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(54) **A method of manufacturing and refining crude lead from arsenic-containing lead raw-materials.**

(57) A method for manufacturing and refining crude lead from arsenic-containing lead raw-materials of a metallic, oxidic, sulphatic or sulphidic nature. In the manufacture of said crude lead, the lead raw-material is melted in a furnace in which strong turbulence can be created in the contents thereof, in the presence of a slag former, whereafter the slag is tapped-off. The furnace used is preferably a top blown rotary converter or a furnace of the Kaldo-type. The invention is characterized in that iron in metallic finely-divided form, such as iron filings, iron powder or finely-divided pieces of iron, is charged to the crude-lead melt whilst creating strong turbulence therein, or said iron is caused to be formed in situ, preferably by adding silicon, silicides, carbon, carbides or ferro-alloys containing carbon and silicon, wherewith arsenic and any antimony present form an iron speiss which is separated from the crude-lead melt in liquid form in direct conjunction with a gravitational separation of speiss and crude lead. Any copper present in the melt can be segregated therefrom as metallic copper or a copper speiss, by cooling the crude-lead melt.

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Croydon Printing Company Ltd.

A method of manufacturing and refining crude lead from arsenic-containing lead raw-materials.

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Although metallic lead is normally produced from sulphidic lead raw-materials, such as concentrates, it is also produced from metallic, oxidic and sulphatic lead raw-materials, such as dust, ashes and slags. The most common furnace for smelting and reducing lead is the shaft furnace, which is charged with lead raw-materials which may have been pre-sintered or roasted to oxidize the sulphidic sulphur with atmospheric oxygen to a content of less than 2% sulphidic sulphur. This smelting and reduction of lead raw-material can also be effected to advantage in a rotary, inclined furnace, such as a furnace of the Kaldo-type as described in Swedish Patent specifications 7317217-3 and 7317219-9, which illustrate processes for producing crude lead from sulphidic and from oxidic and sulphatic lead raw-materials. By crude lead is meant here, generally, a lead product which must be subjected to further purifying or refining stages, in order to be retailed as a normal market product.

When producing crude lead from different raw materials the lead will thus practically always contain impurities undesirable in the finished lead. Examples of such impurities include copper, arsenic and antimony. The crude lead will normally also contain gold and silver.

Thus, irrespective of the method by which it is produced, crude lead must always be refined in order to obtain a sufficiently pure lead, commercially known as a so-called refined lead. Normally, the lead is refined in various chambers or pots specifically designed for such refining work. The copper, and above all the arsenic, present in the crude lead create a particular problem when refining said lead, since these impurities may reach to 15% or, in certain cases, even higher, which give very large quantities of more or less solid powderous products, normally called dross, on the surface of the metal bath, thereby rendering handling difficult. Further, the arsenic represents a direct threat to the environment, since a significant amount thereof is fumed-off from the pots or chambers during the refining process. Thus, it is highly desirable to remove arsenic and copper from the crude lead to the greatest extent possible , before the lead passes to the final refining stage, to be formed into a commercial lead product. Crude lead from shaft furnaces, which are tapped at about 1000-1100°C, can contain the aforementioned impurities , present in the lead raw-material, in quantities which, in the case of copper, correspond to the solubility limit in lead , which is about 10% at 1100°C , and in respect of arsenic correspond to the amount of arsenic present in the lead raw-material with the exception of that which is fumed-off during the smelting process. At the temperatures in question, arsenic is soluble in lead to an unlimited degree.

For the purpose of avoiding the aforementioned problem, a method has been proposed in Swedish Patent specification number 7317218-1 in which crude lead is recovered by smelting and reducing oxidic and/or sulphatic products in a rotatable converter, in which the major part of the tin, arsenic and antimony content of the crude lead is removed from the melt in the actual melt unit, i.e. the converter, by injecting oxygen-gas or air enriched with oxygen-gas on to the surface of the bath in the converter whilst rotating the same, the arsenic, antimony and tin being oxidized and forming a dross which can be removed from the surface of the smelt. Since in this method the tin is oxidized first and then the arsenic and antimony, it is possible to selectively recover tin in the form of tin oxide, which is a valuable product, whereafter arsenic and antimony can be recovered in the form of As_2O_3 and Sb_2O_3 and removed from the smelt individually.

