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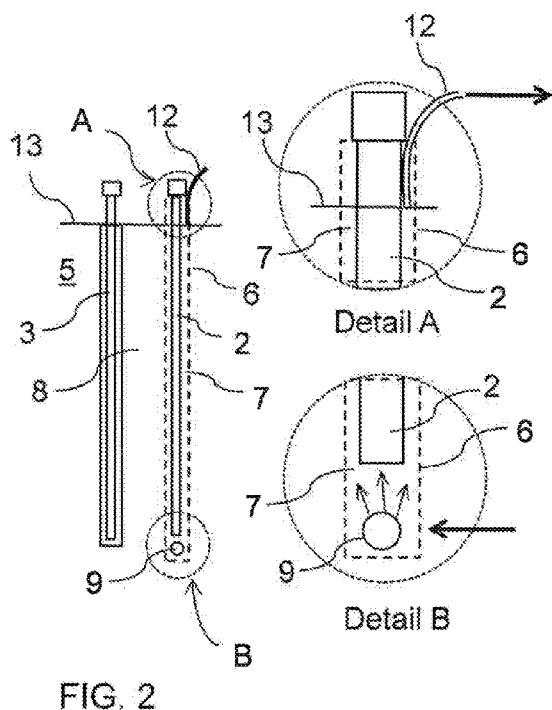
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Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the
earlier application (Rule 4.17(iii))

[Continued on next page]

- (54) **Title:** METHOD FOR METAL ELECTROWINNING AND AN ELECTROWINNING CELL



- (57) **Abstract:** The invention relates to a method for electrowinning a metal from an electrolyte in an electrowinning cell (1) that comprises an electrolysis tank (4), one or more anodes (2), and one or more cathodes (3), which anodes (2) and cathodes (3) are housed in the electrolysis tank (4). The method comprises supplying sulfur dioxide to the anode (2) to depolarize the anode process and to reduce the energy consumption of the electrowinning cell (1).



— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

METHOD FOR METAL ELECTROWINNING AND AN ELECTROWINNING CELL

FIELD OF THE INVENTION

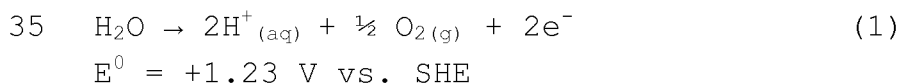
5 The present invention relates to a method for electrowinning a metal from an electrolyte in an electrowinning cell that comprises an electrolysis tank, one or more anodes and one or more cathodes, which anodes and cathodes are housed in the electrolysis tank.
10 The invention also relates to an electrowinning cell for electrowinning a metal.

BACKGROUND OF THE INVENTION

 In metal electrowinning a current is passed
15 from an inert anode to a cathode through a liquid leach solution containing said metal so that the metal is extracted as it is deposited onto the cathode. A significant part of the specific electrical energy consumption (SEEC) for this process is due to the re-
20 action which occurs at the anode. In the case of copper this represents over 25% of the total energy requirement of the copper production.

 In sulfate based electrolytes the anode reaction is oxygen evolution, caused by electrolytic
25 splitting of water into protons and oxygen. This provides electrons for the reduction of metal cations at the cathode. Sulfate based electrolytes are used, for instance, in electrowinning of copper, zinc, nickel, chromium and manganese.

30 In metal electrowinning from sulfate (or sulfuric acid) based electrolytes, the oxygen evolution reaction that occurs at the anode is given by the following equation:



The overall reaction for copper electrowinning with an oxygen-evolving anode is given by equation (2). The reaction produces one mole of cathode copper, one mole of sulfuric acid and half a mole of oxygen gas:



$$E_{\text{cell}} = +1.7 \text{ to } 2.0 \text{ V vs. SHE}$$

10

Efficiency and cost-effectiveness of electrowinning is important for the competitiveness of metal industry. The electrical energy cost of metal electrowinning is almost directly proportional to cell voltage.

15

Attempts have been made to develop anodes that would reduce the energy required for electrowinning. These attempts comprise, for instance, modification of lead anodes and switching to dimensionally stable anodes (DSA). In most cases, the anticipated energy savings have been in the region of a few hundreds of millivolts, or 5-15% of the cell voltage.

