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(54) **A method of refining crude lead.**

(57) A method of refining crude lead from copper-containing lead raw-materials which possibly also contain arsenic and which are of a metallic, oxidic, sulphatic or sulphidic type, in a furnace in which the contents thereof can be subjected to turbulence, preferably in a top blown rotary converter, for example, of the Kaldotype. According to the invention, subsequent to chemical reduction and tapping-off of the slag, the crudelead melt is cooled to a temperature beneath about 700°C whilst strongly agitating said melt, in order to separate out a copper phase or a copper speiss. The coolant used may be an oxidic or sulphatic lead raw-material, a crushed iron-silicate slag, a slag former, and, preferably, water in liquid finely-divided form. Large quantities of arsenic can be removed prior to said cooling, by forming an iron speiss, by adding iron to the crude-lead melt or forming iron in situ therewith.

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A method of refining crude lead

The present invention relates to a method of producing crude lead from copper-containing lead raw-materials of a metallic , oxidic, sulphatic or sulphidic type.

Metallic lead is normally produced from sulphidic lead raw-materials , such as lead concentrates for example, but can also be produced from oxidic and sulphatic lead raw-materials , for example dust, ashes and slags. The most common furnace used for melting and chemically reducing lead is the shaft furnace, to which there is charged a lead raw-material which, if so desired, has been pre-sintered or roasted to simultaneously oxidize the sulphidic sulphur present with atmospheric oxygen to a content of less than 2% sulphur. The lead raw-material can also be melted and reduced, to advantage, in a rotary , inclined furnace, as disclosed in Swedish Patent specification 7317217-3 and 7317219-9, which teach methods for producing crude lead from sulphidic, oxidic and sulphatic lead raw-materials.

When producing crude lead, i.e. lead which must be purified or refined in order to be retailed as a normal market product, the lead will thus practically always contain impurities undesirable in the finished lead, e.g. such impurities as copper, arsenic and antimony, which substances must therefore be removed from the crude lead. Gold and silver are normally also present in the crude lead.

Irrespective of the method by which the crude lead is produced, it must therefore be refined in order that a sufficiently pure, final lead product can be obtained. Normally, the crude lead is refined in so-called pots or chambers of various type , especially designed for refining said lead with respect to said impurities. Copper, and also arsenic and antimony present in the lead , constitute a particular problem when refining said lead. Arsenic and antimony may be present in quantities of up to about 15%, which results in the formation of very large quantities of solid, powderous products which float to the surface of the metal bath during the refining process. This so-called dross renders handling of the crude-lead melt difficult.

When copper is present in the lead raw-materials in large quantities , it is essential that it is possible to remove the copper effectively at an early stage of the process, so as not to render the process more expensive by the fact that the further treatment of the lead to a refined lead is made more difficult and since the copper content of the lead is highly valuable.

According to the invention, crude lead is produced from copper-containing lead raw-materials of a metallic, oxidic, sulphatic or sulphidic type, by melting the raw materials in a furnace in which turbulence can be created in the contents thereof, said raw materials being melted in the presence of a slag former and chemically reduced, whereafter a slag is tapped-off. The novel method is characterized by the fact that subsequent to tapping-off the slag, the crude-lead melt formed is cooled whilst creating a strong turbulence therein, to a temperature above the liquidus point of the lead melt but beneath about 700°C, preferably beneath 500°C, whereafter the copper-containing phase and crude-lead melt separated out when cooling said melt are separated from one another.

