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(54) Process for improving recovery of metals from sulphidic ores or bulk concentrates

(57) The invention relates to a process for improving recovery of metals from ores containing at least two different non-ferrous metal sulphides or from bulk concentrates of such ores, wherein said sulphides are present in different phases, whereby said ores, preferably directly after having been ground, or said bulk concentrates are submitted to a heating step in such conditions to increase the size of at least one of the different phases and/or to oxidise selectively at least one of said metal sulphides, thereafter separating a concentrate of at least one of said metals.

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Description

The invention concerns a process for improving recovery of metals from ores containing at least two different non-ferrous metal sulphides or from bulk concentrates of such ores, wherein said sulphides are present in different phases.

The treatment of copper-zinc ores, and of so-called "complex" sulphides ores containing copper, lead and zinc, joint generally with traces of other elements, such as precious metals, arsenic, antimony, mercury,... is a source of problems due to the fact those ores do not always respond to selective flotation, either directly in three successive steps, or via bulk Cu-Pb or Pb-Zn concentrates. If the production of three separate or bulk concentrates of marketable quality is not feasible for technical reasons, it may even appear that the only solution must be found in the extraction of one bulk copper-lead-zinc concentrate.

For instance, one of the main difficulties concerning the treatment of copper-zinc ores comes from the metallurgical requirements imposed on both copper and zinc concentrates with respect to their respective zinc and copper contents. Such ores contain for instance not more than 8 % Zn in the copper concentrate and not more than 2-3 % Cu in the zinc concentrate.

Mineralogical characteristics of those ores formed by disseminated sulphides not only of copper, lead and zinc, but also iron sulphides, their degree of oxidation, the presence of coatings of supergene cupriferrous minerals on sphalerite grains, etc. may be such that extraction of concentrates of marketable grade is not possible or is too expensive. The amount of middling or unliberated metal sulphides, or in other words of particles containing still different phases of sulphides such as $CuFeS_2$, Cu_2S, ZnS, PbS or FeS_2, is indeed often too high even after a fine grinding and/or a regrinding step of the rougher concentrates. A lack of selectivity is also found in relation to the easy sliming and/or oxidation of some minerals.

The invention has as an aim among others to present a process enabling to extract metal concentrates from an ore or a bulk concentrate with very small sized phases of metal sulphides, whereby ores, being disregarded until now, will become economically interesting.

To this purpose said ores, preferably directly after having been ground, or said bulk concentrates are submitted to a heating step in such conditions to increase the size of the different phases and/or to oxidise selectively at least one of said metal sulphides, thereafter separating a concentrate of at least one of said metals and more specifically of copper and zinc.

Particularly, during the heating step, an intimate contact is realised between particles of said ores or bulk concentrates in order to achieve mass transfer between these particles.

Advantageously, during the heating step said ores or bulk concentrates are submitted, with or without partial smelting depending on the mineralogical composition, to selective oxidising roasting, more particularly in order to oxidise at least one metal sulphide present in this ore or bulk concentrate, especially to oxidise iron which is possibly present in the treated ores or bulk concentrates.

According to a particular embodiment of the invention, the ores or concentrates are heated to a temperature of at least 550°C to volatilise, in a gas phase, at least one of the following elements : lead, mercury, arsenic or antimony, which are possibly present in the ores or bulk concentrates.

According to a preferential embodiment of the invention, at least at the end of the heating step, the temperature is decreased to about 650°C or lower, to minimise mutual solubility of metals present in the ores or bulk concentrates, like copper and/or iron in ZnS.

In a specific embodiment of the invention, at the end of the heating step, the ore or concentrate is roasted at a temperature above the inversion point of sphalerite to wurtzite, if said ore or bulk concentrate contains sphalerite, in order to generate a crystal structure which does not allow solution of elements, like copper or iron, into ZnS.

Other characteristics and advantages of the invention will result from the following description of some specific embodiments of the process for treating ores or bulk concentrates according to the invention; this description is given for the sake of example only, without limiting the scope of the invention; the reference figures quoted below refer to the attached drawings.

