May 30, 1972 G. MILNER 3,666,441

PROCESS FOR DECOPPERIZING LEAD

Filed Nov. 8, 1968 2 Sheets-Sheet 2

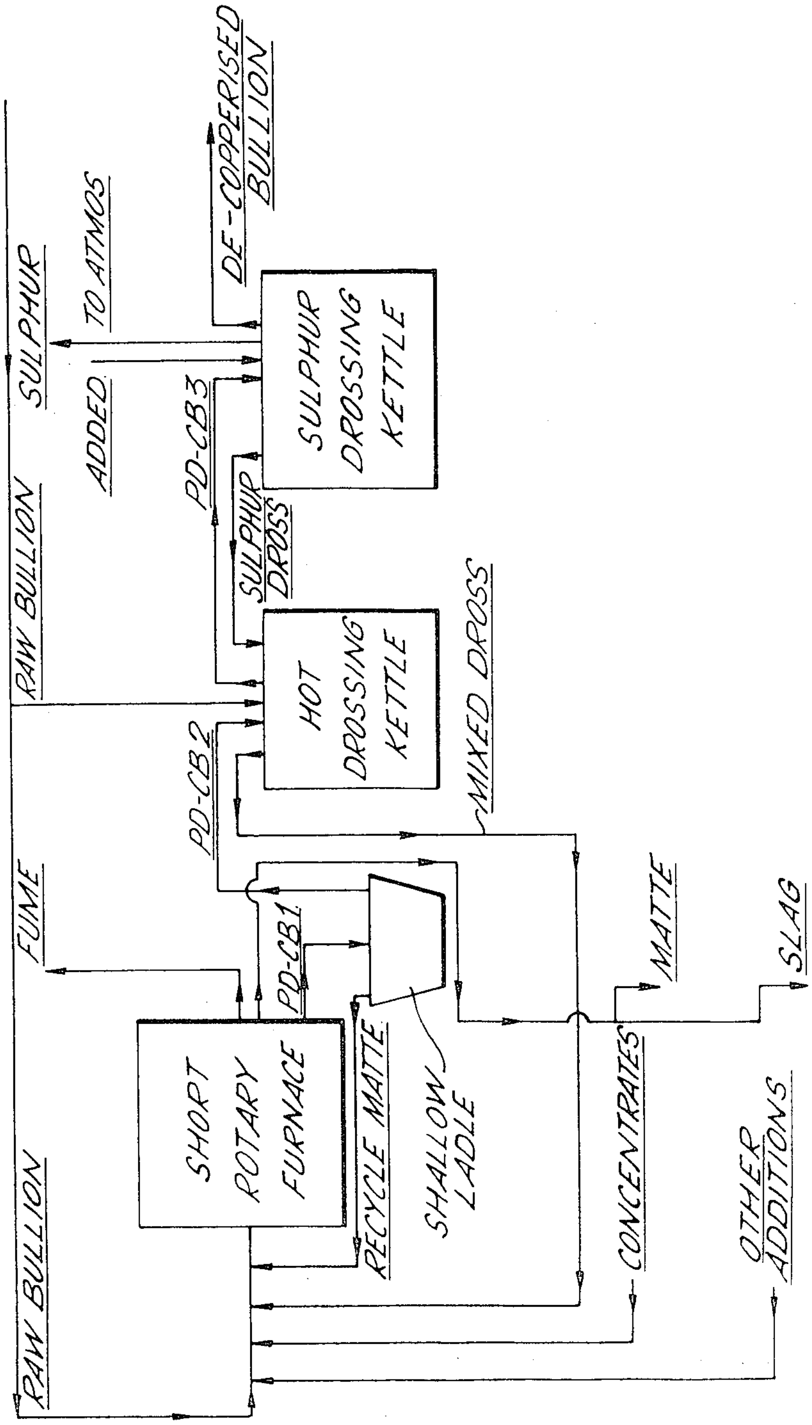

FIG. 2.

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PROCESS FOR DECOPPERIZING LEAD