When melting lead raw-materials containing, inter alia, arsenic, antimony and copper, the arsenic and antimony can be removed in the form of a speiss. A "speiss" is a compound of arsenic and/or antimony with iron metals and copper, i.e. a "speiss" may comprise arsenides and/or antimonides of one or more of the metals copper, iron, nickel and cobalt. Any arsenic or antimony impurities are therefore removed by charging to the melt, whilst creating a strong turbulence therein, iron in a metallic, finely-divided form, or by causing iron to be formed in situ, whereafter the insoluble iron speiss formed in the lead melt is separated therefrom in direct conjunction with gravitational separation of speiss and crude lead, whereafter copperis separated out and removed. If the iron charged to the melt is in powder form or in the form of iron filings or finely-divided pieces, a practically insoluble iron-arsenic speiss or iron-antimony speiss will be formed in the lead melt. By iron in finely-divided form is meant metallic iron in a form such as to present to the lead melt a good specific surface area and that the iron can be charged to the melt in a simple manner. The speiss, which is practically insoluble in lead at the prevailing temperatures, is readily separable and can be tapped-off, preferably at a temperature of 850-1200°C. The iron charged may also have the form of an iron alloy containing 60% iron or more. In this respect, the iron charge may be adapted so that only a part of the arsenic content forms an iron speiss and that there remains in the lead melt a quantity of arsenic corresponding to a molar ratio of copper to arsenic of at least 1.17, so that copper is able to form a copper speiss, which can readily be treated to recover copper and arsenic. Any tin present in the melt will remain therein. The major part of the copper content of the lead raw-materials will remain in the crude-lead melt, however, but, as above mentioned, will be segregated as metallic copper and/or speiss subsequent to cooling the melt under strong turbulence to a temperature above the melting point of the lead-melt but beneath about 700°C, whereafter the crude-lead is tapped-off and recovered.

Cooling of the crude-lead melt can be effected by adding, for example, additional oxidic or sulphatic lead raw materials or crushed iron-silicate slag. Cooling of the crude-lead melt can also be effected by adding a slag former intended for a subsequent melting cycle.

Alternatively , the crude-lead melt can be cooled by spraying water in liquid , finely-divided form directly onto the turbulent crude-lead melt.

It is not necessary to cool the crude-lead melt each time a new charge of lead raw-material is melted down, and removal of slag and any iron-arsenic-speiss formed has been effected. Thus, it is possible to fill the furnace with a crude-lead melt and then segregate the copper-containing phase, whereafter the crude-lead is tapped-off from the furnace and the copper-containing phase recovered.

The melting process, and any possible speiss formation and copper separation, are effected in a furnace in which the melt can be treated whilst being subjected to strong turbulence. Such a furnace is suitably a top blown rotary converter , for example a so-called TBRC or a Kaldo furnace. A TBRC or Kaldo furnace can be rotated at a speed of from 10 to 60 r.p.m . and the choice of suitable rotary speed is controlled by the diameter of the furnace. A suitable turbulence is obtained when the inner surface of the furnace is rotated at a peripheral speed of 0.5 - 7 m/s, preferably 2 - 5 m/s, which enables the melt to accompany the rotating inner surface of the furnace and fall down onto the surface of the bath in a shower of droplets, which results in extremely good contact between solid phase, liquid phase and gas phase. Such good contact is a requisite for rapid chemical and physical sequences, such as a reduction sequence, cooling and separation. The formation of dust is avoided to a surprisingly large extent, by the fact that the shower of droplets drive the dust down, which would otherwise pass out of the furnace with the reaction gases.

Example 1

30 tons of pellets of an oxidic-sulphatic lead raw-material originating from a copper-converter dust having the following analysis: Pb 35%, As 3.5%, Cu 1.15%, S 6.0 %, Bi 1.20%, Au 0.5 mg/kg, Ag 3.38 mg/kg, were melted together with 9.6 tons of granulated fayalite slag (iron-silicate-slag obtained from a fume furnace for treating copper slag) and 3.5 tons of finely-divided limestone in a top blown rotary converter of the Kaldo-type having an inner diameter of 2.5 m, with the aid of an oil-oxygen-gas burner, to form a crude-lead bath and slag. Subsequent to melting the raw material, the slag and the crude-lead bath were reduced chemically with 1.9 tons of coke until the lead content of the slag was about 1.5 % Pb at a temperature of about 1100°C, whereafter the slag was tapped-off.