One disadvantage with the aforedescribed method , however, is that the oxidation of arsenic, antimony and tin is highly exothermic, leading to significant increases in the temperature of the melt, which in turn results in an impaired selectivity, since it is impossible to maintain the temperatures optimal for forming dross. Further, this leads to longer refining times and thus a reduction in the capacity of a given plant. Further, the said method does not solve the problem of the copper which is dissolved in the lead at the temperatures in question, about 1000°C. Refining of crude lead from shaft furnaces is , as with the aforedescribed process, very time consuming , since different refining stages must be incorporated at which work is carried out at different temperatures and at different redox potentials. Thus, considerable time is taken up in the cooling of the crude-lead smelt , from the temperature obtained after the melting process to a temperature suitable for a subsequent refining stage operating at a considerably lower temperature, for example the copper segregation stage. With respect to the various known refining methods and refining stages for crude lead, reference is made to Ullmans "Encyklopädie der technischen Chemie" 4th Edition, volume 8, page 561 and following, where an exhaustive account of the standpoint of techniques is given. Reduction processes in shaft furnaces are described in Winnacker-Küchler, Chemische Technologie, Volume 6, pages 285-288, Munich (1973) , in which the formation of different slags, copper matte and speisses is described, together with analyses.

In the Japanese Patent specification Number 1974-28520 there is described a method for removing arsenic from molten lead, in which iron in the form of iron powder, sponge iron or iron filings, is charged to the melt. For the purpose of lowering the arsenic content, more than 1% iron is charged at a temperature above 450°C, whereafter the lead melt is stirred mechanically . According to the Japanese Patent specification , treatment is carried out in a crucible at temperatures above 450°C and up to 800°C , wherein a finely-divided solid speiss, for example in powder form or in the form of coarse grains , is removed from the melt. With this method it is hardly possible to work at higher temperatures , since the speiss is sticky at temperatures of about 800°C and therefore readily fastens to the walls of the furnace and crucible. Consequently, in the method of the Japanese Patent specification a temperature of about 600°C has obviously been preferred. The purifying effect is considerably lower at temperatures of about 600°C than at somewhat higher temperatures , and thus a method according to the Japanese Patent specification does not result in optimal purification, owing to problems of a process technique nature. In addition, it will be obvious to one of skill in this art that the separation of such a finely-divided solid phase from a lead melt would result in high losses of lead, which is entrained mechanically with said phase, as a result of the lead's adherence and wetting of the solid speiss particles.

The present invention substantially eliminates the aforedescribed problems. Moreover, the method according to the invention enables extremely rapid reaction sequences to be obtained whilst requiring a relatively low energy input, which are important and decisive factors in respect of the economy of the process.

Thus, in accordance with the method, the manufacture and refining of crude lead with respect to copper and arsenic can be effected in one and the same furnace. The lead raw-material may be of the metallic, sulphidic, oxidic or sulphatic type, and may comprise, for example, various dust-products and powderous-products obtained from non-ferrous metallurgical processes. When practicing the method according to the invention, the lead raw-material is melted in a furnace , in which turbulence of the content can be created, in the presence of a slag former, whereafter the slag is drawn-off , said method being characterized by the fact that subsequent to drawing-off the slag , there is charged to the furnace at a temperature of 850-1200°C under strong agitation, iron in a metallic , finely-divided form, or iron is caused to be formed in situ, whereafter the insoluble liquid iron speiss formed in the lead melt is separated therefrom in immediate conjunction with a gravitational separation of speiss and crude lead. By iron in a finely-divided form is meant metallic iron in a form such as to present a relatively high specific surface area to the lead melt and such that the iron can be charged to the lead melt in a simple manner.

When practicing the method according to the invention, the lead raw-material is charged to the furnace prior to or during the smelting process, together with a slag former.