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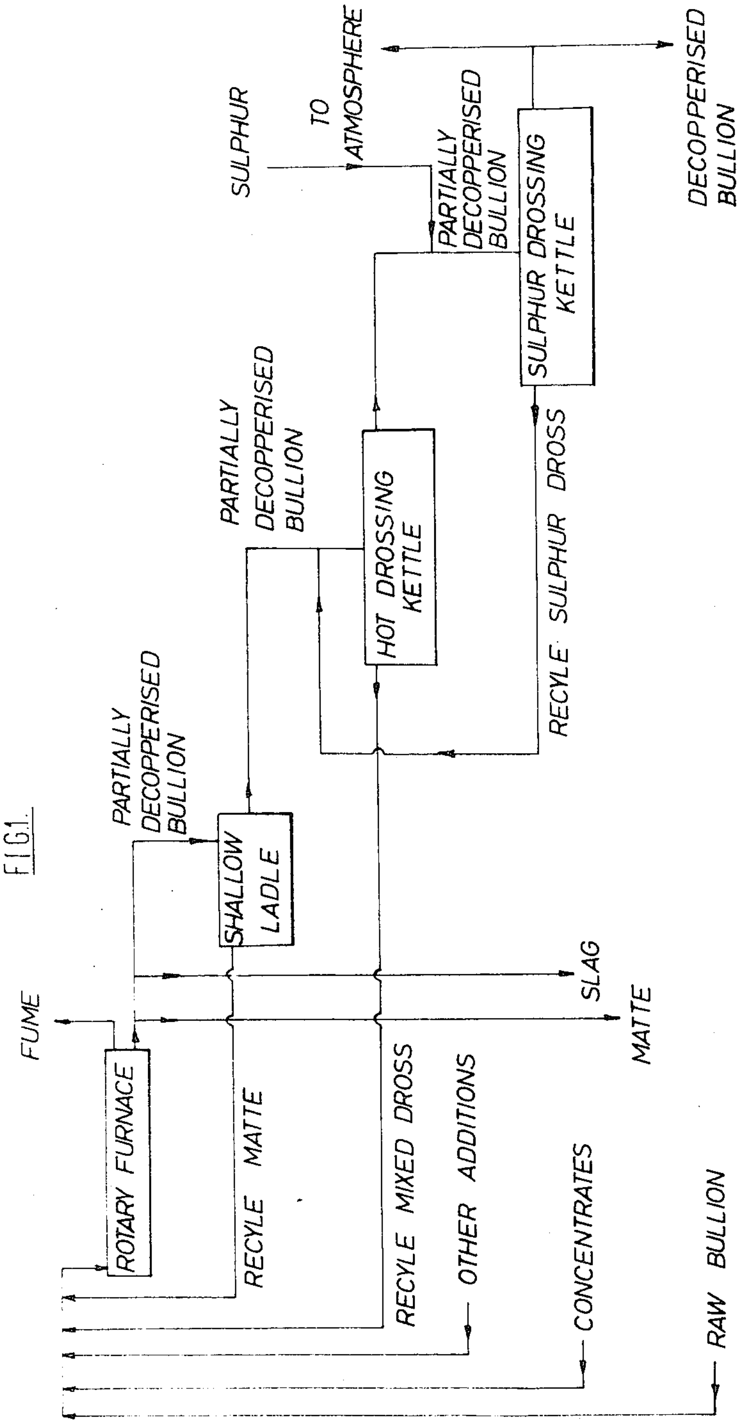
FIG.1.



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PROCESS FOR DECOPPERIZING LEAD

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Continuation-in-part of application Ser. No. 433,651, Feb. 18, 1965. This application Nov. 8, 1968, Ser. No. 774,300

Int. Cl. C22b *13/06*

U.S. Cl. 75—78 12 Claims

ABSTRACT OF THE DISCLOSURE

Decopperizing lead bullion, particularly lead bullion containing more than 2% copper, by adding to the molten lead bullion a sulfur containing compound sufficient to react with the copper to produce cuprous sulfide, allowing the reaction mixture to settle into a first lower layer of molten lead bullion of reduced copper content and an an upper layer of matte containing cuprous sulfide and lead sulfide. Thereafter, the molten lead bullion is isolated and cooled to form a further upper layer of matte containing cuprous sulfide and lead sulfide and a further lower layer of molten lead bullion of further reduced copper content and the latter is then isolated.

The present application is a continuation-in-part application of application Ser. No. 433,651 filed Feb. 18, 1965 and now abandoned.

The present invention relates to a process for decopperizing lead and particularly to the decopperizing of lead bullion of a relatively high copper content.

Crude lead bullion as produced for example in a blast furnace or reverbatory furnace normally contains a large number of impurities, including copper, antimony, arsenic, sulphur, tin, zinc, bismuth, silver, gold, iron oxide and slag.

The processes which have been adopted for the refining of lead bullion are well established but are complicated in that many operations are involved.

A typical first step in the refining of crude lead bullion is the removal of copper from the bullion. It involves the cooling of molten bullion in one or more stages in a drossing kettle or kettles, whereby impurities, which contain copper, separate and are skimmed off as dross. In the final stage of copper removal the bullion is maintained at a temperature just above its freezing point and elemental sulphur in granular form is stirred into the molten bullion. A dross containing cuprous sulphide is formed and is skimmed off and the remaining bullion is of low copper content (the copper content may be as low as 0.005% by weight).

The method of decopperizing lead by drossing is readily applicable to bullions containing up to 1% by weight of copper and can be applied to bullions containing up to 2% by weight of copper.

When the copper content of the bullion exceeds about 3% by weight, decopperizing by drossing becomes progressively more difficult and especially so when the copper content is 6% by weight or higher.

When molten bullion is cooled copper is precipitated from solution and combines with impurities present such as sulphur, arsenic and antimony to form sulphides and/or inter-metallic compounds, which separate in the dross. When the copper content of the bullion is relatively high there are usually not sufficient of said impurities present to combine with all of the copper which is precipitated and consequently free copper will enter the dross, which copper tends to separate in a spongy form, entraining with it substantial quantities of lead.

Under typical operating conditions, where the copper

content of a bullion is from 1% to 1.2% the quantity of dross which is formed and removed during the cooling and sulphur treatment operations is from 8% to 12% by weight of the crude bullion.