Whilst strongly agitating the bath, 2.25 tons of crushed iron-silicate-slag were charged to the furnace, whereupon the temperature of the crude-lead melt fell over a period of time of 60 minutes, from 1100°C to about 850°C, a copper-containing phase segregating from the bath. This phase was then removed from the crude-lead melt, whose copper content was thereby reduced from 5 % Cu to 1.5 % Cu.

A part of the thus obtained crude-lead melt was cooled whilst continuing said agitation, down to a temperature of 400°C, it being possible to segregate out and remove a further copper-containing phase. The resultant copper content of the crude-lead melt was 0.2% Cu.

Example 2

30 tons of pellets of an oxidic-sulphatic lead raw-material having the same composition as that in Example 1 were melted together with 9.6 tons of granulated fayalite slag and 3.5 tons of finely-divided limestone in a top blown rotary converter of the Kaldo-type having an internal diameter of 2.5 m, with the aid of an oil-oxygen-gas burner, to form a crude-lead bath and a slag. Subsequent to melting the raw material, the slag and the crude-lead bath were chemically reduced with 1.9 tons of coke until the lead content of the slag was about 1.5% Pb, at a temperature of about 1100°C, whereafter the slag was tapped-off.

Water in a finely-divided form was then sprayed directly onto the turbulent , agitated crude-lead melt, its temperature being lowered from 1100°C to about 650°C over a period of about 60 minutes, wherewith a copper-containing phase segregated out. This phase was then removed from the crude-lead melt , the copper content being lowered from 5% Cu to 1.5 % Cu.

Example 3

30 tons of pellets of an oxidic-sulphatic lead raw material having the same composition as that in Example 1 were melted together with 9.6 tons of granulated fayalite slag and 3.5 tons of finely-divided limestone in a top blown rotary converter of the Kaldo-type , having an inner diameter of 2.5 m, with the aid of an oil-oxygen-gas-burner, to form a crude-lead bath and a slag. Subsequent to melting the raw material, the slag and the crude-lead bath were chemically reduced with 1.9 tons of coke until the lead content of the slag was about 1.5% Pb at a temperature of about 1100°C, whereafter the slag was tapped-off.

2.25 tons of crushed iron-silicate slag were then charged to the turbulent, agitated crude-lead melt, the temperature of the melt being lowered from 1100°C to about 850°C over a period of about 60 minutes, and a copper-containing phase segregating out. The crude-lead melt, whose copper content decreased from 5% Cu to 1.5 % Cu, was tapped-off whilst the copper-containing phase, together with the iron-silicate slag , were retained in the furnace. A further 30 tons of oxidic-sulphatic lead raw-material and 3.5 tons of finely-divided limestone were then charged to the furnace and melted together with the copper-containing phase and the iron-silicate slag. The resultant slag and crude-lead bath were chemically reduced with 1.9 tons of coke until the lead content in the slag was about 1.5% Pb at a temperature of about 1100°C, whereafter the slag was tapped-off. Whilst strongly agitating the resultant crude-lead melt , a further 2.25 tons of crushed iron-silicate slag were charged to the furnace, the temperature of the crude-lead melt decreasing from 1100°C to about 850 °C over a period of 60 minutes, and a large quantity of copper-containing phase was obtained. This large quantity of copper-containing phase could be separated from the crude-lead melt with less lead losses than when only one freezing or segregation process with iron-silicate slag was carried out. In addition, a considerable saving in time per ton of lead produced was made , since only one segregation process was required.

This method in which the copper-containing phase is retained in the furnace should, of course, be continued until the quantity of copper-containing phase obtained is suitable in respect of the production conditions.

Example 4

30 tons of oxidic-sulphatic lead raw-material having the composition of Example 1 were melted together with 9.6 tons of granulated fayalite slag and 3.5 tons of finely-divided

limestone in a top blown rotary converter of the Kaldo-type having an internal diameter of 2.5 m, with the aid of an oil-oxygen-gas-burner, to form a crude-lead bath and a slag.