During the smelting process, the crude lead is reduced chemically in a known manner and the resultant lead-containing slag is chemically reduced , suitably with coke for example, until the lead content of the slag is sufficiently low , for example less than 2%. The slag , purified from lead, is then tapped off. In order to fill the furnace to the extent desired, further lead raw-material can then be charged to the furnace and the slag reduced to a lead content of less than 2% and the slag tapped-off, in a repeated number of operations. Metallic iron is then charged to the furnace, preferably in the form of iron filings, for example such filings as those obtained when turning and drilling, or in the form of a powder or finely-divided pieces, such as iron clippings, obtained when clipping scrap for example, there being formed a speiss which contains mainly iron and arsenic. A "speiss" is a compound of arsenic and/or antimony with iron metals and/or copper, i.e. a "speiss" may comprise arsenides and/or antimonides of one or more of the metals copper,iron, nickel and cobalt. Formed iron-arsenic-speiss is practically insoluble in a lead melt, and hence it readily separates , floats to the surface and lies above the lead melt and can be poured therefrom in a liquid state at a temperature of 800-1150°C. A temperature range of 950-1000°C is preferred, due to the viscosity of the speiss, which enables rapid separation and tapping. In many cases the iron charged to the furnace may conveniently comprise an iron alloy containing more than about 60% iron.

Any copper impurities present are then suitably segregated or frozen out from the lead melt whilst agitating the same in said furnace, by adding a coolant to the melt, to cool the same suitably to a temperature of between 400 and 600°C, whereafter crude lead is tapped off , said lead being free from copper and arsenic. The coolant may conveniently have the form of an oxidic or sulphatic lead raw-material or a crushed iron-silicate slag. A rapid and effective cooling effect is obtained when the coolant is water, which is injected directly into the furnace in a liquid , finely-divided form. In certain cases , it may also be suitable for the coolant to comprise a slag former intended for a subsequent smelting operation. In respect of minor quantities of copper , it is possible to leave the copper-segregation step until several charges of lead raw-materials have been smelted and treated with iron.

Copper can also be removed from the crude-lead melt as a copper speiss. A copper speiss is formed when the temperature is lowered to less than 1100°C. In order to obtain a copper speiss at all, the mole ratio between copper and free arsenic must be between 1.17 and 4.43. When this mole ratio is lower than 1.17 , iron is suitably added to form an iron speiss in order to raise the mole ratio, to enable segregation of a copper speiss when cooling. Further arsenic can then be removed, by charging more iron to the furnace.

When the melt also contains recoverable quantities of tin, iron is suitably charged in an amount which will ensure that sufficient arsenic remains in the melt to form copper speiss, for example Cu_3As. In this way the risk of forming such copper-tin-compounds as, for example, Cu_3Sn are avoided, it being difficult to recover tin from such compounds. Instead, by means of this preferred method the tin content will exist in a metallic solution in the lead melt, which can be retailed in the form of tin-containing lead , which can demand a higher price on the market. Although the various cooling methods can be applied individually , combinations of two or more cooling methods can be also applied to advantage when importance is placed on short treatment times in the furnace.

In addition to charging to the furnace the quantities of metallic iron necessary to form the speiss from outside the furnace, part of the amount of iron charged, or even the whole of said amount , can be caused to be formed in situ in the melt. When iron is present in the lead raw-materials to be smelted , a substantial part of the iron will be slagged during the melting process. Thus,, when melting of the lead raw-materials is completed, iron can be caused to form in situ in the melt , preferably by adding silicon, silicides, carbon, carbides or ferro-alloys containing carbon and silicon in such quantities that iron present in the slag is reduced out in metallic form prior to removing the slag.

Important advantages are obtained when practising the aforedescribed method. The melting capacity of the furnace can be utilized to the maximum , since the formation of speiss in a charge of about 30-40 tons is obtained already after 30 minutes and , when cooling , the heat content of the lead can be recovered by , as aforementioned , using as the coolant a quantity of slag former intended for a subsequent process, said slag former thus being preheated in readiness for said subsequent process. If so desired, the melt of lead raw-material can also be cooled by charging a part of a subsequent charge of lead raw-material.