If the copper content of the bullion were within the range 5% to 8% the quantity of dross which could be formed and removed during these operations could be from 50% to 70% by weight of the crude bullion. The separation and subsequent treatment of such large quantities of dross is unattractive, because of the arduous manual labour involved, the high cost of fuel and the auxiliary processing equipment required.

It is known that methods have recently been described whereby the copper content of bullions containing about 4% of copper can be reduced to less than 1% of copper in a substantially continuous manner by maintaining a bath of molten bullion in a furnace so that a substantial temperature gradient is maintained between the upper surface and the bottom layers of the bullion, which are withdrawn from the bath as a decopperized bullion. The copper from the bullion separates and floats to the surface, where it can be made to react with suitable sulphur-containing materials, such as iron pyrites, sodium sulphide, or lead concentrates consisting largely of lead sulphide. Such a method has the disadvantages that difficulties may be experienced due to the separation of accretions, especially arsenides, on the walls of the bath below the surface of the bullion, and in working up the copper matte obtained to a suitable content of cuprous sulphide while maintaining substantially continuous operation.

According to the present invention a process for decopperizing lead containing copper comprises adding to the molten lead e.g. lead bullion, which may be contained in a vessel adapted for mixing and provided with heating means, a predetermined amount of a material containing compounded sulphur which can react with copper to yield cuprous sulphide, said predetermined amount preferably including an excess of said compounded sulphur over that required stoichiometrically in the reactions between the compounded sulphur and the copepr in the lead, so that a resultant matte containing cuprous sulphide and lead sulphide will be formed, mixing said added material with the lead and maintaining the mixture at a temperature of at least 540° C. until said reactions are substantially completed and allowing the contents of said vessel to settle into a bottom layer of lead of reduced copper content surmounted by a layer of matte. Bullion may be tapped from said bottom layer for instance into a shallow vessel, and allowed to cool sufficiently to form a further matte containing lead sulphide and cuprous sulphide, which matte separates as a surface layer, and to solidify said further matte, and the solidified matte may be skimmed off from the contents of said shallow vessel to yield a remaining bullion of further reduced copper content.

The bullion of further reduced copper content may be poured from the shallow vessel and cast into ingots, or it may be transferred from the shallow vessel to at least one drossing kettle and cooled and treated in the drossing kettle by known means to form dross, which is skimmed off, to yield a lead bullion of low copper content.

Said compounded sulphur which can react with copper to yield cuprous sulphide may be the sulphur present in lead sulphide (PbS) or half the sulphur present in iron pyrites (FeS_2), or partly elemntal sulphur incorporated in the material, for example as briquettes, and the reactions which take place with the copper in the bullion can be expressed by the equations:

$$PbS+2\ Cu=Cu_2S+Pb \quad (1)$$

$$FeS_2+2\ Cu=Cu_2S+FeS \quad (2)$$

$$S+2\ Cu=Cu_2S \quad (3)$$

It is convenient to use a concentrate of sulphur compounds obtained from metallurgical operations.

The concentrate is preferably rich in lead sulphide and low in the content of zinc, copper and ferrous sulphides, so that the matte which is formed will consist largely of a mixture of lead sulphide and cuprous sulphide. The matte should preferably having a melting point between 540° C., and 850° C. The approximate composition and melting points of mattes consisting of mixtures of lead sulphide and cuprous sulphide are given in Table I:

TABLE I.—LEAD SULPHIDE/CUPROUS SULPHIDE MATTES

Percent by weight lead sulphide	Percent by weight cuprous sulphide	Melting temperature (° C.)
10	90	1,040
20	80	920
30	70	785
40	60	650
48	52	540
50	50	560
60	40	670
70	30	775
80	20	880
90	10	990

Sodium sulphide (Na_2S) may be added with or incorporated in said material containing compounded sulphur. The sulphur in the sodium sulphide does not react with copper to yield cuprous sulphide, but the presence of sodium sulphide in the resultant matte depresses its melting point, so that a matte of suitable fluidity can be obtained which is of high cuprous sulphide and low lead sulphide content.

According to recently published data ("Phase Systems Concerned With the Copper Drossing of Lead" by T. H. A. Davey—Inst. Min. & Met., May 2, 1963, pp. 553–619 and 770–781) it has been established that at a temperature in excess of about 540° C. the solubility of copper in lead in the presence of sulphur is shown by two phase boundaries, between which two liquids are present and outside which liquid and lead sulphide is the stable phase at one boundary and liquid and cuprous sulphide the stable phase at the other boundary. Within the region of two liquid phases the copper and sulphur dissolved in the metal phase appear to be in equilibrium with the composition of the matte phase, so that an increase of lead sulphide content in the matte phase causes a diminution of the solubility of copper in the metal phase and an increase in the solubility of sulphur in this phase.

