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(54) Title: PRODUCTION OF METALLIC COPPER BY REDUCING COPPER (I) OXIDE USING HYDROGEN

(57) Abstract: The invention relates to a method for fabricating metallic copper in connection with the chloride-based hydrometallurgical production of copper. In the method the copper raw material is leached using copper (II) chloride-alkali chloride solution to obtain a solution of copper (I) chloride. Copper is precipitated from the solution as copper (I) oxide and the alkali chloride solution that is formed is routed to chlorine-alkali electrolysis to produce the chlorine, alkali hydroxide and hydrogen required in raw material leaching and copper recovery. Metallic copper is prepared from copper (I) oxide by reducing it from using hydrogen at elevated pressure and temperature in strongly alkaline conditions.



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## PRODUCTION OF METALLIC COPPER BY REDUCING COPPER (I) OXIDE USING HYDROGEN

### FIELD OF THE INVENTION

5 The invention relates to a method for fabricating metallic copper in connection with the chloride-based hydrometallurgical production of copper. In the method the copper raw material is leached using copper (II) chloride-alkali chloride solution to obtain a solution of copper (I) chloride. Copper is precipitated from the solution as copper (I) oxide and the alkali chloride  
10 solution that is formed is routed to chlorine-alkali electrolysis to produce the chlorine, alkali hydroxide and hydrogen required in raw material leaching and copper recovery. Metallic copper is prepared from copper (I) oxide by reducing it from a clearly alkaline solution using hydrogen at elevated pressure as either a batch or continuous process.

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### BACKGROUND OF THE INVENTION

US patent publication 6,007,600 describes a method for producing copper in a hydrometallurgical process from a copper-bearing raw material such as copper sulphide concentrate. According to the method, the raw material is  
20 leached counter-currently with a strong alkali chloride – copper chloride solution in several stages to form a copper (I) chloride solution. Since both divalent copper and some impurities comprising of other metals are always left in the solution, the divalent copper is reduced and solution purification is performed on the solution. The pure cuprous (I) chloride solution is  
25 precipitated by means of alkali hydroxide into copper (I) oxide and the oxide is reduced further into elemental copper. The alkali chloride solution formed during copper (I) oxide precipitation is treated further in chlorine-alkali electrolysis, from where the chlorine gas and/or chloride solution obtained is used for raw material leaching, the alkali hydroxide generated in electrolysis  
30 is used for oxidule precipitation and the hydrogen generated is used for the reduction of the copper to elemental copper. US patent publication 6,007,600 relates to the copper recovery method as a whole, and it is mentioned that

copper may be recovered from copper (I) oxide either in a pyrometallurgical process or in an autoclave. Autoclave reduction is not described further in the publication.

- 5 The fabrication of metallic copper from cuprite ( $\text{Cu}_2\text{O}$ ), an aqueous slurry of it, is described in the congress presentation by Hevia, J.F. & Wadsworth, M. E.: "Hydrothermal Reduction of Copper Oxides", pp. 93-108 in EPD Congress 1994, The Minerals, Metals & Materials Society, Warrendale, 1994. According to the research they described in the presentation, cuprite  
10 i.e. naturally occurring copper (I) oxide, is reduced to metallic copper with hydrogen reduction. Hydrogen reduction takes place in an autoclave at a temperature of approximately  $150^\circ\text{C}$  and at a hydrogen pressure of 1900 kPa (19 bar). There is what is known as dead time or an induction period related to the reduction before the reaction gets underway. The dead time  
15 lasts several hours. The use of certain additives such as hydrazine or anthraquinone may shorten the induction period.

A commercially available copper (I) oxide powder, intended mainly for pigment use, was used in the tests carried out by Hevia and Wadsworth,  
20 which is presumably fairly pure. In practice it has been found that the reduction of the copper (I) oxide generated during the hydrometallurgical fabrication is more difficult than that of commercial, pure  $\text{Cu}_2\text{O}$ . Therefore it has not been possible to estimate the effect of impurities etc. in the reduction tests described in the presentation. In reduction tests, the pH value of the  
25 slurry varied between 7 - 9 and in the article it is stated that the pH value was of no significance.

