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(54) Title: METHOD FOR DECOMPOSING METAL SULPHATE

(57) Abstract: The method of the invention relates to the decomposition in a fluidized bed of metal sulphates generated in the metallurgical industry. The decomposition of metal sulphates is carried out so that the metal oxides generated are recovered in such a pure form that they can be recycled to be reused in the manufacture of metal alloys such as steel. In particular, sulphates containing nickel, iron and chrome are decomposed in oxidising conditions using pyrites or pyrrhotite as the fuel and bed material.

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METHOD FOR DECOMPOSING METAL SULPHATE

FIELD OF THE INVENTION

The method of the invention relates to the decomposition in a fluidised bed of
5 metal sulphates generated in the metallurgical industry. The decomposition
of metal sulphates is carried out so that the metal oxides generated are
recovered in such a pure form that they can be recycled to be used again in
the manufacture of metal alloys such as steel. In particular, sulphates
containing nickel, iron and chrome are decomposed in oxidising conditions
10 using pyrites or pyrrhotite as the former and fuel of the bed material.

BACKGROUND OF THE INVENTION

Metal sulphates are generated in various metallurgical processes such as for
example during steel pickling or in the electrolytic purification of metal into
15 anodic sludge. Mixed sulphate waste containing sulphuric acid cannot be
used as such anywhere, and is largely hazardous waste.

US patent 4,824,655 describes a method for producing sulphur dioxide by
the thermal decomposition of sulphur-containing metal sulphates in a
20 fluidized bed. The metal sulphate is mainly iron sulphate, which includes a
small amount of other metals such as compounds of aluminium, magnesium,
titanium, manganese, chrome and vanadium. The sulphate originates largely
from the manufacture of titanium. The decomposition of metal sulphate
occurs at a temperature of 800 – 1100°C. It is essential that sulphur-
25 containing material, such as sulphur waste or fine pyrites, be used in
sulphate reduction in order to produce the largest possible amount of sulphur
dioxide. The energy required for sulphate reduction is produced with a
carbon-containing fuel such as coal, coke or heavy fuel oil. The majority of
the fuel is introduced with the bed material, but some is fed separately with
30 the carrier gas. The key point in the method is the production of sulphur
dioxide, and there is no mention of the use of the metal-containing solids that
are generated, so they go to waste. The amount of waste generated in this

way is considerable. The feed of extra fuel, particularly of extra liquid or gaseous fuel, makes it difficult to keep the temperature regulated evenly, since localised feeding to the bed may result in hot spots, which cause the sintering of the bed. Carbon-containing fuel creates carbon dioxide emissions, and the aim is to reduce the amount of these emissions.

PURPOSE OF THE INVENTION

The purpose of the method of this invention is to avoid the drawbacks of the method described above. The aim of the method now developed is to decompose metal sulphates generated in the metallurgical industry, particularly mixed sulphates that contain nickel, so that the fuel used in their decomposition produces bed material on oxidising, whereupon the uniform distribution of fuel prevents the generation of hot spots. The fuel does not contain carbon either, so that carbon dioxide emissions are not produced.

SUMMARY OF THE INVENTION

The essential features of the invention will be made apparent in the attached claims.

- The invention relates to a method for the decomposition of a residue generated in the metallurgical industry, containing at least one metal sulphate, into oxides. The decomposition of metal sulphide is performed in a fluidised bed furnace, whereby the energy required for decomposing the sulphate is obtained from roasting the iron sulphide used as the bed material.
- Roasting is performed in oxidising conditions to form an oxide that is essentially free of sulphur for reuse in the steel industry, and the sulphur dioxide that is generated is used in the manufacture of sulphur and/or sulphuric acid.
- According to one embodiment of the invention the metal sulphate is a mixed sulphate, including nickel, chrome and iron sulphate. Mixed sulphate is for instance the mixed sulphate generated during the pickling of steel.

According to another embodiment of the invention the metal sulphate is nickel sulphate. Nickel sulphate is formed for instance during the electrolytic purification of copper.