By adding a predetermined excess of lead sulphide to a bullion rich in copper at a temperature high enough for cuprous sulphide to be formed and at the same time increasing the amount of sulphur dissolved in the metal phase, a matte, consisting of lead sulphide and cuprous sulphide, can be formed of which the melting point can be preselected. The lowest melting point of the matte is 540° C., corresponding to the eutectic composition, but if less lead sulphide than required for the eutectic composition is added the melting point of the matte will increase. If the mixture of matte and metal phase thus formed be cooled until the phase boundary between the "two liquids" and "liquid plus cuprous sulphide" be reached matte will precipitate from the metal phase and the copper content of the metal phase will depend on the freezing point, and consequently the composition, of the matte.

It has been found necessary that a temperature in excess of 540° C. be employed in the reaction between the material containing compounded sulphur and the copper in the lead bullion in order that the matte containing cuprous sulphide and lead sulphide is formed. The vessel in which this reaction is carried out must therefore have a minimum temperature of 540° C.

Resulting from successive operations in said vessel adapted for mixing and provided with heating means, the matte containing cuprous sulphide and slag formed from impurities present in the bullion will accumulate to an extent such that it is not feasible to feed more bullion for treatment. This matte and slag may be tapped or skimmed off into suitable containers and the feeding of bullion into the vessel recommenced. Alternatively and preferably, this matte and slag may be converted by the addition of materials and mixing, into a matte of a different composition to suit the commercial market and a slag of greater fluidity. For example, to a matte consisting largely of a mixture of lead sulphide and cuprous sulphide a suitable amount of scrap iron may be added to form a matte consisting largely of a mixture of ferrous sulphide and cuprous sulphide, and predetermined amounts of slag forming materials such as lime, silica, aluminas and fluor-spar may be added to produce a slag of increased fluidity. Soda ash and a reducing agent such as coke may be added to obtain a matte containing sodium sulphide and an increased content of cuprous sulphide and a reduced content of lead sulphide. The converted matte and slag are removed from the vessel by tapping.

The process of the present invention is suitable for the treatment of lead bullion containing 3% by weight and upwards of copper.

Said vessel adapted for mixing and provided with heating means is conveniently, and preferably, a drum type rotary furnace provided with an internal burner supplied with fuel. However, other vessels than a rotary furnace may be used, for example the bath or crucible of an induction electric furnace, provided with a heat-resisting removable mechanical stirrer.

The lead bullion may be fed to the vessel from the hearth of a blast furnace or reverbatory furnace in the molten state by means of a ladle.

The temperature of the contents of the vesel is preferably maintained between 800° and 900° C. during the reaction period.

The reaction between lead sulphide and iron pyrites in the concentrate and copper in the bullion are rapid at temperatures above 800° C. and the length of time required to complete the reactions will be dependent on the size of the vessel and the speed at which the material can be mixed. Small scale experiments, involving the use of quantities of 50 lb. to 70 lb. of bullion, have shown that the reactions can proceed substantially to completion in a few minutes, for example 3 to 5 minutes.

When using a rotary furnace this may be provided with one tapping hole, suitably located, which is kept plugged when the furnace is rotated during the reaction period. When the reaction has been completed the rotation of the furnace is stopped so that the tapping hole is positioned at or near the bottom of the furnace. After allowing the contents of the furnace to settle the plug is removed from the tapping hole and the bullion of reduced copper content is run into said shallow vessel.

Said shallow vessel is preferably lined with refractory material. It may for example be an iron or steel shallow ladle lined with refractory bricks. The bullion in this vessel is allowed to cool to a temperature of 600° C. or lower, at which temperature a matte containing lead sulphide and cuprous sulphide will have formed and solidified at the surface.

The reason for lining the vessel with refractory material is that the matte containing lead sulphide and cuprous sulphide is corrosive to iron and steel.

When using a shallow ladle, after skimming off the solidified matte the ladle may be used for feeding the bullion of further reduced copper content to a drossing kettle.

When adding scrap iron to convert a lead sulphide/cuprous sulphide matte in the reaction vessel, for example a rotary furnace, the reaction which takes place is expressed by the equation:

$$PbS+Fe=FeS+Pb \quad (4)$$

The ferrous sulphide passes into the matte and the lead separates as a copper-rich bullion.

When the reaction has been completed, the rotation of the furnace is stopped so that the tapping hole is positioned at a point above the newly formed bullion layer. After allowing the contents of the furnace to settle the plug is removed from the tapping hole and first the matte and then the slag are run into suitable containers.

The temperature of the contents of the rotary furnace during this operation may be raised to 1,000° C. or higher, depending on whether matte only or both matte and slag are being produced.

The lead which separates from the reaction will be relatively high in copper content. Such lead bullion may be left in the furnace, after tapping off matte and slag and incorporated with a new charge of lead bullion of relatively high copper content for treatment by the process of the present invention. Alternatively, the separated lead bullion may be withdrawn from the rotary furnace and transferred to a second rotary furnace for processing separately.

By operating two or more rotary furnaces in parallel, it is possible to make the preliminary decopperizing of lead bullion produced in say a blast furnace into a substantially continuous operation.

