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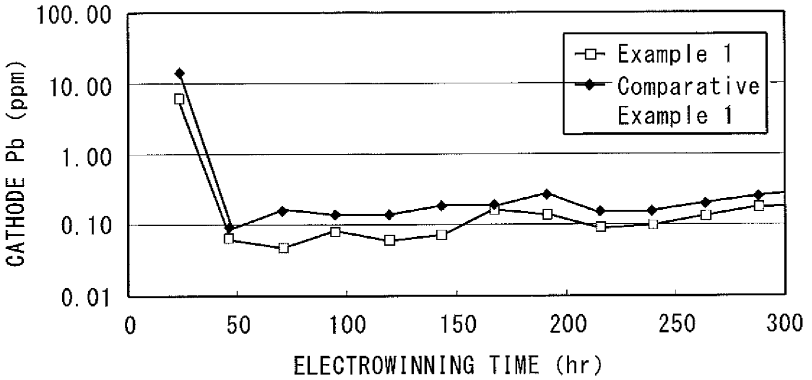
(54) METHOD FOR ELECTROWINNING OF NON-IRON METAL

(57) There is provided an electrowinning process for non-ferrous metals, which can inexpensively and stably recover a non-ferrous metal, such as zinc or copper, containing a very small quantity of lead for a long period of time by electrowinning. In a method for recovering a non-ferrous metal, such as zinc or copper, from an electrolytic solution containing a sulfate of the non-ferrous metal using an anode containing lead, a strontium containing solution prepared by dissolving strontium in concentrated sulfuric acid is added to the electrolytic solution to recover the non-ferrous metal from the electrolytic solution by electrowinning using the anode, the surface of the anode to be soaked in the electrolytic solution being blasted.

FIG.3



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Description

Technical Field

[0001] The present invention relates generally to an electro winning process for non-ferrous metals. More specifically, the invention relates to a method for recovering a non-ferrous metal, such as zinc or copper, from an electrolytic solution containing a sulfate of the non-ferrous metal, such as zinc sulfate or copper sulfate, by electrowinning using an anode containing lead.

Background Art

[0002] As a conventional electrowinning process for non-ferrous metals, there is known a method for depositing or adhering a non-ferrous metal, such as zinc or copper, onto a cathode from an electrolytic solution containing a sulfate of the non-ferrous metal, such as zinc sulfate or copper sulfate, using a plate of lead or lead-silver alloy, which is insoluble in sulfuric acid, as an anode.

[0003] However, in such an electrowinning process for non-ferrous metals, a small number of lead ions are transferred from the anode to the electrolytic solution, and a part of the transferred lead ions are deposited or adhered onto the cathode to be included in an electrodeposited non-ferrous metal, such as electrodeposited zinc or copper.

[0004] In order to reduce the amount of lead included in the electrodeposited zinc, there is known a method for adsorbing and removing lead ions and so forth in the electrolytic solution by adding a small amount of additives, such as strontium carbonate, to the electrolytic solution (see, e.g., Japanese Patent Laid-Open No. 9-20989), and there is also known a method for recovering high-purity zinc by electrowinning using a dimensional stable electrode (DSE), which contains no lead, as an anode (see, e.g., Japanese Patent Laid-Open No. 10-46274).

[0005] However, in the method for adding strontium carbonate to the electrolytic solution, it is not possible to uniformly disperse strontium in the electrolytic solution due to the very low solubility of strontium carbonate in water, so that it is difficult to further reduce the quantity of lead in the electrodeposited zinc on the cathode. In addition, it is desired to further reduce the quantity of lead in the electrodeposited zinc on the cathode by using an inexpensive plate of lead or lead-silver alloy (containing 1 to 3 wt% of silver) without using any relatively expensive dimensional stable electrode (DSE).

[0006] Therefore, in a method for recovering zinc from an electrolytic solution containing zinc sulfate by electrowinning using an anode containing lead, the inventors have proposed a method for carrying out the electrowinning of zinc after an aqueous solution containing strontium ions is added to the electrolytic solution (Japanese Patent Application No. 2009-277394) and a method for blasting the surface of the anode, which is to be soaked in the electrolytic solution, before electrowinning (Japanese Patent Application No. 2010-63445).