Figure 1 represents a classic very schematic flowsheet applied at a mine site.

Figure 2 represents the same flowsheet which is amended with the process according to the invention.

The invention concerns a process for upgrading ores and especially bulk concentrates in which the size of the individual sulphide-phases (Cu-sulphide, Zn-sulphide) is too small to have a good recovery of metals out of these ores or bulk concentrates by physical separation methods. Moreover, the invention is also relating to a process for separating some valuable metals, like lead, or undesired metals, like iron, mercury, arsenic or antimony, at the mining site itself.

By bulk concentrate is, in this specification, understood the concentrate obtained after separating most of the gangue and containing mainly particles which are composed of several phases from different metals, whereby these phases are to be separated. By "phase" is to be understood : a part of a particle with a substantially homogeneous chemical composition separated by interfaces from adjacent phases. Such a phase can contain one or more crystals.

More particularly, an ore is exploited from a mine and is submitted to a crushing step to reduce parts from up to 1,5 m to particles sized from about 0,5 cm to 2 cm. Subsequently, grinding reduces these particles to particles with a size between about 300 µm and 10 µm. After separation of the ore into, respectively, a valuable fraction and a non-valuable fraction, respectively, a bulk concentrate and a tailing are obtained.

According to the invention, the ores or bulk concentrates are brought, by grinding, into an appropriate form for selective roasting.

In roasting a mixture of several metal sulphides, e.g. ZnS, $CuFeS_2$ and FeS_2, oxidation and elimination of S will proceed in a predetermined order. This order is determined by the relative thermodynamic stabilities of the metals and their respective oxides and sulphides. For the mixture suggested above the roasting will first produce SO_2 and Fe-oxide. Cu and Zn will remain sulphidic. Not until large part of the Fe present in the feed is oxidised (even the Fe mixed at atomic scale within the marmatite or chalcopyrite), ZnS will oxidise. Finally when all the ZnS is oxidised, the remaining Cu_2S will oxidise. These differences in thermodynamic stability can be used to obtain a mixture in which only part of the material is oxidised, resulting in different chemical and/or physical behaviour. The process as mentioned above in which the roasting is stopped before dead roast (complete oxidation) is called hereafter selective roasting.

The ores or bulk concentrates are, more particularly, brought to a particle size necessary for separating gangue from sulphides without substantial loss of recovery. This particle size is preferentially comprised between 500 µm and 50 µm. Subsequently, these ores or bulk concentrates are submitted to selective oxidising roasting. If the ores or bulk concentrates contain iron sulphide (FeS_2) this iron will be oxidised to form magnetite, while the sulphur bound to iron will form SO_2 contained in a gas phase. The heat liberated by these reactions will increase diffusion in the particles and between these particles of the ores or bulk concentrates. This will involve a grain growth in said particles and, as a consequence, the size of the phases present in such particles will increase or become more regular. To realise a good recovery of metals, said heating step is controlled in such a way that most of said phases obtain, for instance, a d_{80} value of at least 20 µm and preferably of at least 30 µm.

This is especially very interesting for ores which contain very fine intergrown phases of metal sulphides. For instance, for an ore consisting mainly of $CuFeS_2$, ZnS and PbS, which are very finely disseminated and/or very finely intergrown, an economical separation of these metals with good recoveries was practically impossible.

Therefore, achieving a grain growth or phase growth is very desirable for the exploitation of such ores. To this end, to obtain sufficient mass transfer between particles of the ore or bulk concentrate and thus said grain or phase growth, an intimate contact between these particles is realised by using for example a multiple hearth furnace or kiln. Preferably, roasting is performed in such conditions that said particles are partially melted, or at least some of them, so as to enhance diffusion and consequently preferential phase and grain growth.

The use of fluidised bed roasting is less suitable because there is very few contact and diffusion between particles. Furthermore, managing precisely retention time in fluidised bed roasting is difficult and an important pre-treatment of the feed, to obtain a narrow distributed particle size, is required. This pre-treatment is not necessary when roasting takes place in a hearth furnace or kiln.

