison of the results of Experiment Example 26 and
15 Experiment Example 25, it was understood that although the Au recovery efficiency was approximately same, use of the grooved rotary cathode in place of the titanium mesh could improve the durability of the cylindrical rotary cathode.

20 INDUSTRIAL APPLICABILITY

[0177] According to the present invention, it is made possible to provide an apparatus to be used for recovering a metal from a metal-containing solution by electrolysis, which can be installed in a saved installation space and reduce equipment load and is remarkably excellent in recovery efficiency to
25 recovery the metal within a short time.

CLAIMS

1. An apparatus for recovering a metal from a metal-containing solution by electrolysis is characterized in that:

5 the apparatus comprises

a columnar or tubular rotary cathode rotating on a shaft;

an anode arranged opposite to the rotary cathode; and

a metal mesh with an average aperture size of 0.5 to 3 mm and with an average wire diameter of 0.3 to 0.5 mm,

10 at least a portion of a surface of said rotary cathode arranged opposite to said anode is coated with said metal mesh.

2. The recovery apparatus according to Claim 1, wherein said metal is a noble metal.

15

3. An apparatus for recovering a metal from a metal-containing solution by electrolysis is characterized in that:

the apparatus comprises:

a columnar or tubular rotary cathode rotating on a shaft; and

20 an anode arranged opposite to the rotary cathode

at least a portion of a surface of said rotary cathode arranged opposite to said anode is processed so as to be roughened (rugged).

25 4. The recovery apparatus according to Claim 3, wherein said roughness formed on the surface of said rotary cathode has following size:

the width of a recesses formed by the roughness measured as the maximum value of the distance between wall faces in the horizontal direction, concerning to a cross-section vertical to the cathode surface is 0.5 to 1.5 mm,

- 5 the interval between neighboring recesses is 0.5 to 1.5 mm, and the depth of the recesses measured as the maximum value of the distance in the vertical direction from the aperture parts concerning to a cross-section vertical to the cathode surface is 0.5 to 3 mm.

10

5. The recovery apparatus according to Claims 3 or 4, wherein said roughness formed on the surface of said rotary cathode is grooves formed continuously along the cathode surface.

15

6. The recovery apparatus according to any one of Claims 3 to 5, wherein at least a portion of the surface of said rotary cathode arranged opposite to said anode is coated with a metal mesh with an average aperture size of 0.5 to 3 mm and
20 with an average wire diameter of 0.3 to 0.5 mm.