[0007] In these methods, as an aqueous solution containing strontium ions, there are used an aqueous solution obtained by dissolving strontium carbonate in water by adding strontium carbonate to water into which sulfur dioxide gas is blown, a suspension obtained by dissolving a part of strontium carbonate in water while suspending the rest thereof by adding excessive strontium carbonate to water into which sulfur dioxide gas is blown, or an aqueous solution obtained by dissolving strontium hydroxide in water by adding strontium hydroxide to water into which hydrogen sulfide gas is blown. By these methods, it is possible to inexpensively and stably recover a non-ferrous metal, such as zinc or copper, containing a very small quantity of lead for a long period of time by electrowinning, but it is desired to provide a method capable of inexpensively and stably recovering a non-ferrous metal, such as zinc or copper, containing a smaller quantity of lead for a long period of time.

Disclosure of the Invention

[0008] It is therefore an object of the present invention to eliminate such conventional problems and to provide an electrowinning process for non-ferrous metals, which can inexpensively and stably recover a non-ferrous metal, such as zinc or copper, containing a very small quantity of lead for a long period of time by electrowinning.

[0009] In order to accomplish the aforementioned object, the inventors have diligently studied and found that it is possible to inexpensively and stably recover a non-ferrous metal, such as zinc or copper, containing a very small quantity of lead for a long period of time by electrowinning if the electrowinning of the non-ferrous metal is carried out using an electrolytic solution, to which a strontium containing solution obtained by dissolving strontium in concentrated sulfuric acid is added, in a method for recovering the non-ferrous metal from the electrolytic solution containing a sulfate of the non-ferrous metal by electrowinning using an anode containing lead. Thus, the inventors have made the present invention.

[0010] A method for recovering a non-ferrous metal by electrowinning according to the present invention, comprises the steps of: preparing an electrolytic solution containing a sulfate of the non-ferrous metal; preparing a strontium containing solution by dissolving strontium in concentrated sulfuric acid; and adding the strontium containing solution to the electrolytic solution to recover the non-ferrous metal from the electrolytic solution by electrowinning using an anode containing lead.

[0011] In this method for recovering a non-ferrous metal by electrowinning, the strontium containing solution is preferably prepared by adding strontium carbonate to concentrated sulfuric acid. Preferably, the concentration of sulfuric acid in the concentrated sulfuric acid is not less than 98 % by weight. The concentration of strontium ions in the strontium containing solution is preferably in the range of from 5 g/L to 20 g/L. The surface of the anode to be soaked in the electrolytic solution is preferably blasted. In this case, the surface of the anode is preferably blasted using particles of silica sand, zinc or alumina powder. Moreover, the non-ferrous metal is preferably zinc, and the sulfate of the non-ferrous metal is preferably zinc sulfate.

[0012] According to the present invention, it is possible to inexpensively and stably recover a non-ferrous metal, such as zinc or copper, containing a very small quantity of lead for a long period of time by electrowinning. In particular, it is possible to inexpensively and stably recover a lead-free non-ferrous metal, such as zinc or copper, containing a very small quantity (0.1 ppm or less) of lead for a long period of time by electrowinning.

Brief Description of the Drawings

[0013]

FIG. 1 is a graph showing the relationship between the stirring time and the concentration of strontium ions in an electrolytic solution when a strontium containing solution obtained in each of Example 1 and Comparative Example 1 is added to the electrolytic solution to be stirred;

FIG. 2 is a graph showing the relationship between the stirring time and the concentration of lead ions in the electrolytic solution when the strontium containing solution obtained in each of Example 1 and Comparative Example 1 is added to the electrolytic solution to be stirred; and

FIG. 3 is a graph showing the quantity of lead in zinc electrodeposited on a cathode with respect to electrolyzing time in Example 2 and Comparative Example 2.