In the subsequent processing of the ores or bulk concentrates, the separation of the different phases present in the ore or bulk concentrate, and the recovery of metal sulphides present in said phases, will be easier and cheaper due to a more regular and/or greater phase size.

For a sulphidic ore, containing chalcopyrite, marmatite and pyrite, after selective roasting in such a way that all iron sulphide is oxidised while maintaining at least one non-ferrous metal sulphide, mainly particles were obtained with a central core of respectively Cu_2S or ZnS covered by a layer of magnetite. To liberate the different phases, these particles are ground. Afterwards, they are separated by a physical separation method for instance first magnetic separation, flotation or cycloning of magnetite, followed by for instance flotation to separate sphalerite from bornite and/or chalcocite, which is obtained by oxidation of chalcopyrite.

By the heat, generated by the selective roasting, impurities like mercury, arsenic or antimony, are volatilised in a gas phase as from about 550°C. If they are present in relatively high amounts, they can possibly be recovered economically from the gas phase. An ore containing lead can be heated to a higher temperature so as to obtain a sufficient volatilisation of the lead as PbS by forming lead sulphate in the gas phase. It has been found that volatilisation of PbS increases with a factor of 10 with an increase of 100°C in the roasting temperature range. At 900°C lead is almost completely eliminated (< 0,1 %) within one hour. At 800°C lead is almost eliminated within six hours, while at 700°C still 85 % of the lead is present after six hours. The degree of lead volatilisation is a function of temperature and retention time.

Preferably, the ore or bulk concentrate is roasted at a temperature of at least 800°C to volatilise the lead sulphide. If the ore contains enough lead to recover it economically, the lead is, as lead sulphate, extracted from the gas phase.

In certain cases it is possible to maintain the lead sulphide as a phase in the concentrate so as to be separated according to known physical separation methods in the same way as the copper and zinc sulphides.

By heating the ores or bulk concentrates during selective roasting, mutual solubility of metals can cause difficulties in the further recovery of these metals. Therefore, in the process, according to this invention, the temperature at the end of the heating step is preferably decreased to about 650°C or lower to reduce mutual solubility. More particularly, at the end of the heating step the temperature is decreased to a temperature between 650°C and 550°C to obtain a separation of Cu_2S and ZnS due to a lower solubility.

In another embodiment of the process, according to this invention, from the beginning of the heating step roasting is executed at a temperature between 550°C and 650°C and preferably at a temperature of about 600°C.

In still another embodiment of the invention, in order to overcome this mutual solubility of metals present in the ore or bulk concentrate, the ore or bulk concentrate is heated so as to obtain a new crystal structure. It is expected that this crystal structure minimises or prevents said mutual solubility. For example, in an sulphidic ore containing copper and zinc, the zinc is present as sphalerite (ZnS) which has an isometric face centred cubic structure, while copper is present as chalcopyrite ($CuFeS_2$) which has a similar structure with one half of the zinc atoms replaced by copper atoms and the other half replaced by iron atoms. Due to the high similarity of these two structures, important problems in roasting could arise. In simply heating up the ore or concentrate, Cu and Fe will migrate substantially into the sphalerite.

To overcome this problem, according to the invention, the ore or bulk concentrate is heated to a temperature above the inversion temperature to obtain another crystal structure for which it is assumed that it does not allow mutual solubility of metals present. For example, in the above ore, containing sphalerite and chalcopyrite, at very high temperature sphalerite will be transformed to wurtzite which has a hexagonal closest packing. This structure of wurtzite is supposed to decrease solubility of Cu or Fe. The inversion temperature of pure sphalerite to wurtzite is 1020°C. Consequently, the ore or bulk concentrate is to be heated to a temperature above this inversion point. Because the inversion temperature depends upon the impurities present in the ore or bulk concentrate, this temperature can vary as a function of the composition of the ore or bulk concentrate. For an iron containing ore, this temperature is decreased. However, the iron present in other phases than sphalerite has no influence on the inversion temperature.