20

Dimensionally stable anodes comprise a thin active coating, usually few microns, deposited on a base metal, such as Ti, Zr, Ta, Nb. The coating enables the electrical charge transport between the base metal and the electrode/electrolyte interface, and is chosen for its high chemical and electrochemical stability and its ability to catalyze the desired electrochemical reaction.

30

PURPOSE OF THE INVENTION

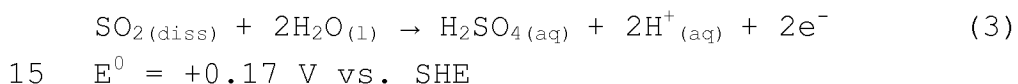
The object of the present invention is to reduce the electrical power consumption in metal electrowinning.

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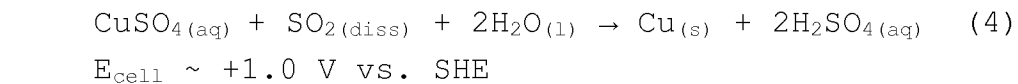
SUMMARY

The invention comprises the use of sulfur dioxide depolarized electrolysis (SDE) to lower the cell voltage for metal electrowinning, thereby lowering the electrical power needed to win metals from a solution. Anodic oxidation of SO₂ is used to depolarize the anode reaction and to decrease the energy required for electrowinning.

By comparison with the oxygen evolution reaction (1), sulfur dioxide oxidation reaction (3) has a much lower standard electrode potential than oxygen evolution:



The overall reaction for sulfur dioxide depolarized copper electrowinning would then be the production of one mole of cathode copper, two moles of acid and no oxygen. The cell voltage is considerably lower than for standard copper electrowinning technology:



The method according to the present invention is characterized by what is presented in claim 1.

The electrowinning cell according to the present invention is characterized by what is presented in claim 10.

In the present invention, anolyte and catholyte are separated from each other by a diaphragm or membrane, and sulfur dioxide is supplied to the anode to depolarize the anode process and to reduce the energy consumption of the electrowinning cell.

In one embodiment of the invention, sulfur dioxide is introduced in gas form into the electrolysis tank in the vicinity of the anode.

5 In another embodiment of the invention, sulfur dioxide is dissolved into an electrolyte before said electrolyte is introduced into the electrolysis tank in the vicinity of the anode.

10 In an advantageous embodiment of the present invention, each anode is housed in an anode bag of its own and sulfur dioxide is introduced into the lower part of the anode bag.

In one embodiment of the present invention, the anode comprises a titanium mesh coated with platinum.

15 In another embodiment of the present invention, the anode comprises a titanium mesh coated with gold.

20 In an advantageous embodiment of the present invention, the titanium mesh comprises 0.10-0.50 g/cm² Ti, advantageously about 0.15 g/cm² Ti.

In one embodiment of the present invention, the anode is a standard PbCaSn anode spray-coated with platinum powder. Alternatively, the standard PbCaSn anode can be spray-coated with gold powder.

25 In another embodiment of the present invention, the anode comprises a stainless steel anode coated with platinum or gold. Coating can be carried out, for instance, by powder coating, electrolytical precipitation, or any other suitable technology.

30 The present invention may be employed, for instance, in copper or zinc electrowinning carried out in a strong H₂SO₄ based electrolyte. The new method can also be suitable for use in nickel, chromium or manganese electrowinning, depending on the impact of SO₂ on
35 the solution chemistry of those processes.

With sulfur dioxide depolarized electrowinning technology (SDD-EW), it is possible to de-

polarize the electrowinning anode reaction by as much as 1 volt and so decrease the cell voltage and energy consumption in copper electrowinning by approximately 50%.

5

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are included to provide a further understanding of the invention and constitute a part of this specification, illustrate embodiments of the invention and together with the description help to explain the principles of the invention. In the drawings:

FIG. 1 is a schematic cross-sectional view of a sulfur dioxide depolarized electrowinning cell comprising bagged anodes.

FIG. 2 is an enlarged view of two electrodes, illustrating the flow of dissolved SO_2 containing anolyte through an anode bag, with two enlarged detail drawings.

FIG. 3 is a diagram illustrating current densities as a function of applied potential with three tested anode materials in degassed electrolyte and an electrolyte with SO_2 .