Best Mode for Carrying Out the Invention

[0014] In a preferred embodiment of an electrowinning process for non-ferrous metals according to the present invention, the electrowinning of a non-ferrous metal is carried out using an electrolytic solution, to which a strontium containing solution obtained by dissolving strontium in concentrated sulfuric acid is added, in a method for recovering the non-ferrous metal from the electrolytic solution containing a sulfate of the non-ferrous metal, such as zinc sulfate or copper sulfate, by electro winning using an anode containing lead. Although the strontium containing solution can be obtained by adding strontium carbonate, strontium sulfate or strontium hydroxide to concentrated sulfuric acid (the concentration of sulfuric acid of which is preferably 98 wt% or more), it is preferably obtained by adding strontium carbonate to the concentrated sulfuric acid in view of costs.

[0015] Inthis electrowinningprocess for non-ferrous metals, strontium carbonate is added to concentrated sulfuric acid to be lightly stirred (to such an extent that the vessel is turned by hand) to dissolve strontium in the concentrated sulfuric acid to obtain a strontium containing solution of strontium hydrogen sulfate ($Sr(HSO_4)_2$). The concentration of strontium ions in the strontium containing solution is preferably in the range of from 1 g/L to 90 g/L, more preferably in the range of 5 g/L to 20 g/L, since a sulfate is formed if it is too high. The strontium containing solution thus obtained is preferably added directly to the electrolytic solution without being diluted.

[0016] The anode containing lead is preferably an anode of a lead alloy, such as a lead-silver-calcium alloy or a lead-silver alloy, which is usually used in electrowinning processes for non-ferrous metals, such as zinc and copper. The surface of the anode containing lead, which is to be soaked in the electrolytic solution, is preferably blasted. That is, the blasting of the surface of the anode is preferably carried out by colliding hard particles (media), such as particles of sand, alumina (aluminum oxide) powder or a metal, with the surface thereof by compressed air. By this blasting, it is possible to cause the surface of the anode to be rough while removing contaminants and deteriorated layers from the surface thereof. In this blasting, although the particles of sand, alumina (aluminum oxide) powder or a metal are preferably used as the media in view of the diameter and shape of the particles, sand blasting is more preferably carried out using alumina powder or sand which can inexpensively and relatively uniformly work the surface of the anode. Although the particles of silica sand (No.4 silica sand having particle sizes of 10-23 meshes, 1.2-0.6 mm) can be sufficiently used if the particles of sand are used as the media, the particles of alumina powder are preferably used since they can cause the surface of the anode to be rough and are non-consumable and easily handled in comparative with the particles of sand. If the particles of alumina powder are used, the coarse particles of alumina powder of #24 to #14 (particle sizes of 710 μm to 2.8 mm) are preferably used. The conditions of the blasting can be controlled by the discharge pressure due to the pressure of compressed air, the discharge amount, discharge area and discharge time of the media, and so forth. The surface roughness of the anode can be controlled by changing at least one of these conditions. Furthermore, it is not always required to carry out the blasting with respect to the whole surface of the anode, but the blasting may be also carried out with respect to at least part of the surface of the anode, which is to be soaked in the electrolytic solution. The blasting is preferably carried out with respect to regions of the surface of the anode, which is near the liquid level of the electrolytic solution and which is to be soaked in the electrolytic solution. Since there are some cases where the media are attached to the surface of the anode after the blasting, the media adhered thereto are preferably dropped with air or the like, or the anode is preferably washed with water, dilute acid or the like.

[0017] Examples of an electrowinning process for non-ferrous metals according to the present invention will be described below in detail.

Example 1

[0018] An electrolytic solution (Zn: 65 g/L, FA: 170 g/L, total Pb: 1.0 mg/L, Sr: 15 mg/L) delivered from a zinc smelting process was prepared as an electrolytic solution containing zinc sulfate. The temperature of the delivered electrolytic solution was raised to 42 °C to be held. Also, 1.5 g of strontium carbonate was added to 18.4 g of concentrated sulfuric acid having a sulfuric acid concentration of 98 wt% to be stirred to prepare a strontium containing solution (Sr^{2+}: 90 g/L). Then, 0.6 mL of the strontium containing solution was added to 1L of the electrolytic solution by means of a measuring pipette to be stirred at 300 rpm by three blades for two hours.