Alternatively a single vessel adapted for mixing and provided with heating means, for example a rotary furnace, may be employed for both decopperizing the raw bullion rich in copper and working up the matte formed in said vessel, whilst maintaining a substantially continuous flow of bullion from the primary producer (e.g. a blast furnace or reverbatory furnace), by incorporating a heated holding vessel in the system. During a given period, or say 12 hours, decopperizing of the bullion is carried out during a first half period (6 hours) and working up of the matte is carried out during a second half period (6 hours). During the second half period hot raw bullion from the primary producer is stored in a suitably heated holding vessel maintained at a temperature above that at which copper could separate, either as cuprous sulphide, an intermetallic compound or metallic copper, while matte is worked up in the rotary furnace or alternative vessel. Each batch or ladle of bullion received from the primary producer is poured into the heated holding vessel until the decopperizing operation in the rotary furnace, or alternative vessel, and shallow vessel is recommenced during the next first half period. During a first half period when decopperizing is carried out in the rotary furnace, or alternative vessel, and shallow vessel both the raw bullion received direct from the primary producer and that from the heated holding vessel are fed to the rotary furnace, or alternative vessel, in quantities equivalent to twice the average rate of production of bullion in the primary producer. Thus the whole of the bullion stored in the heated holding vessel during the preceding second half period will pass to the rotary furnace, or alternative vessel, for decopperizing, and the heated holding vessel will be emptied so that it will be ready for receiving hot raw bullion from the primary producer during the following second half period.

According to a further form of the present invention a process for decopperizing lead of a relatively high copper content e.g. more than 5% by weight, comprises decopperizing a part of the raw lead bullion by the process described above to yield a molten bullion of reduced copper content, passing said molten bullion of reduced copper content and the remaining part of molten raw lead bullion to a drossing vessel such as a drossing kettle, cooling the mixed molten bullion in the drossing vessel to form a dross at the surface, skimming off or otherwise removing said dross to yield a lead bullion of further reduced copper content and recycling said dross as feed material to the process described above so that said molten bullion of reduced copper content produced thereby contains arsenic in solution. Preferably the arsenic in solution in said molten bullion of reduced copper content is in excess of that required to form copper arsenide with the free copper in said mixed bullion prior to separation of dross.

The free copper in the mixed bullion in this instance is defined as that which is in excess of the copper which can combine with the sulphur dissolved in the bullion. The arsenic dissolved in the mixed bullion combines with free copper to form copper arsenide (Cu_3As) which separates out in the dross. Preferably the arsenic in the mixed bullion should be in excess of the amount required to combine with the free copper by at least 0.07 percent by weight of the bullion.

The mixed lead bullion usually contains copper, sulphur, arsenic, antimony and other elements in solution, the amount of copper being in excess of that which can combine with the sulphur to form cuprous sulphide. On cooling to the drossing temperature the copper combines preferentially first with the sulphur, next with the arsenic and then with the antimony. It is preferred that there is an excess of arsenic in the mixed bullion over that which can combine with the copper remaining after the sulphur has combined with copper, to form copper arsenide because in this instance a relatively small proportion of the antimony in the bullion combines with the copper to form a copper-antimony compound which separates out in the dross. Copper arsenide is preferred to a copper-antimony compound in the dross which is recycled to the rotary furnace because a dross containing a relatively large amount of a copper-antimony compound is difficult to handle.

It is assumed that the raw bullion from the primary producer, e.g. a blast furnace, contains some arsenic, and this is usually the case. By building up the arsenic content in the molten bullion tapped from the rotary furnace, the build up of a copper-antimony compound in the dross of the first or hot drossing kettle is reduced to a minimum.

In starting up the process, the building up of the arsenic content of the molten bullion tapped from the rotary furnace can be hastened by feeding to the rotary furnace a suitable amount of a dross comparatively rich in copper arsenide and comparatively poor in a copper-antimony compound. Thereafter the build up of the arsenic content is achieved by recycling to the rotary furnace or like vessel, the dross skimmed from the hot drossing kettle.

The bullion of further reduced copper content in the drossing kettle may be transferred to a sulphur drossing kettle, where it is cooled to just above its freezing point and mixed with added granular sulphur to form a sulphur dross and yield a bullion of low copper content. The sulphur dross is skimmed off and is preferably recycled to the first drossing kettle.

The process of the present invention may be carried out so that during a period when a part of the raw lead bullion is decopperized by the process first described above the resultant molten bullion of reduced copper content is passed to the first drossing kettle and the remaining part of molten raw lead bullion is added to the drossing kettle during another period when matte and slag are worked up in the vessel adapted for mixing and provided with heating means pertaining to the process first described above. In this way a single vessel adapted for mixing and provided with heating means, for example a rotary furnace, may be employed for decopperizing a part of the raw bullion rich in copper and working up the matte and slag formed in said vessel, whilst maintaining a substantially continuous flow of bullion from the primary producer (e.g. a blast furnace or reverbatory furnace). Furthermore, by feeding part of the raw lead bullion into the first drossing kettle, the drossing kettle also takes the place of the heated holding vessel of the process first described above and the need for such a separate holding vessel for continuous operation of the decopperizing process is dispensed with.

The invention is illustrated by, but not limited to the following examples, in which reference will be made to the accompanying drawings wherein

FIGS. 1 and 2 are flow diagrams.