#### PURPOSE OF THE INVENTION

The purpose of the method according to the present invention is to reduce  
30 copper (I) oxide generated during the hydrometallurgical production of copper into pure metallic copper using hydrogen. The induction time related to the reduction of copper (I) oxide generated during hydrometallurgical

production may be cut considerably without additives by applying reduction in strongly alkaline conditions.

#### SUMMARY OF THE INVENTION

5 The purpose of this invention is to achieve a simple and inexpensive method of producing metallic copper from the copper (I) oxide generated during the hydrometallurgical production of copper. Sulphidic copper concentrate is the preferred feed material used in hydrometallurgical production. Copper concentrate is leached using an alkali chloride – copper (II) chloride solution and the copper (I) chloride solution generated is cleaned from impurities. Copper (I) oxide is precipitated from the copper (I) chloride solution by means of alkali hydroxide by known methods. The alkali chloride solution formed during copper (I) oxide precipitation is routed to chlorine-alkali electrolysis to produce the chlorine, alkali hydroxide and hydrogen required in raw material leaching and copper recovery. The pH of the copper (I) oxide slurry is adjusted to be strongly alkaline by means of alkali hydroxide generated in electrolysis, after which the reduction of copper (I) oxide into metallic copper is carried out in a pressurised space using the hydrogen obtained from electrolysis.

20

One essential factor of the invention is that the slurry to be fed to reduction is strongly alkaline. The pH value of the slurry is preferably in the range 9.5 – 13.5.

25 Due to the method of production, the copper (I) oxide always also includes chlorides, which react with alkali hydroxide to form the corresponding alkali salt, which then remains in the solution. The amount of chloride is around 0.1 – 1.5%.

30 The precipitated  $\text{Cu}_2\text{O}$  slurry in a strong alkali chloride solution may be routed to a pressurised space as it is without thickening or the slurry may be thickened. The slurry may also be fed to reduction as thickened, filtered and

washed and reslurried in water. The alkalinity of the slurry is achieved either during  $\text{Cu}_2\text{O}$  precipitation, by adding alkali hydroxide to the  $\text{Cu}_2\text{O}$  slurry to be fed into the pressurised space or by feeding the alkali hydroxide directly into the pressurised space.

5

The reduction of copper (I) oxide can be performed either as a batch or continuous process.

The essential features of the invention will become apparent in the attached  
10 claims.

#### DETAILED DESCRIPTION OF THE INVENTION

In the chloride-based hydrometallurgical production of copper, as described in the above-mentioned US patent 6,007,600, it is advantageous to get the  
15 copper in solution in monovalent form i.e. as copper (I) chloride. When chlorine-alkali electrolysis is connected to the process, the alkali chloride solution generated in the process stages is routed to chlorine-alkali electrolysis, which produces chlorine gas that is used in the leaching of the raw material, alkali hydroxide, which is used to precipitate copper (I) oxide  
20 and hydrogen, used to produce metallic copper.

Copper (I) oxide is reduced into metallic copper in the method according to the invention using hydrogen at an elevated pressure. Current autoclave technology has advanced and utilisation of higher pressure and temperature  
25 does not produce any great problems. Copper (I) oxide reduction can therefore be performed at a partial hydrogen pressure of 40 – 50 bar and at a temperature between 140 – 220 °C, preferably 170 – 220 °C.