DETAILED DESCRIPTION OF THE INVENTION

FIG. 1 shows an electrolytic cell 1 that can be used in SO_2 depolarized electrowinning of copper from an acid electrolyte 5 that contains sulfuric acid and its copper salt. The electrolytic cell 1 comprises a plurality of anodes 2 and a plurality of cathodes 3, which are arranged alternately in an electrolysis tank 4 filled with the electrolyte 5. The anodes 2 can be, for instance, platinum or gold plated titanium mesh anodes, or of any other suitable type. Each anode 2 is contained in an anode bag 6 of its own. The anode bags 6 are formed of a material that permeates the electro-

lyte 5 in a controlled manner. The cathodes 3 are preferably permanent cathodes, which are made of acid-resistant special steel. The cathodes 3 are in direct contact with the electrolyte 5 in the tank 4.

5 Catholyte, which contains copper sulfate and sulfuric acid, is fed to the bottom of the tank 4 via a main feed manifold 10. After flowing through the tank 4, the spent catholyte is removed as an overflow 11 from the upper part of the tank 4. Anolyte, together with dissolved SO_2 , is fed into the lower part of each anode bag 6 via an anolyte feed manifold 9. The spent anolyte is removed from the upper part of the anode bag 6 via a conduit 12 with the aid of vacuum. The anolyte and the catholyte are separated from each other by the anode bag 6, which can comprise a diaphragm cloth bag or an ion exchange membrane, such as Nafion 117. The ion exchange membrane is a functionally fixed electrolyte that serves as an electric insulator and as a proton conductor that prevents gases from flowing from one side of the membrane to the other side of it.

FIG. 2 shows on a larger scale the structure of the anode 2 placed in the anode bag 6 and the cathode 3 placed outside the anode bag 6. The anode bag 6 defines an anodic space 7 on its inside and a cathodic space 8 on its outside. In the lower part of the anodic space 7 there is a manifold 9 through which anolyte is fed into the anode bag 6 together with SO_2 gas dissolved in the anolyte. Copper is precipitated on the surface of the cathode 3 and sulfuric acid is generated at the anode 2.

The spent anolyte, along with any excess gas including SO_2 , is removed from the anode bag 6 with the aid of suction via the conduit 12 arranged in connection with the air/electrolyte interface 13 in the upper part of the anode bag 6. The spent anolyte with

increased concentration of H_2SO_4 is conducted to recirculation.

The aqueous solution introduced into the anodic space 7 together with the sulfur dioxide results in oxidation of gaseous sulfur dioxide (SO_2) to form sulfur acid (H_2SO_4) with a sulfur dioxide depolarized anode.

In a preferred embodiment of the invention, the apparatus comprises means for adding sulfur dioxide to the anolyte solution, which solution is fed to the anodic space 7 via anolyte feed manifold 9.

As sulfur dioxide is consumed in electrolysis, some SO_2 make up is needed in the process.

In metallurgical industry, a large amount of sulfur dioxide is formed in roasting and smelting processes, i.e. the exhaust gases contain essentially large amounts of sulfur dioxide. The present invention is suitable for use in connection with metal production processes involving a pyrometallurgical step producing SO_2 and an electrowinning step to deposit metal on cathodes. The SO_2 producing step may comprise, for instance, roasting or smelting of sulfidic raw materials. Normally, the new type of electrowinning step would be suitable for zinc or nickel production, whereby SO_2 would be used in sulfur dioxide depolarized anodes in the electrowinning part of the process. If there is no SO_2 available from the process, then other sources of SO_2 can be considered. Sulfur dioxide can be transported from a near-by process plant, or a sulfur burner can be used to generate the necessary SO_2 . Furthermore, sulfuric acid evolved in the electrolytic cell can be re-circulated to a leaching stage.

In principle, there are several alternative ways of supplying SO_2 to the anodes in an electrolytic cell. The first alternative, illustrated in FIGS. 1 and 2, comprises dissolving SO_2 gas in the anolyte be-

fore the electrolytic cell 1 and feeding the solution via the manifold 9 to the bottom of the anode bag 6. Spent anolyte that contains residual SO_2 will then be re-circulated separately from the bulk electrolyte (catholyte). Any emissions will be handled by removal of electrolyte from the top of the anode bag 6. Fresh anolyte that contains dissolved SO_2 can be fed into the lower part of the anode bag 6 via the manifold 9 consisting of a steel tube, or by a device similar to that used in air sparging. Alternatively, SO_2 gas can be supplied directly into the anode bag without prior dissolution in an electrolyte.