EXAMPLE 1

Laboratory experiments were carried out treating batches of 56 to 65 lb. of lead bullion containing 6.3 to 6.5% by weight of copper with a lead concentrate of the following composition:

	Percent by weight
Zn	5.5
Pb	53.0
Cu	6.2
S	21.0
Fe	7.0
SiO_2	2.0
Al_2O_3	0.5
CaO	0.5

A sulphur balance of the composition of the lead concentrate indicates that virtually all of the iron present is present as iron pyrites (FeS_2).

Compounded sulphur available for forming cuprous sulphide:

	Percent by weight of concentrate
From PbS	8.19
From FeS_2	4.01
Total	12.20

The lead concentrate was ground to pass through a 52 B.S.S. sieve and a known weight of the concentrate was placed in a refractory lined crucible which had been previously heated to about 700° C. Molten lead bullion which had previously been heated to about 1020° C., was poured on to the concentrate in the crucible and the mixture gently stirred for about 4 minutes and then allowed to separate. The weight of bullion poured into the crucible was determined by the difference in the weight of the crucible prior to and after pouring. The bullion was sampled immediately before pouring and again after the separated matte had been removed by skimming, exposing a clean bright surface of bullion. Owing to the small scale of the experiments it was not possible to separate matte and bullion completely; the products obtained were (a) decopperized bullion, (b) matte and (c) a residue adhering to the crucible, which was removed by chipping and reheating and melting. This residue was found to contain matte, bullion, and some lead oxide and refractory material.

Three tests (1 to 3) werec arried out as described above and the following results were obtained.

Test Number	1	2	3
Pounds			
Weight of bullion poured	56.07	64.37	65.22
Weight of concentrate used	13.00	9.50	6.82
Weight of decopperized bullion recovered	47.22	47.68	49.76
Weight of matte recovered	18.90	18.28	18.96
Weight of residue recovered	1.83	6.08	4.86
Unaccounted loss (or gain)	1.12	1.83	(1.54)
Copper analysis (wt percent)			
Copper in bullion	6.54	6.31	6.38
Copper in decopperized bullion	0.40	0.97	1.42
Copper in matte	19.70	17.97	17.65
Copper in residue	4.93	10.20	6.34
Copper in concentrate	61.7	6.23	6.23
Copper balance (lbs)			
Copper in bullion	3.66	4.05	4.14
Copper in concentrate	0.80	0.59	0.42
Total	4.46	4.64	4.56
Copper in decopperized bullion	0.19	0.46	0.71
Copper in matte	3.72	3.28	3.34
Copper in residue	0.09	0.62	0.31
Copper unaccounted for	0.46	0.28	0.20
Total	4.46	4.64	4.56
Compounded sulphur (lbs.)			
S required stoichiometrically for reacting with copper in bullion to form Cu_2S	0.922	1.021	1.044
S provided from PbS and FeS_2 in concentrate	1.585	1.160	0.832
Ratio, S provided: S required	1.72	1.41	0.80

The temperature of the bullion after pouring and mixing with the concentrate in the crucible was estimated to be above 740° C. and below 900° C.

The melting temperature of the mattes was estimated to be in the range 830° C. (test 1) to 860° C. (test 3).

In tests 1 and 2 the compounded sulphur from PbS and FeS_2 in the concentrate is in excess of that required for reacting with the copper in the bullion to form Cu_2S and the copper content of the decopperized bullion obtained is in each case below 1% by weight, being only 0.4% in test 1 where the excess is greater.

In test 3 the compounded sulphur in the concentrate is less than that required for reacting with the copper in the bullion and the copper content of the decopperized bullion is higher (1.42%).

EXAMPLE 2

Laboratory experiments were carried out treating batches of 65 to 68 lb. of lead bullion containing 6.4 to 7.1% by weight of copper with a lead concentrate of the following composition:

	Percent by weight
Zn	2.5
Pb	79.0
Cu	0.2
S	15.0
Fe	4.0
SiO_2	0.7
Al_2O_3	0.5
CaO	0.5

A sulphur balance of the composition of the lead concentrate indicates that virtually all of the iron present is present as ferrous sulphide (FeS), iron pyrites being absent.

Compounded sulphur for forming cuprous sulphide is available solely from PbS, being 12.23% by weight of concentrate.

The experiments were carried out in the same way as described for Example 1 and two tests (4 and 5) were carried out and the following results obtained:

Test Number	4	5
Pounds:		
Weight of bullion poured	64.87	68.16
Weight of concentrate used	11.10	7.00
Weight of decopperized bullion recovered	53.91	54.90
Weight of matte recovered	15.35	8.47
Weight of residue recovered	5.51	11.43
Unaccounted loss	1.20	0.36
Copper analysis (wt. percent):		
Copper in bullion	7.13	6.36
Copper in decopperized bullion	0.78	2.10
Copper in matte	16.61	15.00
Copper in residue	11.55	11.13
Copper in concentrate	0.23	0.23
Copper balance (lbs.):		
Copper in bullion	4.62	4.33
Copper in concentrate	0.03	0.02
Total	4.65	4.35
Copper in decopperized bullion	0.42	1.15
Copper in matte	2.55	1.27
Copper in residue	0.64	1.28
Copper unaccounted for	1.04	0.65
Total	4.65	4.35
Compounded sulphur (lbs.):		
S required stoichiometrically for reacting with copper in bullion to form Cu_2S	1.165	1.090
S provided from PbS in concentrate	1.358	0.855
Ratio, S provided:S required	1.16	0.78

In test 4 the compounded sulphur from the PbS in the concentrate is in excess of that required for reacting with the copper in the bullion to form Cu_2S and the copper content of the decopperized bullion obtained is 0.78% by weight.