The melting process , and also the formation of speiss and the segregation of copper, are effected in a furnace in which the melt can be treated whilst being strongly agitated. One suitable furnace in this respect is a top-blown rotary converter, known as a TBRC converter or a Kaldo furnace. A TBRC converter or a Kaldo furnace can be rotated at a speed of from 10 to 60 r.p.m., the choice of suitable rotary speed being controlled by the diameter of the furnace. A suitable turbulence or agitation can be obtained when the inside of the furnace moves 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 droplet form, which results in extremely good contact between solid phase, liquid phase and gas phase. Good contact is a prerequisite of rapid chemical and physical sequences, such as reduction sequence, cooling and separation. The formation of dust is avoided to a surprisingly high degree, owing to the fact that the showerof droplets falling down onto said surface drive down that dust which would otherwise leave the furnace with the reaction gases.

Example 1

30 tons of pellets of oxidic-sulphatic lead raw-material originating from 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 and Ag 3.38 mg/kg, were melted together with 9 tons of granulated fayalite slag and 2.25 tons of finely divided limestone in a top-blown 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 slag. After melting the lead raw-material, the slag and the crude-lead bath were chemically reduced with 1.3 tons of coke until the lead content of the slag was about 1.5 % at a temperature of about 1000°C, whereafter the slag was tapped off. 3.0 tons of iron filings were then charged to the furnace , the arsenic content of the melt during rotation of the converter at a speed of about 30 r.p.m. falling from 7.3% to less than 0.01 %. Thus, it is extremely important that the speiss formation is effected with good contact between the iron and lead phase and with an iron surplus of at least 20% above the stoichometric value. The temperature during the formation of speiss was in excess of 1000°C. The formed and segregated speiss phase was tapped-off immediately the converter stopped rotating, since in a stationary crude-lead bath some arsenic will re-dissolve in the crude-lead melt from the speiss.

The resultant speiss was tapped-off and slag former intended for the next charge was charged to the furnace, whereupon the temperature of the crude lead fell to 450°C . The solubility of copper in the lead decreases greatly at this temperature, and hence the copper in the crude lead segregated out when cooling , the lead tapped-off containing

0.26% copper subsequent to said segregation.

Example 2

30 tons of oxidic-sulphatic pellets of the kind and composition recited in Example 1 were melted in a manner similar to that described in Example 1, with 9 tons of fayalite slag and 2.25 tons of limestone in a Kaldo converter, whilst burning oil with oxygen. Subsequent to melting the pellets, the slag and crude lead were chemically reduced at a temperature of 1000°C with 1.3 tons of coke, until the lead content of the slag was about 1.5 %, whereafter about 70% of the slag was tapped-off from the converter. About 1.5 tons of silicon iron , FeSi, were then charged to the converter, to reduce the remainder of the slag and to form a speiss. The converter was rotated at a speed of about 25 r.p.m., whereupon the arsenic content fell from an original 5%, firstly to about 1.3 % and then , during the rotation of the converter for about one hour and subsequent to the charge of silicon iron, to about 0.4%.

It will be evident from these two examples , that as a result of adding metallic iron the speiss was formed much more quickly and resulted in a more effective removal of arsenic than when the iron is formed by the reduction of slag, although even this latter method of procedure resulted in a fully acceptable result.

Example 3

Oxidic-sulphatic pellets mixed with pellets of metallic and sulphidic type were melted with fayalite slag and limestone in a manner similar to that described in Example 1, resulting in a crude-lead melt of about 15 tons having the following composition: lead 84.4%, copper 2.7 %, arsenic 5.5% and tin 1.4%.

The melt was rolled at 1100°C and 1200 kg of iron filings were added and rolling of the melt continued at 30 r.p.m for some minutes, an iron speiss being formed. The speiss was tapped-off and the resultant lead melt had the following composition: lead 86.1 %, copper 2.4%, arsenic 1.1%, tin 1.3%. The mole ratio of copper to arsenic was 2.6. The melt was then cooled to 450°C by injecting water thereinto whilst the furnace was rotating, a copper-speiss-copper-dross segregating out. The resultant lead melt had the following composition: lead 96.3%, copper 0.1%, arsenic 0.01% and tin 1.3 %.

In a further experiment , 3000 kg of iron filings were used instead of 1200 kg , there being obtained an arsenic content of 0.01% and thus a very high copper/arsenic mole ratio. Subsequent to cooling and separating copper from the melt, the composition of the crude-lead melt was : lead 98.0%, copper 0.1%, arsenic 0.01% and tin 0.2%.