[0019] A part of the electrolytic solution, to which the strontium containing solution was added every predetermined elapsed time during the stirring, was extracted to measure the concentration of strontium ions therein by means of inductively coupled plasma (ICP) and to measure the concentration of lead ions therein by means of an ICP mass spectrometer (ICP-MS). As a result, the concentration of strontium ions was 15.0 mg/L immediately after the addition of the strontium containing solution, 27.6 mg/L after the stirring for 1 minute, 17.1 mg/L after the stirring for 10 minutes, 15.2 mg/L after the stirring for 30 minutes, 13.5 mg/L after the stirring for 60 minutes, and 13.1 mg/L after the stirring for 120 minutes. The concentration of lead was 0.40 mg/L immediately after the addition of the strontium containing solution, 0.26 mg/L after the stirring for 1 minute, 0.32 mg/L after the stirring for 10 minutes, 0.25 mg/L after the stirring for 30 minutes, 0.34 mg/L after the stirring for 60 minutes, and 0.39 mg/L after the stirring for 120 minutes. These results are shown in Table 1, Table 2, FIG. 1 and FIG. 2.

Table 1

Sr^{2+} (mg/L)

	0min	1min	10min	30min	60min	120min
Ex. 1	15.0	27.6	17.1	15.2	13.5	13.1
Comp. 1	15.0	50.1	38.9	32.9	29.8	27.2

Table 2

Pb^{2+}(mg/L)

	0min	1min	10min	30min	60min	120min
Ex. 1	0.40	0.26	0.32	0.25	0.34	0.39
Comp. 1	0.40	0.37	0.35	0.37	0.35	0.45

[0020] As can be seen from Table 2 and FIG.2, the concentration of lead ions decreases immediately after the addition of the strontium containing solution to the electrolytic solution until the stirring is carried out for 1 minute, so that it is possible to reduce the concentration of lead ions in a short period of time after the addition of the strontium containing solution.

Comparative Example 1

[0021] A strontium containing solution was added to an electrolytic solution to be stirred by the same methods as those in Example 1, except that 6 mL of the strontium containing solution (Sr^{2+}: 9 g/L), which was obtained by dividing and adding 15 g of strontium carbonate to 1 L of pure water so as to maintain a pH of 2.0 by blowing SO_2 gas into the solution at a flow rate of 200 mL/min while stirring the solution at 300 rpm by means of three blades, was used in place of the strontium containing solution in Example 1.

[0022] A part of the electrolytic solution, to which the strontium containing solution was added every predetermined elapsed time during the stirring, was extracted to measure the concentrations of strontium ions and lead ions therein by the same methods as those in Example 1. As a result, the concentration of strontium ions was 15.0 mg/L immediately after the addition of the strontium containing solution, 50.1 mg/L after the stirring for 1 minute, 38.9 mg/L after the stirring for 10 minutes, 32.9 mg/L after the stirring for 30 minutes, 29.8 mg/L after the stirring for 60 minutes, and 27.2 mg/L after the stirring for 120 minutes. The concentration of lead was 0.40 mg/L immediately after the addition of the strontium containing solution, 0.37 mg/L after the stirring for 1 minute, 0.35 mg/L after the stirring for 10 minutes, 0.37 mg/L after the stirring for 30 minutes, 0.35 mg/L after the stirring for 60 minutes, and 0.45 mg/L after the stirring for 120 minutes. These results are shown in Table 1, Table 2, FIG. 1 and FIG. 2.

[0023] As can be seen from Table 2 and FIG.2, in this comparative example, the decreased amount of the concentration of lead ions is smaller and it takes a longer period of time to decrease the concentration thereof in comparative with those in Example 1, so that the concentration of lead ions during the stirring for 2 hours is high, although the concentration of lead ions decreases after the addition of the strontium containing solution to the electrolytic solution. In addition, in this comparative example, it can be seen that the degree of the depression of increase of the concentration of lead ions due to the redissolution of lead ions is smaller than that in Example 1. That is, it can be seen that, in Example 1 in comparative with Comparative Example 1, the concentration of lead ions in a shorter period of time after the addition of the strontium containing solution is greatly decreased, and the concentration of lead ions during the stirring for 2 hours is lower, so that the degree of the depression of increase of the concentration of lead ions due to the redissolution of lead ions is greater.