Subsequent to melting the raw material, the slag and the crude-lead bath were chemically reduced with 1.9 tons of coke until the lead content of the slag was about 1.5% Pb at a temperature of about 1100°C, whereafter the slag was tapped-off.

The crude lead obtained contained 7% As and 3% Cu. 3 tons of iron in a metallic, finely-divided form was charged to the turbulent crude-lead melt, to form an iron speiss at about 1000°C, which speiss was then tapped-off in liquid form.

A crushed iron-silicate slag was then charged to the furnace whilst strongly agitating the crude-lead melt, as in Example 1, the temperature of the bath decreasing, a copper-containing phase segregating out and being removed from the melt.

What we claim is:-

1. A method of producing crude lead from copper-containing lead raw-materials of a metallic, oxidic, sulphatic or sulphidic type, by melting said materials in a furnace in which a turbulence can be created in the contents thereof, the lead raw-material being melted in the presence of a slag former and chemically reduced, whereafter a slag is tapped-off, characterized in that subsequent to tapping-off said slag, the lead melt is cooled, whilst being strongly agitated, from melting temperature to a temperature above the liquidus point of the lead melt but beneath about 700°C, whereafter the copper-containing phase segregating from the crude-lead melt during the cooling sequence is removed from said melt.

2. A method according to claim 1, characterized inthat the lead melt is cooled to a temperature of less than about 500°C.

3. A method according to claim 1, characterized in that the coolant used is an oxidic or sulphatic lead raw-material or a crushed iron-silicate slag.

4. A method according to claim 1, characterized in that the coolant used is said slag former for a subsequent melting of lead raw-material.

5. A method according to claim 1, characterized in that cooling is effected by spraying water in liquid, finely-divided form directly onto the turbulent crude-lead melt.

6. A method according to claim 1, characterized in that the copper-containing phase which segregates out from the melt is retained in the furnace during at least one further melting cycle.

7. A method according to claim 1, characterized in that melting of said raw material and the elimination of copper is effected in a rotary, inclined furnace of the Kaldo-type.

8. A method according to claim 1, characterized in that any arsenic impurities in the lead raw-materials are at least partially removed by supplying to said melt, whilst strongly agitating the same, iron in a metallic finely-divided form or by causing iron to be formed in situ in said melt, whereafter the insoluble iron speiss formed in the lead melt is separated therefrom in direct conjunction with a gravitational separation of speiss and crude lead, whereafter copper segregates out and is removed.

9. A method according to claim 8, characterized in that said iron is charged to said melt in the form of iron filings, iron powder or finely-divided iron pieces.

10. A method according to claim 8, characterized in that said iron is charged to said furnace in the form of an iron alloy containing more than 60% iron.

11. A method according to claim 8, characterized in that the iron is formed in situ by charging silicon, silicides, carbon or ferro-alloys having silicon or carbon in quantities such that the iron present in the slag is reduced out in a metallic form prior to tapping-off the slag.

12. A method according to claim 8, characterized inthat the speiss is tapped-off at a temperature of 850 - 1200°C.

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EUROPEAN SEARCH REPORT

0006832

Application number

EP 79 850 059.1

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	DE - B - 1 174 511 (THE BROKEN HILL ASSOCIATED SMELTERS PROPRIETARY LTD.) --	
A	DE - B - 1 189 279 (BREVETS METALLURGIQUES) --	
A	DE - B - 1 199 003 (METALLGESELLSCHAFT) --	
A D	DE - B2 - 2 459 756 (BOLIDEN) & SE - A - 7 317 219 --	
A D	DE - B2 - 2 459 832 (BOLIDEN) & SE - A - 7 317 217 --	
A	US - A - 3 666 441 (POWER-GAS) ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl.3)

C 22 B 13/02
C 22 B 13/06

TECHNICAL FIELDS SEARCHED (Int.Cl.3)

C 22 B 13/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

☒ The present search report has been drawn up for all claims

Place of search Berlin	Date of completion of the search 05-10-1979	Examiner SUTOR

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