At least at the end of the roasting process, the temperature is raised above the inversion temperature from sphalerite to wurtzite and preferably above 950°C.

In a favourable embodiment of the invention, said temperature is applied from the starting of the roasting.

Afterwards, when most or all of the sphalerite has been transformed to wurtzite, the ore or bulk concentrate is cooled down quickly to a temperature at which diffusion is very low so as to avoid solution of copper or other metals in ZnS. Depending on the cooling conditions, it is possible to retain ZnS as wurtzite in a metastable form, which contains less dissolved copper.

In another embodiment of the process, according to the invention, this problem of mutual solubility of metals is avoided by selective oxidising roasting. For instance, by selective oxidising an ore or bulk concentrate which contains zinc and copper, a rejection of Cu_2S from the newly formed ZnO phase is obtained. To this end, roasting conditions are managed so as to oxidise only zinc and elements present which are less noble than zinc, whereby roasting is performed until at the very most all sulphur bound to zinc is oxidised. In such a way, copper is not oxidised and remains in sulphidic form. In a next process step, zinc oxide can be separated easily from copper sulphide, for example, by flotation after grinding or milling.

In a specific embodiment of the invention, if iron is present in the ore or bulk concentrate, first iron is oxidised, to form magnetite, and, subsequently, this magnetite is separated from the rest of the ore or bulk concentrate by a physical separation method, for example by magnetic separation. In a next step of the process, the ore or bulk concentrate is further roasted if it contains zinc and copper, so as to oxidise zinc, in such a way that the subsequently separation into a copper and a zinc concentrate will be simplified.

The following example illustrates the selective roasting of a Cu-Zn-bulk concentrate with 27 % Zn, 20 % Cu, 24 % Fe, 35 % S, 1 % Pb and 2 % SiO_2. The minerals present are marmatite (Zn,Fe)S, chalcopyrite $CuFeS_2$, pyrite FeS_2 and minor amounts of PbS and quartz SiO_2.

Roasting is performed in a mono hearth pilot roasting furnace at a temperature of 800°C.

At the start of selective roasting, FeS and ZnS will diffuse into the chalcopyrite and Cu and Fe will diffuse into the blende (ZnS). The removal of S as SO_2 will oxidise preferably the Fe to Fe_3O_4. For instance, at the point where 30 % of the S is removed, the phases present are bornite (Cu_5FeS_4) with 5 % Zn, blende (ZnS) with 4,37 % Cu and 15 % Fe, blende with low Cu and Zn, resp. 1,97 and 3,82 %, and a solid solution $Cu_9Fe_9S_{16}$ with 7,82 % Zn (at room temperature this ZnS is finely disseminated in the $Cu_9Fe_9S_{16}$).

After removal of 50 % of the S present Cu_2S appears next to bornite (Cu_5FeS_4). The blende present has 6 % Fe left and 4,2 % Cu.

At this point, roasting is stopped and the product is milled to liberate, as much as possible, the different phases.

Microscopy samples of the treated material show that the individual grain size of the remaining Cu_2S, ZnS and Cu_5FeS_4 is larger than the $CuFeS_2$ and (Zn, Fe)S in the original untreated material which is a clear indication for the desired preferential growth.

As can be seen, the process allows using ores which contain copper and zinc in a finely intergrown or dispersed structure to win copper as well as zinc.

The process according to the invention is normally inserted in a classic flowsheet. An example of such a classic flowsheet is represented in figure 1.

The ore 5 with d_{80} = 10 cm is in a grinding and milling treatment 1 reduced to d_{80} = 110 µm. The notation d_{80} = x means that 80 % of the particles of the ore 1 can pass through a sieve with a mesh-size of x. In a following step 2, tailings 6 are separated from the ore 5 by means of, for example, flotation to obtain a bulk concentrate. This bulk concentrate is further ground and/or milled to liberate the different phases present so as to obtain, in step 3, a concentrate containing sulphides with d_{80} = 40 µm. In a last step 4, a flotation is for instance applied to separate tailings 6 and different metal sulphides 7 and to collect concentrates 7 which will be transported to a refinery plant.