Example 2

[0024] The same electrolytic solution (Zn: 65 g/L, FA: 170 g/L, total Pb: 1.0 mg/L, Sr: 15 mg/L), which was delivered from the zinc smelting process, as that in Example 1, was prepared as an electrolytic solution containing zinc sulfate. The temperature of the delivered electrolytic solution was allowed to be stand to be cooled to a room temperature to precipitate impurities to be filtered. Thus, 1.2 L of an electrolytic solution for electrowinning (Zn: 65 g/L, FA: 170 g/L, total Pb: 0.6 mg/L, Sr: 12 mg/L) was prepared, and the temperature thereof was raised to 42 °C to be held.

[0025] Also, 1.0 g of strontium carbonate was added to 184 g of concentrated sulfuric acid having a sulfuric acid concentration of 98 wt% to be stirred to prepare a strontium containing solution (Sr^{2+}: 6 g/L).

[0026] Moreover, particles of alumina powder were collided with a region of the surface of an anode of a Pb-Ag alloy, the region being caused to contact the electrolytic solution, by compressed air at the maximum air pressure of 0.9 MPa to carry out the blasting of the anode. Then, the alumina powder attached to the anode was removed, and the anode was washed with water. Thus, two blasted anode plates were prepared.

[0027] Then, the electrolytic solution was transferred into an electrolysis vessel to be held at 40-42 °C while being circulated at a flow rate of 200 mL/min, and the blasted anode plate and a cathode of aluminum were placed in the electrolysis vessel so as to be spaced from each other at an interval of 25 mm. In this state, a current was flowed between the anode and the cathode at a current density of 600 A/m^2 to start the electrowinning of zinc. At the substantially same time, 10 mL of the strontium containing solution was continuously added to the electrolytic solution at a rate of 0.2 mL/min.

[0028] The cathode was replaced with a new cathode every day (every 24 hours) from the start of the flowing of the current while the current was flowed. Then, the quantity of lead in zinc electrodeposited on the cathode was measured by means of the ICP mass spectrometer (ICP-MS). As a result, the quantity of lead in the electrodeposited zinc was 5.8 ppm after 24 hours, 0.06 ppm after 48 hours, 0.05 ppm after 72 hours, 0.09 ppm after 96 hours and 0.06 ppm after 120 hours from the start of the addition of the strontium containing solution. These results are shown in FIG. 3. As shown in FIG. 3, the quantity of lead in the electrodeposited zinc was not higher than 1.0 ppm after 30 hours from the start of the flowing of the current, and thereafter, the electrodeposited zinc having a very low quantity (not higher than 0.1 ppm) of lead was stably recovered for a long period of time (not less than 120 hours).

Comparative Example 2

[0029] The strontium containing solution in Example 2 was substituted for 10 mL of a strontium containing solution (Sr^{2+}: 9 g/L) which was prepared by dividing and adding 5.0 g of strontium carbonate to 500 mL of pure water so as to maintain a pH of 2.0 by blowing SO_2 gas into the solution at a flow rate of 200 mL/min while stirring the solution at 300 rpm by means of three blades. The prepared strontium containing solution was used to carry out the electrowinning of zinc to measure the quantity of lead in zinc electrodeposited on the cathode, by the same methods as those in Example 2. As a result, the quantity of lead in the electrodeposited zinc was 16.1 ppm after 24 hours, 0.10 ppm after 48 hours, 0.17 ppm after 72 hours, 0.14 ppm after 96 hours and 0.15 ppm after 120 hours from the start of the addition of the strontium containing solution. These results are shown in FIG. 3. As can be seen from FIG. 3, the quantity of lead in the electrodeposited zinc after 24 hours from the start of the flowing of the current in this comparative example was higher than that in Example 2, and it took a longer period of time to decrease the quantity of lead than that in Example 2. In addition, it can be seen that the quantity of lead in the electrodeposited zinc was not higher than 1.0 ppm after 30 hours from the start of the flowing of the current, and thereafter, it was possible to stably recover the electrodeposited zinc having a low quantity of lead for a long period of time, but it was not possible to stably recover the electrodeposited zinc having a very low quantity (not higher than 0.1 ppm) of lead, which was stably recovered in Example 2, for a long period of time (not less than 120 hours).

