Title: PREPARATION OF ZINC CHEMICALS FROM THE MINOR FLOW OF A PROCESS

Abstract: The invention is a novel process arrangement for producing pure zinc chemicals from the minor flow of a calcining-dissolving-electrolysis type of a preparation process of zinc. The invention is based on the fact that part of the production of the zinc sulphate-containing solution obtained from the dissolution of the calcining-dissolving-electrolysis plant is directed to the preparation of zinc chemicals. The actual recovery process of zinc, which is based on electrolysis, is not disturbed, as only part of the production of the zinc sulphate solution is directed to the preparation of zinc chemicals. The extraction process is based on the use of any organically substituted phosphoric acid or organically substituted thio phosphoric acid. The strong acid solution, which is generated as a by-product in the extraction process of zinc, is recycled back to the calcining-dissolving-electrolysis type of a preparation process of zinc.
Preparation of zinc chemicals from the minor flow of a process

The invention relates to the preparation processes of zinc and zinc chemicals. To be more precise, the invention relates to a process arrangement and circuit for preparing zinc chemicals in connection with a hydrometallurgical purification and preparation process of zinc.

In connection with zinc preparation, primary and secondary preparations are often mentioned. The primary production refers to various dissolutions of zinc ores, zinc concentrates and calcines and the treatment of solutions obtained therefrom by means of various hydrometallurgical methods, including liquid-liquid extraction. The secondary production refers to the use of various raw materials of lesser volumes, such as particulates of electric furnaces, Waeltz oxides and galvanizing cinders, as raw material.

In the primary production of zinc, traditional original materials, such as sulphide zinc ores, are concentrated, i.e., a zinc concentrate, and when so desired, also zinc calcine are further prepared from them. Further, a concentrated zinc sulphate solution is often produced from the zinc concentrate and the zinc calcine, being well-suited for the electrolytic preparation of zinc metal. The present invention relates to the traditional hydrometallurgical primary production of zinc.

In the traditional hydrometallurgical production of zinc, complex solution purification is needed after the dissolution of the raw material, comprising the preparation of a pure zinciferous solution. The electrolytic preparation of zinc is very sensitive to certain impurity agents. Therefore, it is important to prepare a sufficiently pure solution for the zinc electrolysis.

For the preparation of zinc, a method is widely used, wherein zinc concentrate is calcined to form zinc oxide, the zinc oxide is dissolved in a diluted sulphuric-acid solution in a so-called neutral dissolution, the zinciferous solution is purified, and zinc is separated from the purified solution by electrolytic separation.
At the dissolving stage of the zinc calcine, the zinc dissolves and the major part of the iron contained by the zinc calcine can be separated as zinc ferrite that does not dissolve in the diluted acid. In addition to the zinc, the solution obtained from the neutral dissolution contains bivalent iron, cadmium, copper, cobalt, nickel, calcium, manganese and chlorides.

To obtain a solution that is suitable for the electrolytic recovery of zinc, the solution obtained from the neutral dissolution is purified by a multi-stage solution purification process. Normally, the solution purification comprises three stages, wherein copper, cobalt, nickel, and finally, cadmium are removed.

The zinciferous sulphate solution obtained from the neutral dissolution is also suitable for a feed material in the leaching method of zinc. Until recently, the liquid-liquid extraction has been used for zinc preparation mainly in small-scale processes that employ secondary raw materials. The US Patent 5,135,652, for example, describes a solvent extraction that can be used to selectively separate zinc from the zinc sulphate solution, which may contain zinc sulphate up to its saturation concentration, and one or more of a group containing the following: bivalent iron, trivalent iron, calcium, magnesium, manganese, sodium, potassium, arsenic, antimony, copper, cadmium, germanium, and indium.

The purpose of this invention is to provide a new kind of a process arrangement for producing pure zinc chemicals from the minor flow of a zinc preparation process of a calcining-dissolving-electrolysis type. The invention is based on the fact that part of the production of the zinc sulphate-containing solution obtained from the dissolving of the calcining-dissolving-electrolysis plant is directed to the preparation of zinc chemicals. As only part of the production of the zinc sulphate solution is directed to the preparation of zinc chemicals, the actual recovery process of zinc that is based on the electrolysis is not disturbed.

In the process arrangement according to the invention, the preparation process of zinc chemicals is based on a selective separation of zinc by extraction with
known extraction techniques. The known extraction process is based on the use of any organically substituted phosphoric acid or organically substituted thiophosphinic acid. According to the invention, the extraction process is connected to the calcining-dissolving-electrolysis process described above.