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The iron sulphide used as the fluidised bed material and energy producer is pyrite and/or pyrrhotite. The decomposition of sulphate is carried out at a temperature of 800 – 900°C and the residence time in the bed is around 1 – 5 h. The sulphur concentration of the alloy of the oxide or oxides formed is a maximum of 0.5%.

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DETAILED DESCRIPTION OF THE INVENTION

Impure sulphate sediments are generated in the metallurgical industry, such as in steel manufacture and the electrolytic purification of metals, which contain sulphates of nickel, chrome and iron etc. Sulphates are soluble enough that they cannot be removed from the circuit as they are but in addition their metal content should be recovered in an environment-friendly way. As described in the prior art, sulphate residues, in particular those generated during the manufacture of titanium, are treated in a fluidised bed furnace, but mainly in order to produce sulphur dioxide gas for the manufacture of sulphuric acid.

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Mixed sulphate precipitate is generated in the pickling stage of steel manufacture, containing in addition to iron sulphates ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3$) also nickel and chrome sulphate (NiSO_4 , $\text{Cr}_2(\text{SO}_4)_3$) and sulphuric acid. In oxidising conditions iron sulphates and chrome sulphate decompose at a far lower temperature than nickel sulphate. Nickel sulphate may also decompose at lower temperatures in reducing conditions, but then there is a danger that in addition to oxides, sulphides will also form. When the purpose is to produce a product fit for a steelworks for example, its sulphur content must be quite low i.e. below 0.5 %.

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The end product of the pyrometallurgical fabrication of copper is copper anode, which is further purified electrolytically into pure cathode copper. The anode sludge that is generated contains the impurities of the anode, of which nickel in the form of nickel sulphate is one of the most significant.

5

The decomposition of sulphates into oxides is an endothermic reaction. In the method according to the prior art, the bed of the fluidised bed furnace was formed so that reducing sulphur-containing material and some of the carbon-containing fuel were mixed with the sulphates, pelletised and then fed
10 into the furnace. In addition, part of the fuel was fed separately. In the method now developed the fuel required for decomposition acts as the bed material i.e. no separate carbon-containing fuel is required at all. Iron sulphide such as pyrite or pyrrhotite acts as the fuel and bed material, which is roasted and, simultaneously, the sulphates fed into the bed are
15 decomposed into their oxides. The reactions that occur in iron sulphide roasting are so exothermic that the heat generated is enough for the endothermic reactions required in sulphate decomposition without the need for any extra heat.

20 Sulphate decomposition is carried out at a temperature of 800 – 900°C and the residence time in the bed is around 1 – 5 h. In particular the decomposition of nickel sulphate requires the temperature mentioned above, in order for the decomposition into oxides to take place in a reasonable time. The invention relates thus to a method for the decomposition of one or more
25 metal sulphates, where nickel sulphate is preferably one of the sulphates. Sulphate decomposition is carried out in oxidising conditions, in order to avoid sulphur remaining in any form among the oxides. Sulphur-free oxides are fit for reuse e.g. in a steelworks. The sulphur dioxide-containing gases that are formed are routed to sulphur and/or sulphuric acid manufacture, but
30 the process is regulated on the basis of producing metal oxides that are as pure as possible rather than sulphur dioxide production.

It is preferable to keep the sulphur content of the oxide alloy to be fed to the steelworks as small as possible, since it will reduce the demand for oxygen used for sulphur removal in conversion.

- 5 When all the energy required for sulphate decomposition is brought in the form of bed material, the drawbacks that can arise from feeding fuel to the bed separately can be avoided. The use of separate fuel is awkward because it is difficult to feed it into the bed so evenly that no localised hot spots are generated where the bed material and sulphates would be
10 sintered. Hot localised points are also harmful to the equipment. Introducing a separate fuel to the fluidised bed means carbon-containing material, generally feeding gas into the bed. The drawback of carbon-containing fuel is that the fuel produces carbon dioxide emissions and in addition it requires a post-combustion chamber as additional equipment.

15

- When iron sulphides are used as the energy producer in the fluidised bed decomposition of sulphates, it is easy to control the shutdown of the bed nor does a malfunction in the sulphate feed cause problems. When using iron sulphides the operation is run in oxidising conditions, and there are no
20 additional sulphides to be burnt in the bed. If the operation is run in reducing conditions and there is a malfunction, then the sulphides burn and hot spots, molten phase and sintering occur.