Another option of supplying SO_2 to anodes in the electrolytic cell comprises using stacked membrane electrolyser assemblies (MEA), such as those related to descending packed bed electrowinning cell technology. In this cell design, anolyte and catholyte are treated as separate feeds and anolyte gas handling is part of the cell design. An example of this is presented in S. Robinson et al. "Commercial development of a descending packed bed electrowinning cell, part 2: Cell operation", Hydrometallurgy 2003 - Fifth International Conference in Honor of Professor Ian Ritchie - Volume 2: Electrometallurgy and Environmental Hydrometallurgy, TMS, 2003.

One more option would be dissolving SO_2 gas in the electrolyte feed prior to its addition to an undivided cell. An acid mist capture hood would then be needed to control the tankhouse atmosphere.

The potential at which the reactions (2) and (3) occur depends strongly on the anode material. For example, in an electrowinning tankhouse of prior art, reaction (2) typically occurs on lead based anodes (PbCaSn for copper electrowinning; PbAg for zinc electrowinning). Lead, or more specifically lead oxide on the surface of the lead anode is not a particularly good catalyst for oxygen evolution; platinum and gold

would be much better catalysts. The use of lead-based anodes persists in electrowinning applications for cost reasons - lead is a low cost option.

5 The material costs of anodes suitable for use in sulfur dioxide depolarized (SDD) metal electrowinning can be very high. The SDD anode itself appears to be competitive with conventional dimensionally stable anode (DSA), and there may be even cost reduction if it is possible to use light titanium mesh
10 based SDD anodes.

It is estimated that sulfur dioxide depolarized copper electrowinning would potentially save about 49% on the energy by using the oxidation of sulfur dioxide as the anode reaction.

15 The benefits achieved by the new method are numerous. Electrical energy consumption is reduced by approximately half over standard PbCaSn based copper electrowinning. There is no oxygen evolution at the anode. Together with the use of anode bags, this will
20 yield elimination of acid mists and better environmental control, which is especially important for instance in nickel electrowinning. As there are no lead anodes, no lead impurities are present in the electrolytic cell. Cathode finish and the quality of the
25 cathodes can be better than in conventional electrowinning. No anode sludges are created.

The new process is most suitable for use in connection with plants where SO₂ is generated at a location close to the electrowinning plant. If no other
30 source is available, sulfur burning can be used to generate SO₂. Extra plant and extra investment costs for SO₂ handling may be necessary. A good option might be the utilization of anode bag technology. Another promising alternative would be the utilization of descending packed bed electrowinning cells.
35

The following examples are presented to illustrate but not to limit the present invention.

EXAMPLE 1

The effect of anode material on the sulfur dioxide depolarized electrolysis reaction was tested using a standard PbAg electrode normally used in zinc electrowinning, an oxygen evolving dimensionally stable anode (titanium mesh coated with IrO_2 and Ta_2O_5), and a platinum coated titanium mesh electrode for comparison. Polarization curves were measured in 100 g/dm³ sulfuric acid, either degassed with nitrogen or saturated with SO_2 . FIG. 3 discloses a summary of the current density as a function of applied potential from 10 mV/s scans of the tested three anode materials in degassed electrolyte and in an electrolyte with SO_2 .

The results in FIG. 3 indicate that the least active electrode combination is a standard PbAg anode in a nitrogen degassed electrolyte. The most active combination so far was Pt in the presence of SO_2 , giving high currents at a much lower voltage than the other combinations tested.

Other possible anode materials that can be used in sulfur dioxide depolarized electrolysis comprise a platinum coated dimensionally stable anode (Ti coated with Pt), which is an industrial version of bulk platinum anode, and a gold electrode. So far, the tests performed in laboratory scale suggest that gold is an active catalyst for the sulfur dioxide depolarized electrolysis reaction. The gold electrode can be made, for instance, by electroplating a substrate of stainless steel, titanium mesh, or any other suitable metal or metal alloy. Also other suitable coating methods can be employed, such as physical vapor deposition method and multiple layer coating.

Consequently, the most probable anode materials usable on industrial scale comprise a coated titanium anode (also known as a dimensionally stable an-

ode, DSA) with a mixed metal and platinum or gold based coating, and a standard PbCaSn anode spray coated with platinum or gold powder, for instance by a method taught in WO 2007045716 A1. Also anodes produced by electrolytically plating stainless steel anode plates with gold or platinum, as well as anodes produced by physical vapor deposition of gold or platinum on a stainless steel anode can be used in the method according to the present invention.