The process, according to the invention, is normally inserted in this flow-sheet after separation of tailings in step 2 and before the separation of the individual sulphides. In figure 2 the process according to the invention is represented by a rectangle 8.

For ores having a relative low content of tailings, separation thereof can possibly be omitted. In that case, more sulphur will have to be oxidised which will provide enough heat to volatilise impurities, as mentioned hereinbefore, and possibly to reach said inversion temperature for changing the crystal structure, so as to decrease mutual solubility of metals.

The invention is of course not limited to the examples and description of the embodiments of the process given. Indeed, the process can be used for a wide variety of ores and to win other metals than those mentioned in this description.

Claims

1. Process for improving recovery of metals from ores containing at least two different non-ferrous metal sulphides or from bulk concentrates of such ores, wherein said sulphides are present in different phases, characterised in that said ores, preferably directly after having been ground, or said bulk concentrates are submitted to a heating step in such conditions to increase the size of at least one of the different phases and/or to oxidise selectively at least one of said metal sulphides, thereafter separating a concentrate of at least one of said metals.

2. Process according to claim 1, characterised in that, during the heating step, an intimate contact is realised between particles of said ores or bulk concentrates in order to achieve mass transfer between these particles.

3. Process according to claim 1 or 2, characterised in that said ores or bulk concentrates are heated in a multiple hearth furnace or kiln.

4. Process according to any one of claims 1 to 3, characterised in that, during said heating step, particles of said ores or bulk concentrates are partially melted.

5. Process according to any one of claims 1 to 4, characterised in that, during the heating step, said ores or bulk concentrates are submitted to selective oxidising roasting, more particularly in order to oxidise the iron which is possibly present in the treated ores or bulk concentrates.

6. Process according to any one of claims 1 to 5, characterised in that the ores or bulk concentrates are heated to a temperature of at least 550°C to volatilise, in a gas phase, at least one of the following elements : mercury, arsenic or antimony, which are possibly present in the ores or bulk concentrates.

7. Process according to any one of claims 1 to 6, characterised in that, if the ores or bulk concentrates contain lead sulphide, they are heated to a temperature of at least 750°C, and preferably at least 800°C, to volatilise said lead sulphide.

8. Process according to claim 7, characterised in that, if the ores or bulk concentrates contain lead, lead sulphate is extracted from the gas phase.

9. Process according to any one of claims 1 to 8, characterised in that, before applying the heating step to the ores, they are ground to a particle size necessary for separating gangue from sulphides without substantial loss of recovery.

10. Process according to claim 9, characterised in that, before the heating step, the ores or bulk concentrates are ground to obtain a particle size comprised between 500 µm and 50 µm.

11. Process according to any one of claims 1 to 10, characterised in that the heating step is controlled in such a way that most of said phases have a d_{80} value of at least 20 µm and preferably of at least 30 µm.

12. Process according to any one of claims 1 to 11, characterised in that, after having heated the ores or bulk concentrates, they are ground to a particle size that allows separation of the different phases present in the ores or bulk concentrates by applying a physical separation method.

13. Process according to one of the claims 1 to 12, characterised in that, after the heating step, an iron containing phase, mainly consisting of magnetite, is separated by magnetic separation, cycloning or flotation.

14. Process according to one of claims 1 to 13, characterised in that, at the end of the heating step, temperature is decreased to about 650°C or lower to minimise mutual solubility of metals present in the ores or bulk concentrates.

15. Process according to one of the claims 1 to 14, characterised in that, at the end of the heating step,

the temperature is decreased to a temperature between 650°C and 550°C.

16. Process according to any one of claims 1 to 15, characterised in that roasting is performed at a temperature between 550°C and 650°C and preferably a temperature of about 600°C.