Claims

1. A method for recovering a non-ferrous metal by electrowinning, the method comprising the steps of :

   preparing an electrolytic solution containing a sulfate of the non-ferrous metal;
   preparing a strontium containing solution by dissolving strontium in concentrated sulfuric acid; and
   adding the strontium containing solution to the electrolytic solution to recover the non-ferrous metal from the electrolytic solution by electrowinning using an anode containing lead.

2. A method for recovering a non-ferrous metal by electrowinning as set forth in claim 1, wherein said strontium containing solution is prepared by adding strontium carbonate to concentrated sulfuric acid.

3. A method for recovering a non-ferrous metal by electrowinning as set forth in claim 1, wherein the concentration of sulfuric acid in said concentrated sulfuric acid is not less than 98 % by weight.

4. A method for recovering a non-ferrous metal by electrowinning as set forth in claim 1, wherein the concentration of strontium ions in said strontium containing solution is in the range of from 5 g/L to 20 g/L.

5. A method for recovering a non-ferrous metal by electrowinning as set forth in claim 1, wherein a surface of said anode to be soaked in said electrolytic solution is blasted.

6. A method for recovering a non-ferrous metal by electrowinning as set forth in claim 5, wherein said surface of the anode is blasted using particles of silica sand, zinc or alumina powder.

7. A method for recovering a non-ferrous metal by electrowinning as set forth in claim 1, wherein said non-ferrous metal is zinc, and said sulfate of the non-ferrous metal is zinc sulfate.

FIG.1

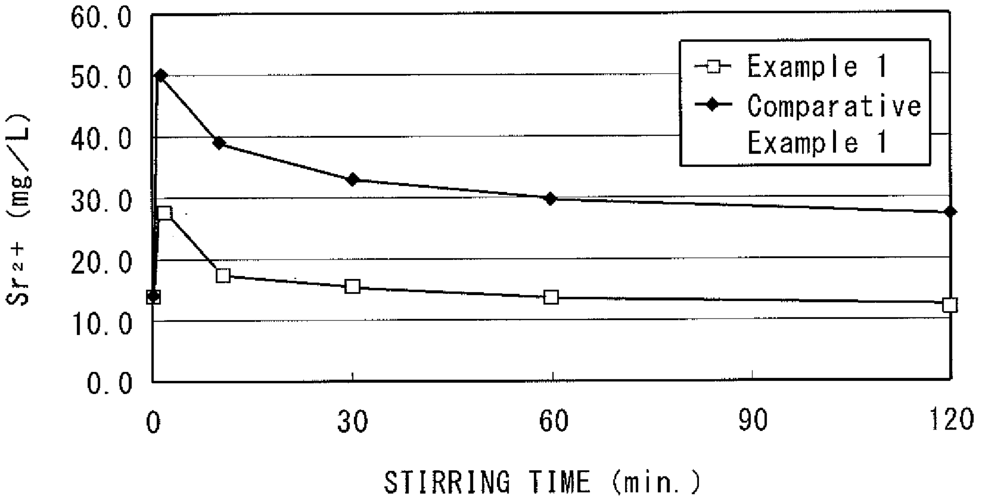

60.0
50.0
40.0
30.0
20.0
10.0
0.0
Sr2+ (mg/L)
0
30
60
90
120
STIRRING TIME (min.)
Example 1
Comparative Example 1