EXAMPLE 2

To get an idea of the electrical energy consumption in copper electrowinning, the overall cell voltages (U_{cell}) and standard electrical energy consumptions (SEEC) of three different anodes were calculated for copper electrowinning. A summary of the results of these calculations is shown in Table 1. The calculations were made for the use of: a standard PbCaSn electrode in connection with oxygen evolving copper electrowinning; a dimensionally stable $\text{IrO}_2/\text{Ta}_2\text{O}_5$ electrode in connection with oxygen evolving copper electrowinning; and a platinum coated titanium electrode in connection with sulfur dioxide depolarized (SDD) copper electrowinning.

TABLE 1

	PbCaSn	DSA $\text{IrO}_2/\text{Ta}_2\text{O}_5$	Pt SDD with SO_2
U_{cell} , [V]	2.065	1.815	1.055
SEEC/t Cu, [kWh/t]	1834	1612	987

The results indicate that by using new platinum coated titanium electrodes in connection with sulfur dioxide depolarized copper electrowinning, remarkable reduction in the overall cell voltage and standard electrical energy consumption can be achieved.

It is obvious to a person skilled in the art that with the advancement of technology, the basic idea of the invention may be implemented in various ways. The invention and its embodiments are thus not
5 limited to the examples described above; instead they may vary within the scope of the claims.

CLAIMS

1. A method for electrowinning a metal from an electrolyte in an electrowinning cell (1) that comprises an electrolysis tank (4), one or more anodes (2), and one or more cathodes (3), which anodes (2) and cathodes (3) are housed in the electrolysis tank (4), the method comprising supplying sulfur dioxide to the anode (2) to depolarize the anode process and to reduce the energy consumption of the electrowinning cell (1), **characterized** by housing each anode (2) in an anode bag (6) of its own and introducing sulfur dioxide into the lower part of the anode bag (6).

2. A method according to claim 1, **characterized** by introducing sulfur dioxide in gas form into the electrolysis tank (4) in the vicinity of the anode (2).

3. A method according to claim 1, **characterized** by dissolving sulfur dioxide into an electrolyte before introducing said electrolyte into the electrolysis tank (4) in the vicinity of the anode (2).

4. A method according to any one of claims 1 to 3, **characterized** by using anodes (2) of platinum coated titanium mesh.

5. A method according to any one of claims 1 to 3, **characterized** by using anodes (2) of gold coated titanium mesh.

6. A method according to any one of claims 1 to 3, **characterized** by using standard PbCaSn anodes spray-coated with platinum powder.

7. A method according to any one of claims 1 to 3, **characterized** by using standard PbCaSn anodes spray-coated with gold powder.

8. A method according to any one of claims 1 to 3, **characterized** by using stainless steel anodes with platinum coating.

9. A method according to any one of claims 1 to 3, **characterized** by using stainless steel anodes with gold coating.

10. An electrowinning cell for electrowinning a metal from an electrolyte, comprising an electrolysis tank (4), one or more anodes (2) and one or more cathodes (3), which anodes (2) and cathodes (3) are housed in the electrolysis tank (4), and means (9) for supplying sulfur dioxide to the anode (2) to depolarize the anode process, **characterized** in that each anode (2) is housed in an anode bag (6) of its own and the sulfur dioxide is supplied into the lower part of the anode bag (6).

11. An electrowinning cell according to claim 10, **characterized** in that the means for supplying sulfur dioxide into the electrolysis tank (4) comprises a manifold (9) arranged to introduce sulfur dioxide into the vicinity of each anode (2).

12. An electrowinning cell according to claim 10 or 11, **characterized** in that the anode (2) comprises a titanium mesh provided with a platinum coating.

13. An electrowinning cell according to claim 10 or 11, **characterized** in that the anode (2) comprises a titanium mesh provided with a gold coating.

14. An electrowinning cell according to claim 12 or 13, **characterized** in that the titanium mesh comprises 0.10-0.50 g/cm² titanium, advantageously about 0.15 g/m² of titanium.

15. An electrowinning cell according to claim 10 or 11, **characterized** in that the anode (2) is a standard PbCaSn anode spray-coated with platinum powder.