17. Process according to any one of claims 1 to 16, characterised in that, if said ores or bulk concentrates contain sphalerite, at the end of the heating step, the ores or bulk concentrates are roasted at a temperature above the inversion point of sphalerite to wurtzite in order to generate a crystal structure decreasing the solution of elements, such as Cu and/or Fe, into ZnS present in the ore or bulk concentrate.

18. Process according to claim 17, characterised in that the end of the roasting is carried out at a temperature above 950°C.

19. Process according to claim 17 or 18, characterised in that said temperature is applied from the starting of the roasting.

20. Process according to any one of claims 1 to 19, characterised in that, if the ores or bulk concentrates contain iron, roasting is carried out until at substantially all sulphur bound to iron has been oxidised.

21. Process according to claim 20, characterised in that, after the roasting, iron, mainly present as magnetite, is separated from the bulk concentrates or ores.

22. Process according to any one of claims 1 to 21, characterised in that, during the heating step, at least one of the metals present in the ores or bulk concentrates are oxidised to decrease mutual solubility of metals.

23. Process according to claim 22, characterised in that, if the ores or bulk concentrates contain zinc and copper, zinc is oxidised to decrease solution of copper in zinc.

24. Process according to any one of claims 1 to 23, characterised in that the ores or bulk concentrates are roasted until at the very most all sulphur bound to zinc has been oxidised.

25. Process according to any one of claims 1 to 24, characterised in that, after the heating step, the copper containing phase is separated from the zinc containing phase for instance by a physical separation method.

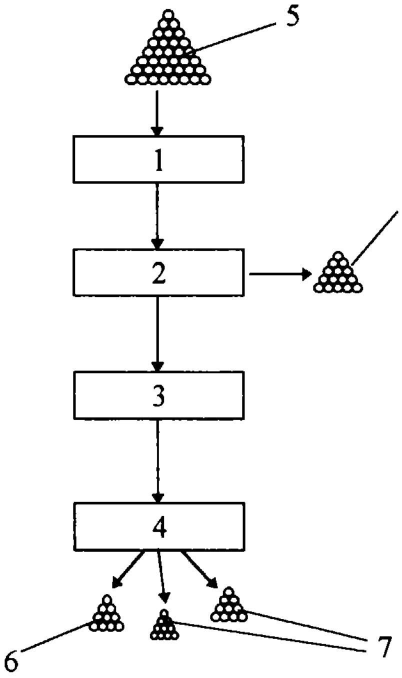

Fig. 1

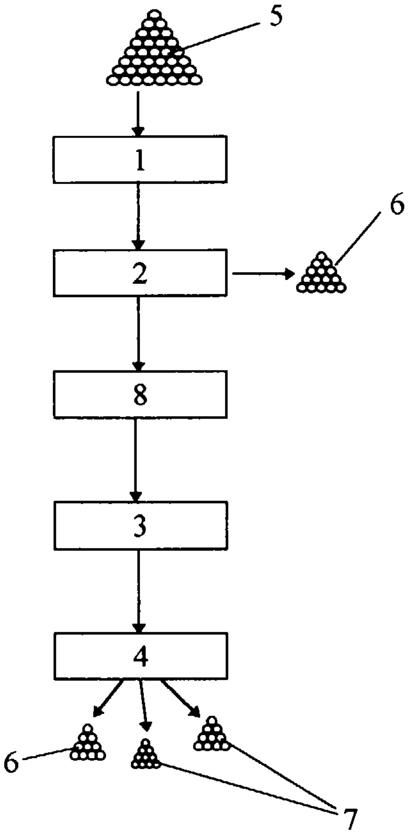

Fig. 2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 20 0177

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US-A-4 368 176 (D. N. ABISHEV ET AL.) * claim 1 * ---	1	C22B1/02
A	US-A-4 201 748 (G. M. SWINKELS ET AL.) * claim 1 * ---	1	
A	AU-B-491 430 (OUTOKUMPU) * claim 1 * ---	1	
A	US-A-3 961 941 (R. D. BAKER ET AL.) * claim 1 * ---	1	
A	DE-C-9 166 (C. HABER) * claim * -----	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C22B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	20 June 1996	Sutor, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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