The biggest problem in the hydrogen reduction of copper (I) oxide is what is  
30 known as dead time, i.e. the reactions get underway very slowly. It is mentioned in the prior art that this induction time has been shortened by using an additive, e.g. hydrazine or anthraquinone. Hydrazine is classified as

an environmental toxin, so its use is always to be avoided. Now it has been found that the induction time required for reduction can be considerably lessened even without additives, when the solution to be reduced is catalysed by making it strongly alkaline. In contrast to the impression given in the prior art, we have found that raising the pH has a powerful effect on the progression of reduction. According to the method now developed, the pH of the solution entering the autoclave is adjusted preferably to a value of 9.5 – 13.5 by means of the alkali hydroxide generated in the process. The pH adjustment of the slurry can be made in connection with the precipitation of copper (I) oxide that occurs using alkali hydroxide. Alkali hydroxide can also be added to the slurry before it is routed to the autoclave or the alkali hydroxide can be fed directly into the autoclave.

Raising the pH of the solution to be fed to reduction by means of alkali hydroxide is advantageous to the process not only in shortening induction time but also in other regards. In the chloride-based production of copper (I) chloride and further in that of copper (I) oxide, a small amount of chloride, about 0.1 – 1.5%, always remains in the oxide powder. When alkali hydroxide is fed into the oxide slurry entering reduction, the chloride in the oxide powder leaches into the water and is made to react to its salt by means of the hydroxide. When the sodium hydroxide generated in chlorine-alkali electrolysis is beneficially used as the hydroxide, sodium chloride is generated, which does not precipitate with the copper but stays in solution. The copper powder is separated from the slurry after reduction and the solution is circulated back to copper concentrate leaching. Although we speak of sodium in the description, other alkalis such as potassium may be used in its place.

For process economy it is advantageous that copper (I) oxide reduction can also be performed either directly from the alkali chloride solution or from a thickened slurry without filtration, washing and reslurrying of the precipitate with water. Of course the copper (I) oxide may be filtered, washed and

reslurried in an aqueous solution before reduction within the framework of the method now developed. Copper (I) oxide reduction may be implemented either as a batch or continuous process.

- 5 Another benefit of this method that is worthy of mention is the fact that nothing is generated in any of the stages that has to be removed from the internal circulation of the process. Furthermore, the alkali hydroxide used as additive and the hydrogen required in reduction are obtained as products of chlorine-alkali electrolysis, as described in US patent publication 6,007,600.

10

## EXAMPLES

### Example 1

- In order to clarify the method according to the invention, a series of tests was made, in which an aqueous slurry of copper (I) oxide was fed into an  
15 autoclave. The amount of copper (I) oxide in each test was 100 g/l. The partial pressure of hydrogen in every test was 45 bar and the temperature 200°C. The chloride content of the starting material was about 1 %. The pH of the solution fed into the autoclave in the tests varied between 8.3 – 13.2. The pH was raised by routing sodium hydroxide into the aqueous solution  
20 before it was fed into the autoclave. The other results are presented in Table 1 below. One indicator of the success of the test is the oxygen content of the copper powder produced, in other words, the lower the oxygen content, the more successful the reduction has been.

25

30

Table 1

| Test                                     | 1    | 2     | 3      | 4     | 5     | 6     | 7     | 8    | 9    |
|------------------------------------------|------|-------|--------|-------|-------|-------|-------|------|------|
| Particle size,<br>$\mu\text{m}$          | 50   | 50    | 50     | 30    | 50    | 50    | 50    | 50   | 50   |
| pH                                       | 8.3  | 12.5  | 12.5   | 12.5  | 12.5  | 12.5  | 13.2  | 12.5 | 9.6  |
| Hydrazine,<br>mg/l                       | 0    | 250   | 1000   | 0     | 0     | 0     | 0     | 600  | 600  |
| Duration of<br>test, min                 | 120  | 60    | 60     | 60    | 60    | 60    | 60    | 60   | 60   |
| Cl <sub>2</sub> content of<br>product, % | 0.54 | 0.007 | <0.005 | 0.007 | 0.035 | 0.037 | 0.011 | 0.25 | 0.80 |
| O <sub>2</sub> content of<br>product, %  | 10.5 | 1.5   | 4.1    | 1.3   | 1.6   | 1.3   | 0.84  | 9.5  | 12.3 |

The table shows that the best result was achieved in tests 4-7, when the pH of the solution was high and no additives were fed into the solution.