In test 5 the compounded sulphur in the concentrate is less than that required for reacting with the copper in the bullion and the copper content of the decopperized bullion is higher (2.1%).

EXAMPLE 3

FIG. 1 illustrates a scheme for decopperizing lead bullion containing 5.6% by weight of copper. Molten raw bullion and concentrates containing lead sulphide and iron pyrites are fed to a rotary furnace in which these are mixed and heated to carry out the reactions for forming a matte containing cuprous sulphide. Partially decopperized bullion is tapped from the rotary furnace and run into a shallow ladle where it is allowed to cool until a matte containing lead sulphide and cuprous sulphide which has separated at the surface solidifies. The solidified matte is broken and recycled to the rotary furnace. The remaining further partially decopperized bullion in the shallow ladle is fed to a hot drossing kettle where it is cooled and a dross allowed to form. The still further partially decopperized bullion in the hot drossing kettle is pumped from this vessel into a sulphur drossing kettle where it is cooled to just above its freezing point and mixed with added granular sulphur to form a sulphur dross. The sulphur dross is skimmed off the kettle and recycled to the hot drossing kettle to mix with the dross which is formed there. The mixed dross from the hot drossing kettle is recycled to the rotary furnace. Decopperized bullion, containing 0.1% by weight or less of copper, is pumped from the sulphur drossing kettle and cast into ingots.

The matte and slag which are formed and accumulate in the rotary furnace are periodically worked up. During this working up scrap iron is added to convert some of the lead sulphide in the matte to ferrous sulphide, lead being formed at the same time, and sand and lime are added to obtain a slag of suitable fluidity. A certain amount of coke is added to act as a reducing agent for lead oxide, some of which has formed. When worked up, the matte and slag are tapped from the rotary furnace and allowed to cool into matte and slag products.

The hot products of combustion leaving the rotary furnace contain a fume comprising lead and other elements obtained by the volatilisation and entrainment of material in the furnace. The hot products of combustion are diluted with air and further cooled and then passed through bag filters in which the fume is retained and recovered.

Quantity and composition figures for the various materials specified in the flow diagram are given in the following table and relate to 100 parts by weight of lead in the raw bullion.

TABLE II

Raw bullion

Lead	100.0
Copper	6.0
Arsenic	0.2
Iron	0.2
Sulphur	0.2
Antimony	0.4
"Others"	0.3
	107.3

"Others" additions

Coke FC	0.47
Ash	0.11
H_2O+VM	0.07
	0.65

Iron	1.18
Sand	As necessary
Lime	As necessary

Concentrates

Lead	11.97
Copper	0.57
Zinc	0.665
Iron	1.615
Sulphur	3.80
"Others"	0.38
	19.00

Matte

Lead	1.58
Copper	6.53
Zinc	0.63
Iron	2.71
Sulphur	3.62
	15.07

Slag

Lead	0.05
Iron	0.20
Arsenic	0.08
"Others"	1.18
	1.51

Recycle matte

Lead	2.096
Copper	1.86
Iron	0.08
Arsenic	0.04
Sulphur	0.637
"Others"	0.404
	5.117

Mixed dross

Lead	3.17
Copper	0.39
Arsenic	0.16
Sulphur	0.116
Antimony	0.044
"Others"	0.036
	3.916
Iron	Trace

Sulphur dross

Lead	3.60
Copper	0.05
Sulphur	0.07
	3.72

Fume

Lead	3.53
Copper	0.030
Zinc	0.035
Iron	0.085
Sulphur	0.45
"Others"	1.30
	5.43

Sulphur

To sulphur drossing kettle	0.1
To atmosphere	0.03

Partially decopperised bullion

	(a) From rotary furnace	(b) From shallow ladle	(c) From hotdrossing kettle
Lead	112.075	109.979	110.409
Copper	2.36	0.40	0.060
Arsenic	0.32	0.28	0.12
Irom	0.08	trace	trace
Sulphur	0.68	0.043	0.001
Antimony	0.448	0.444	0.40
"Others"	0.440	0.036	trace
Total	116.305	111.182	110.990

De-copperised bullion

Lead	106.81
Copper	0.01
Arsenic	0.12
Antimony	0.40
	107.34

It will be noted that the concentrates contain 11.97 parts by weight of lead and the de-copperised bullion contains 106.81 parts by weight of lead.

The concentrates have the following average composition:

	Percent by weight
Zn	3.5
Pb	63.0
Cu	3.0
S	20.0
Fe	8.5
SiO_2	0.8
Al_2O_3	0.7
CaO	0.5

A sulphur balance of the concentrates indicates that they contain 72.6% by weight of PbS and 10.97% of FeS_2.