It will be evident from Example 3 that by limiting the iron charge in a manner such as to obtain in the crude-lead melt a copper/arsenic mole ratio of 2.6, it is possible to avoid losing the tin content to speiss phases in the form of copper-tin-compounds from which tin is not readily recoverable. A lead which contains tin has a very high commercial value.

When the crude-lead melt obtained subsequent to melting and reduction in accordance with the aforegoing, contained so much copper in relation to arsenic that the mole ratio of copper to arsenic exceeds about 4 it is possible , in order to avoid losses of tin through the formation of copper-tin-compounds, either to charge to the melt arsenic in some form or other, e.g. in the form of a speiss rich in arsenic, or to remove copper from the melt, by adding sulphur in an elementary form or in the form of a compound which contains sulphur, for example pyrites, thereby to form a copper-matte phase in which copper will be present in the form of di-copper sulphide, which copper-matte phase can then be tapped-off.

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What we claim is:-

1. A method of manufacturing and refining crude lead from arsenic-containing lead raw-materials of a metallic, oxidic, sulphatic or sulphidic nature, the lead raw-material being melted in a furnace in the presence of a slag former, said furnace being of the type in which turbulence can be created in the contents thereof, whereafter the slag is drawn-off, characterized in that subsequent to drawing off said slag, iron in a metallic finely-divided form is charged to the melt or caused to be formed in situ therein, at a temperature of 800-1200°C during strong turbulence of the melt, whereafter the insoluble iron speiss formed in the lead melt is separated in liquid form from said melt in direct conjunction with a gravitational separation of speiss and crude lead.

2. A method according to claim 1, characterized in that the iron charged to the furnace is in the form of iron filings, iron powder or finely-divided pieces.

3. A method according to claim 1, characterized in that the iron comprises an iron alloy containing more than 60% iron.

4. A method according to claim 1, characterized in that the iron is caused to be formed in situ in the melt by adding silicon , silicides, carbon, carbides or ferro-alloys having carbon and silicon in such quantities that the iron in the slag is reduced out in metallic form before the slag is tapped-off.

5. A method according to claim 1, characterized in that the speiss is tapped-off at a temperature of 950-1000°C.

6. A method according to any one of claims 1-5, characterized in that any copper impurities are segregated or frozen out from the lead melt during turbulence thereof in said furnace by adding a coolant, whereafter crude lead is tapped-off.

7. A method according to claim 1, characterized in that when copper is present in the crude-lead melt a copper speiss is formed prior to forming said iron speiss, by cooling the melt to a temperature below 1100°C, whereafter the copper speiss formed is tapped-off.

8. A method according to claim 7, characterized in that iron is charged to the lead melt in a quantity below that required to form an iron speiss with residual arsenic before the temperature is lowered to form said copper speiss, whereafter said copper speiss is tapped-off and further iron charged to the furnace to fully remove the arsenic.

9. A method according to claim 6, characterized in that the coolant used is an oxidic or sulphatic lead raw-material or crushed iron-silicate slag.

10. A method according to claim 6, characterized in that the coolant used is water , which is injected directly into the furnace in a liquid, finely-divided form.

11. A method according to claim 6, characterized in that the coolant used is a slag former for a subsequent melting of the lead raw-material.

12. A method according to claim 6, characterized in that the melt is cooled to a temperature of 400-600°C.

13. A method according to claim 6, characterized in that

segregated copper or copper and speiss is or are retained in the furnace during at least one further melting cycle.

14. A method according to claim 1, characterized in that the manufacturing and refining processes are effected in a rotary, inclined furnace of the Kaldo type.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 79 850 058.3

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.3)
A D	DE - A1 - 2 459 756 (BOLIDEN) & SE - A - 7 317 219 --		C 22 B 13/02 C 22 B 13/06
A D	DE - A1 - 2 459 832 (BOLIDEN) & SE - A - 7 317 217 --		
A	DE - A1 - 2 705 654 (MITSUBISHI METAL AND ELECTROLYTIC ZINC CO. OF AUSTRALIA) --		
A	US - A - 1 283 427 (F.A. STIEF) ----		

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