## PATENT CLAIMS

1. A method for the recovery of metallic copper from copper (I) oxide in connection with a chloride-based hydrometallurgical production of copper, whereby a copper raw material is leached with a solution of alkali chloride and copper (II) chloride to obtain copper (I) chloride solution, said solution is treated with alkali hydroxide to form copper (I) oxide, and the alkali chloride solution formed in copper (I) oxide precipitation is routed to chlorine-alkali electrolysis to produce the chlorine, alkali hydroxide and hydrogen required in raw material leaching and copper recovery, **characterised in that** the pH of the copper (I) oxide slurry is adjusted to be strongly alkaline by means of the alkali hydroxide generated in the method, after which the reduction of copper (I) oxide into metallic copper is performed in a pressurised space by means of hydrogen.
2. A method according to claim 1, **characterised in that** the pH of the slurry to be reduced is adjusted to a value of 9.5 – 13.5.
3. A method according to claim 1 or 2, **characterised in that** reduction is carried out at a partial pressure of hydrogen of 40 – 50 bar.
4. A method according to any of claims 1-3, **characterised in that** the reduction temperature is adjusted to be in the range of 140 – 220°C.
5. A method according to claim 4, **characterised in that** the reduction temperature is adjusted to be in the range of 140 – 220°C.
6. A method according to any of claims 1-5, **characterised in that** the copper (I) oxide routed to reduction contains chloride.

7. A method according to claim 6, **characterised in that** the amount of chloride is 0.1 – 1.5%.
8. A method according to claim 6 or 7, **characterised in that** the chloride in the copper (I) oxide dissolves and, in reaction with alkali hydroxide, forms the equivalent salt, which remains dissolved in solution.
9. A method according to any of claims 1-8, **characterised in that** the alkali used is sodium.
10. A method according to any of claims 1-8, **characterised in that** the alkali used is potassium.
11. A method according to any of claims 1-10, **characterised in that** copper (I) oxide is reduced from a concentrated alkali chloride solution.
12. A method according to any of claims 1-10, **characterised in that** copper (I) oxide is precipitated from a concentrated alkali chloride solution before reduction.
13. A method according to any of claims 1-10, **characterised in that** copper (I) oxide is precipitated from a concentrated alkali chloride solution, filtered, washed and slurried into an aqueous solution before reduction.
14. A method according to any of claims 1-13, **characterised in that** the reduction of copper (I) oxide is performed as a batch process.
15. A method according to any of claims 1-13, **characterised in that** the reduction of copper (I) oxide is performed as a continuous process.

16. A method according to any of claims 1-15, **characterised in that** the pH of the copper (I) oxide slurry is adjusted to be strongly alkaline during copper (I) oxide precipitation.

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17. A method according to any of claims 1-15, **characterised in that** the pH of the copper (I) oxide slurry is adjusted to be strongly alkaline by feeding alkali hydroxide into the copper (I) oxide slurry that is to be routed into a pressurised space.

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18. A method according to any of claims 1-15, **characterised in that** the pH of the copper (I) oxide slurry is adjusted to be strongly alkaline by feeding alkali hydroxide into a pressurised space.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2005/000400

## A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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)

IPC: C22B

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

SE,DK,FI,NO classes as above

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

EPO-INTERNAL, WPI DATA, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| Y         | US 4097271 A (GODEFRIDUS M. SWINKELS ET AL),<br>27 June 1978 (27.06.1978), column 7,<br>line 32 - line 35, claim 1, abstract<br>--- | 1-18                  |
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☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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- "&" document member of the same patent family

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

26/11/2005

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