16. An electrowinning cell according to claim 10 or 11, **characterized** in that the anode (2) is a standard PbCaSn anode spray-coated with gold powder.

17. An electrowinning cell according to claim 10 or 11, **characterized** in that the anode (2) is a stainless steel anode coated with platinum.

5 18. An electrowinning cell according to claim 10 or 11, **characterized** in that the anode (2) is stainless steel anode coated with gold.

19. An electrowinning cell according to any one of claims 10 to 18, **characterized** in that at least one of the anode bags (6) comprises a diaphragm cloth
10 bag or an ion exchange membrane.

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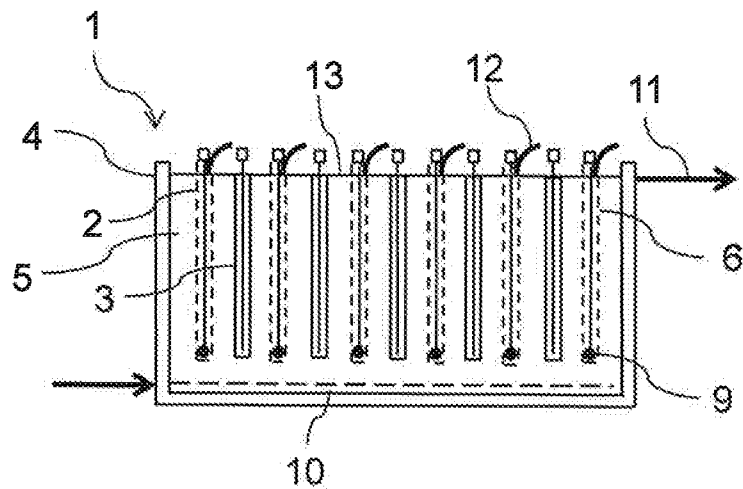