EXAMPLES

25 Example 1

- The decomposition of impure nickel sulphate was carried out in a fluidised bed furnace using pyrite as bed material and fuel. Air was used as the fluidising air and fluidising was carried out at a rate of 0.2 m/s in slightly oxidising conditions. After 1.5 h the sulphur concentration of the nickel oxide
30 removed from the furnace was 0.34 % and after 3 h it was 0.15 %, so that it was highly suitable for recycling to the steel industry.

Example 2

The decomposition of mixed sulphate was performed in a fluidised bed furnace, where the composition of the mixed sulphate was Fe 12.8%, Cr 1.8%, Ni 1.8%, Mo 0.08% and SO₄ 44.4%. Pyrite was used as fuel and bed material. Air was used as the fluidising air and fluidising was carried out at a rate of 0.2 m/s in slightly oxidising conditions. After 1.5 h the sulphur concentration of the oxide mixture removed from the furnace was 0.32 % and after 3 h it was 0.17 %, so it was highly suitable for recycling to the steel industry.

PATENT CLAIMS

1. A method for decomposing a residue generated in the metallurgical industry that includes at least one metal sulphate into oxide,
5 **characterised in that** the decomposition of the metal sulphate is carried out in a fluidised bed furnace, whereby the energy required for sulphate decomposition is obtained from roasting of an iron sulphide used as the furnace bed material, the decomposition is carried out in oxidising conditions to form an essentially sulphur-free
10 oxide for recycling to the steel industry, and the sulphur dioxide that is generated is used for the manufacture of sulphur and/or sulphuric acid.
2. A method according to claim 1, **characterised in that** the metal
15 sulphate is a mixed sulphate, which includes nickel, chrome and iron sulphates.
3. A method according to claim 1 or 4, **characterised in that** the metal
20 sulphate is the nickel-chrome-iron sulphate generated during pickling in steel industry.
4. A method according to claim 1, **characterised in that** the metal
sulphate is nickel sulphate.
- 25 5. A method according to claim 1 or 4, **characterised in that** the metal sulphate is the nickel sulphate generated in an electrolytic purification of copper.
- 30 6. A method according to any of claims 1 – 5, **characterised in that** the iron sulphide is pyrite and/or pyrrhotite.

7. A method according to any of claims 1 – 6, **characterised in that** the sulphate decomposition is carried out at a temperature of 800 – 900°C.
- 5 8. A method according to any of claims 1 – 7, **characterised in that** the decomposition time is 1 – 5 h.
9. A method according to any of claims 1 – 8, **characterised in that** the sulphur concentration of the oxide formed in the fluidised bed furnace
10 is a maximum of 0.5%.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2006/000361

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: C01B, C01F, C01G, C22B, F27B, C23C, C23F, C23G,
C25B, C25D, C25F

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 1484811 A (METALLGESELLSCHAFT AKTIENGESELLSCHAFT), 8 Sept 1977 (08.09.1977) --	1-9
Y	GB 727799 A (THE DORR COMPANY), 6 April 1955 (06.04.1955) --	1-9
A	GB 721591 A (BRITISH TITAN PRODUCTS COMPANY LIMITED), 12 January 1955 (12.01.1955) --	1-9
A	US 3053626 A (JOHN A. PATTERSON), 11 Sept 1962 (11.09.1962) --	1-9

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

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

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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	EP 0262564 A2 (BAYER AG), 6 Apr 11 1988 (06.04.1988) -- -----	1-9

International patent classification (IPC)**C01B 13/32** (2006.01)**C01B 17/52** (2006.01)**C01B 17/58** (2006.01)**C23G 1/36** (2006.01)**Download your patent documents at www.prv.se**

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Use the application number as username.

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Paper copies can be ordered at a cost of 50 SEK per copy from PRV InterPat (telephone number 08-782 28 85).

Cited literature, if any, will be enclosed in paper form.

INTERNATIONAL SEARCH REPORT

Information on patent family members

26/01/2007

International application No.

PCT/FI2006/000361

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