The invention provides considerable advantages. In the conventional calcining-dissolving-electrolysis process, the bottleneck of the production lies in the electrolysis process. Accordingly, the solution according to the invention for taking the minor flow to the preparation line of zinc chemicals adds value to the actual production process of zinc. The invention provides an advantageous process solution for the preparation of zinc chemicals of a lesser demand. In the extraction process of zinc used in the invention, a strong acid solution is generated as a by-product, which can simply be recycled to be exploited in the preparation process of zinc. In that case, no separate investments for the final treatment of the acid solution are needed.

The invention comprises a process circuit and arrangement for preparing pure zinc chemicals from a zinc sulphate-containing solution by an extraction method, whereby the raw material flow of the extraction is separated as a minor flow from the calcining-dissolving-electrolysis type process line of zinc primary production after the neutral dissolving stage.

Fig. 1 shows a simplified process chart of the calcining-dissolving-electrolysis type preparation process of zinc and the preparation stage of zinc chemicals connected thereto.

In the following, the invention is described in detail with reference to the appended drawing.

In the preparation of zinc, a calcine 10 containing zinc oxide is dissolved in a sulphuric-acid solution in a neutral dissolution. The neutral dissolution is typically carried out in several stages. A solution residue 12, which is not soluble in
the dissolution and contains iron, among others, is directed to a strong acid dissolution. A zinc sulphate-containing solution 11 is directed to a multi-stage solution purification, wherein a zinc powder 14 is used to precipitate copper, cobalt, nickel and cadmium. The solution-purified zinc sulphate solution 15 is directed to an electrolysis plant, wherein the zinc is recovered at cathodes 16 by means of electrolysis. The electrolyte, from which the zinc was recovered 17, contains a considerable amount of sulphuric acid, which is reintroduced by directing it to the strong acid dissolution, among others. In the strong acid dissolution, the acid is used up in reactions. Accordingly, in addition to the recycled acid, a certain amount of pure acid is added into the process. In the neutral dissolution, the pH of the solution should not be raised too high. It is reasonable to adjust the pH of the neutral dissolution with fresh acid and, in addition, with an acid 18 that is obtained from the strong acid dissolution.

According to the invention, a minor flow 13 is separated from the main flow 11 of the zinc sulphate-containing solution obtained from the neutral dissolution, and directed to the extraction of zinc. In the extraction, diethylhexylphosphoric acid (DEHPA) or di-2-ethylhexylphosphoric acid (D2EHPA) is exploited. Towards the end of the dissolving stage, the pH of the solution that is going to the extraction can be raised to a level suitable for the extraction, when needed, by means of the calcine. Zinc is separated from the organic phase by stripping it with an acid-containing solution 21. The raffinate 19, which is generated in the extraction, contains sulphuric acid, among others, and is directed to the strong acid stage to be reused.

In stripping, wherein pure acid is used, the pure zinc can be recovered in a sulphuric-acid solution, wherein the content of zinc can be up to 150g/l. Various pure zinc products can be prepared from this solution 20 by any known methods, such as by chemical precipitation or evaporation.
CLAIMS:

1. A process circuit for preparing pure zinc chemicals from a zinc sulphate-containing solution by means of an extraction method, characterized in that the raw material flow of the extraction is separated as a minor flow (13) from the calcining-dissolving-electrolysis type of a process line (11) of the zinc primary production after a neutral dissolution stage.

2. A process arrangement according to Claim 1, characterized in that a raffinate (19) that is generated in the extraction is directed to be reused in the strong acid dissolution of the said calcining-dissolving-electrolysis type of a process.

3. A process arrangement according to Claim 1, characterized in that diethylhexylphosphoric acid (DEHPA) or di-2-ethylhexylphosphoric acid (D2EHPA) is exploited in the extraction.

4. A process arrangement according to Claim 1, characterized in that towards the end of the dissolving stage, the pH of the solution going to the extraction is raised to a level suitable for the extraction by means of a calcine.
Fig. 1
INTERNATIONAL SEARCH REPORT

International application No. PCT/FI 2005/000380

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: C01G, C22B, C25C

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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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>A</td>
<td>US 5135652 A (DANIEL A.D. BOATENG), 4 August 1992 (04.08.1992), abstract</td>
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<td>US 3989607 A (PHILIP D. BUSH ET AL), 2 November 1976 (02.11.1976), abstract</td>
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* Further documents are listed in the continuation of Box C.  
X See patent family annex.

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent published on or after the international filing date
"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"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

Date of the actual completion of the international search: 20 December 2005
Date of mailing of the international search report: 22 -12- 2005

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