FIG. 1

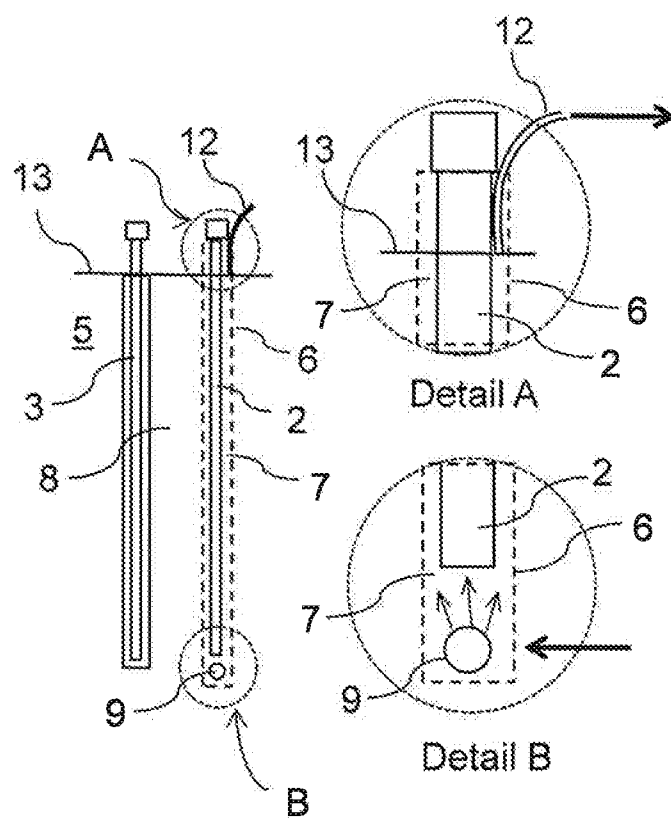


FIG. 2

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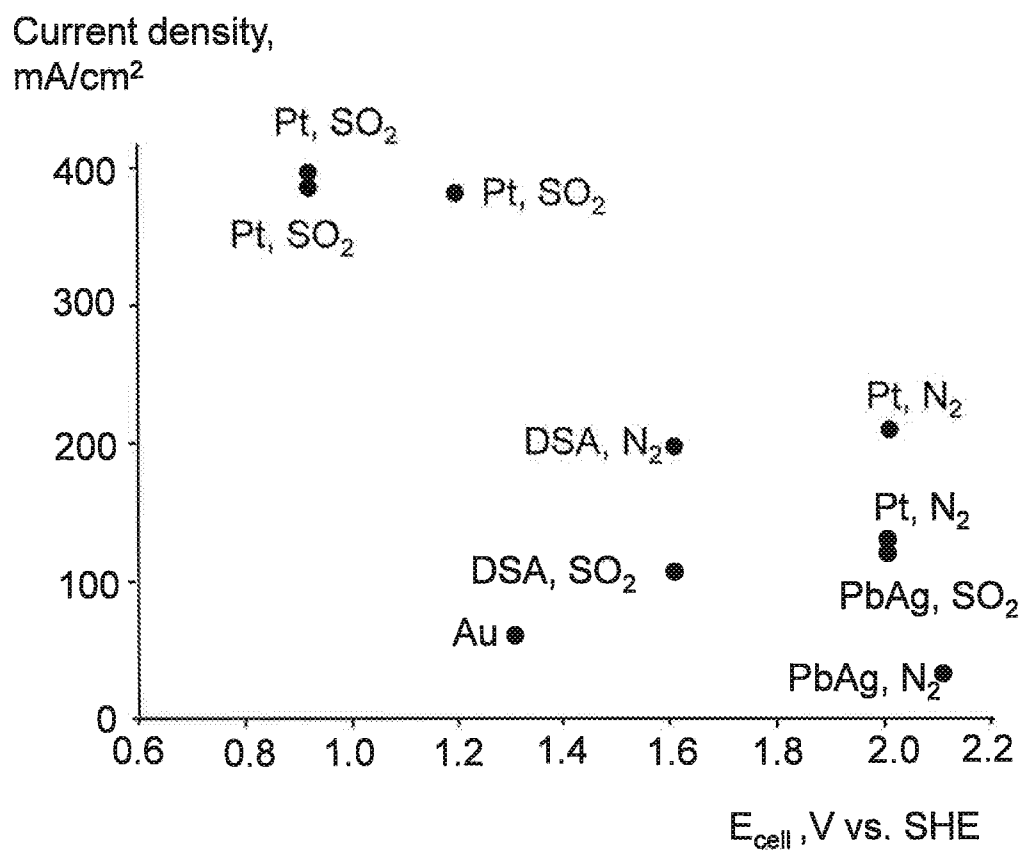


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2014/050439

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25C1/06 C25C7/02
ADD.

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)
C25C

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

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

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 1 120 423 A1 (MAJESTY THE QUEEN HER IN RIGHT) 23 March 1982 (1982-03-23)	1,2,10
Y	abstract; claims 1, 4, 7, 12; figures 1-6 page 2, line 20 - page 13, line 14	3-5,8,9, 11-13, 17-19
Y	----- US 1 260 830 A (STUDT FRANZ EDWARD [GB]) 26 March 1918 (1918-03-26) page 1, line 19 - page 3, line 52; claim 1; figures 1-4	11
Y	----- US 2006/021880 A1 (SANDOVAL SCOT P [US] ET AL) 2 February 2006 (2006-02-02) abstract page 2, paragraph 0019 - paragraph 0024 page 5, paragraph 0060 - paragraph 0062 ----- -/--	4,5,8,9, 12,13, 17,18