FIG.2

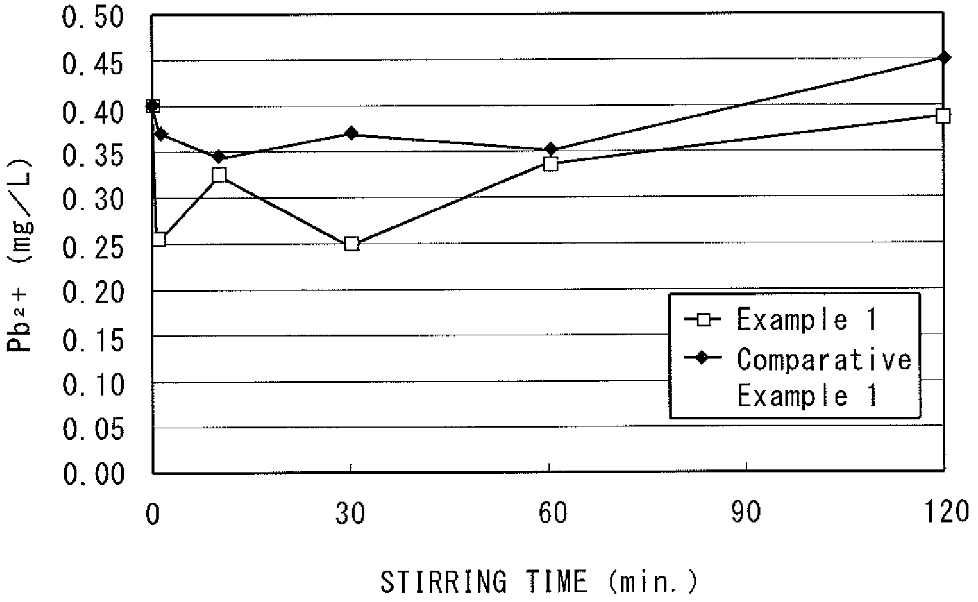
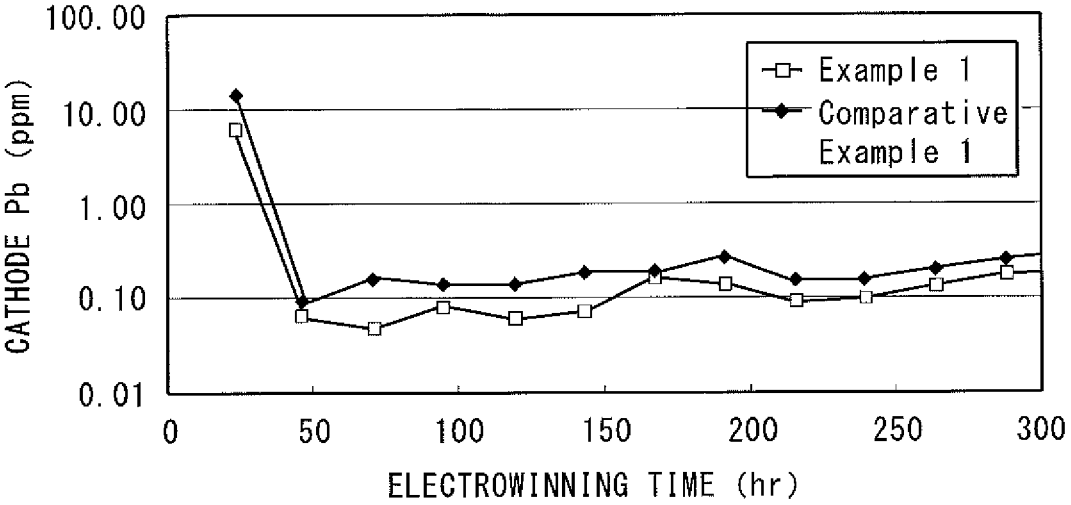

0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Pb2+ (mg/L)
0
30
60
90
120
STIRRING TIME (min.)
Example 1
Comparative Example 1

FIG.3


100.00
10.00
1.00
0.10
0.01
CATHODE Pb (ppm)
0
50
100
150
200
250
300
ELECTROWINNING TIME (hr)
Example 1
Comparative Example 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/068584

A. CLASSIFICATION OF SUBJECT MATTER
C25C1/16(2006.01)i, *C25C7/02*(2006.01)i, *C25C7/06*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25C1/16, C25C7/02, C25C7/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 54-119327 A (Outokumpu Oy), 17 September 1979 (17.09.1979), & ES 473919 A1 & SE 7810593 A & DE 2844289 A & FI 772999 A & BR 7806699 A & US 4157946 A & ZM 8878 A & ZA 7805405 A & DD 139727 A & AU 4056878 A & CA 1121301 A & AU 522663 B & IN 150544 A & PH 15537 A & MX 150596 A & SE 444005 B	1-7

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search 28 October, 2011 (28.10.11)	Date of mailing of the international search report 08 November, 2011 (08.11.11)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/068584

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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- JP 2010063445 A **[0006]**