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

5 September 2014

Date of mailing of the international search report

11/09/2014

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2014/050439

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CA 2 175 270 A1 (ENGITEC SPA [IT]; SEITAL S R L [IT]) 9 November 1996 (1996-11-09) abstract; claims 1, 3, 5, 8; figures 1-8 page 1, line 19 - page 20, line 27 -----	19
Y	US 4 087 339 A (ELLIOTT ROBERT WILLIAM ET AL) 2 May 1978 (1978-05-02) abstract; claim 1; figures 1-3 column 1, line 54 - column 2, line 34 -----	3
A	US 4 431 496 A (REMICK ROBERT J [US]) 14 February 1984 (1984-02-14) the whole document -----	1-19
A	US 4 019 968 A (SPAZIANTE PLACIDO M ET AL) 26 April 1977 (1977-04-26) the whole document -----	1-19
A	US 4 149 944 A (GODDARD JOHN B ET AL) 17 April 1979 (1979-04-17) the whole document -----	1-19
A	PANDA B ET AL: "Electrowinning of copper from sulfate electrolyte in presence of sulfurous acid", HYDROMETALLURGY, ELSEVIER SCIENTIFIC PUBLISHING CY. AMSTERDAM, NL, vol. 59, no. 1, 1 January 2001 (2001-01-01), pages 55-67, XP004220601, ISSN: 0304-386X, DOI: 10.1016/S0304-386X(00)00140-7 the whole document -----	1-19
A	KNERR L A: "SULFUR DIOXIDE DEPOLARIZED GAS DIFFUSION ELECTRODES FOR COPPER ELECTROWINING", EXTENDED ABSTRACTS, ELECTROCHEMICAL SOCIETY. PRINCETON, NEW JERSEY, US, vol. 87-1, 21 March 1987 (1987-03-21), page 474/475, XP000027717, ISSN: 0160-4619 the whole document -----	1-19
A	WO 2007/045716 A1 (OUTOKUMPU TECHNOLOGY OYJ [FI]; BARKER MICHAEL HAROLD [FI]; HYVAERINEN) 26 April 2007 (2007-04-26) cited in the application the whole document -----	1-19
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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Douglas Robinson ET AL: "COMMERCIAL DEVELOPMENT OF A DESCENDING PACKED BED ELECTROWINNING CELL, PART 2: CELL OPERATION" In: "Electrometallurgy and Environmental Hydrometallurgy, Volume 2", 1 August 2003 (2003-08-01), John Wiley & Sons, Inc., Hoboken, NJ, USA, XP055138373, ISBN: 978-1-11-882060-5 pages 1395-1403, DOI: 10.1002/9781118804407.ch25, cited in the application the whole document -----	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/FI2014/050439

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CA 1120423	A1	23-03-1982	NONE
US 1260830	A	26-03-1918	NONE
US 2006021880	A1	02-02-2006	US 2006021880 A1 02-02-2006 US 2008047839 A1 28-02-2008
CA 2175270	A1	09-11-1996	AU 5209696 A 21-11-1996 CA 2175270 A1 09-11-1996 DE 19618517 A1 14-11-1996 IT M1950916 A1 08-11-1996
US 4087339	A	02-05-1978	CA 1062653 A1 18-09-1979 FI 772040 A 03-01-1978 FR 2356746 A1 27-01-1978 JP S535019 A 18-01-1978 JP S6053116 B2 22-11-1985 NO 772310 A 03-01-1978 PH 13006 A 09-11-1979 US 4087339 A 02-05-1978
US 4431496	A	14-02-1984	NONE
US 4019968	A	26-04-1977	AU 8147675 A 25-11-1976 BE 829721 A1 01-12-1975 CA 1043732 A1 05-12-1978 DE 2523950 A1 18-12-1975 DK 239575 A 01-12-1975 FI 751590 A 01-12-1975 FR 2273089 A1 26-12-1975 GB 1497542 A 12-01-1978 IE 41068 B1 10-10-1979 IT 1041375 B 10-01-1980 JP S512632 A 10-01-1976 LU 72595 A1 11-11-1976 NL 7506395 A 02-12-1975 PL 107640 B1 29-02-1980 SE 415281 B 22-09-1980 US 4019968 A 26-04-1977 ZA 7503322 A 26-05-1976
US 4149944	A	17-04-1979	BE 865641 A1 03-10-1978 CA 1108554 A1 08-09-1981 DE 2814364 A1 12-10-1978 FR 2386619 A1 03-11-1978 GB 1580877 A 10-12-1980 IN 148381 A1 31-01-1981 IT 1102465 B 07-10-1985 JP S5736358 B2 03-08-1982 JP S53149831 A 27-12-1978 NO 781166 A 05-10-1978 US 4149944 A 17-04-1979 ZA 7801916 A 25-04-1979
WO 2007045716	A1	26-04-2007	AU 2006303250 A1 26-04-2007 BR PI0617694 A2 02-08-2011 CA 2626720 A1 26-04-2007 CN 101292057 A 22-10-2008

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/FI2014/050439

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		EA 200800705 A1	30-10-2008
		EP 1937864 A1	02-07-2008
		FI 20051059 A	22-04-2007
		JP 4834103 B2	14-12-2011
		JP 2009512781 A	26-03-2009
		KR 20080058414 A	25-06-2008
		PE 08622007 A1	05-09-2007
		US 2008237036 A1	02-10-2008
		WO 2007045716 A1	26-04-2007
		ZA 200803109 A	25-02-2009