Compounded sulphur available from—	Percent by weight of concentrates
PbS	9.73
FeS_2	2.93
Total compounded sulphur available for forming Cu_2S	12.66

The raw bullion contains 6.0 parts by weight of copper per 100 parts by weight of lead, which copper requires stoichiometrically, 1.644 parts by weight of compounded sulphur to form Cu_2S.

The raw bullion is treated with 19.0 parts by weight of concentrates of which 1 part is taken as entrained in the fume from the rotary furnace, leaving 18 parts by weight of concentrates containing 2.28 parts by weight of compounded sulphur available for forming Cu_2S.

Ratio of compounded sulphur provided:compounded sulphur required=2.28/1.644=1.39.

There is thus an ample excess of the requisite compounded sulphur in the concentrates over that required for reacting with the copper in the bullion to form Cu_2S.

EXAMPLE 4

FIG. 2 illustrates a scheme for de-copperizing raw lead bullion containing 5.65% by weight of copper. The molten bullion is received in batches from the primary producer at an average rate of 3 tonnes per hour, amounting to 36 tonnes in 12 hours. For a period of 7 hours approximately 21 tonnes of the molten raw bullion is fed at intervals of 1 hour, together with concentrates containing lead sulphide and iron pyrites, reducing agents such as coke, and recycle matte and mixed dross, to a drum type rotary furnace in which these are mixed and heated to carry out the reactions for forming a matte containing cuprous sulphide and lead sulphide. Partially decopperized bullion (PD—CB1) is tapped at hourly intervals from the rotary furnace and run into shallow ladles where it is allowed to cool until a matte containing lead sulphide and cuprous sulphide which has separated at the surface solidifies. The solidified matte is broken up and recycled to the rotary furnace. The remaining further partially decopperized bullion (PD—CB2) in the shallow ladles is fed to a hot drossing kettle, where it is stored, until approximately 30 to 31 tonnes of said further partially decopperized bullion has accumulated. Prior to feeding the further partially decopperized bullion to the hot drossing kettle, approximately 1¼ tonnes of sulphur dross, from a previous sulphur treatment operation, is charged into the kettle.

For a period of the next 5 hours approximately 15 tonnes of molten raw bullion from the primary producer is fed to the hot drossing kettle and mixes with said further partially decopperized bullion contained therein, so that approximately 47 tonnes of mixed bullion containing about 2% to 2.1% by weight of copper will be in the hot drossing kettle. This mixed bullion is allowed to cool in the kettle until its temperature falls to a suitable value between 375° C. and 450° C., when the drossing operation is carried out resulting in the removal by skimming off 9 to 10 tonnes of mixed dross. After drossing the still further partially decopperized bullion (PD—CB3) is passed to a sulphur drossing kettle for sulphur treatment. The sulphur dross from the sulphur drossing kettle is recycled to the hot drossing kettle and the final decopperized bullion passes out from the sulphur drossing kettle.

During said period of the next 5 hours, the matte and slag which have accumulated in the rotary furnace during the preceding 7 hours are worked up ("upgraded") by raising the temperature of the furnace and adding materials such as scrap iron, sand and lime or soda so that the lead content of the matte is susbtantially reduced and a slag of good fluidity and low in lead and copper content is obtained. The worked up slag and matte are tapped from the furnace during the last one or two hours of the 5 hours period leaving in the rotary furnace a copper-rich lead bullion formed by the reaction between lead sulphide in the initial matte and the added iron. During the last hour of this period and after tapping slag and matte from the furnace the recycle matte and a part of the mixed dross which have accumulated, together with a portion of the concentrates containing lead sulphide and iron pyrites required for the succeeding decopperizing operation are added to the rotary furnace, prior to feeding molten raw bullion at the commencement of the next 7 hours period. During the next 7 hours period, when molten raw bullion is fed to the rotary furnace, the remainder of the accumulated mixed dross and the required concentrates, together with slag forming fluxes, are added.

In a preferred method of operation the whole of the recycle matte, one-quarter of the accumulated mixed dross and one-sixth of the required concentrates are added to the rotary furnace during the last hour of the preceding 5 hour "upgrading" period, after draining the furnace free of slag and matte. During the following 7 hours period the furnace is fed at intervals of 1 hour with approximately 3 tonnes of molten raw bullion, together with one-quarter of the accumulated mixed dross and one-sixth of the required concentrates until all the mixed dross accumulated during a previous 12 hours period and all the required concentrates have been added, after which only molten raw bullion is fed during the last 2 hours of the 7 hours period. During the 7 hours period, at intervals of 1 hour, following the feeding of molten raw bullion, mixed dross and concentrates, partially decopperized bullion is tapped from the furnace and run into shallow ladles for cooling and separation of the recycle matte. thus avoiding the accumulation of too much fluid material in the furnace and allowing the furnace to be operated so that its content of fluid material at any instant does not exceed 75% to 80% by volume of its working capacity.

In the operation of the process as described, an equilibrium will be attained after three or four complete cycles of 12 hour periods, whereby the copper entering the hot drossing kettle in excess of that which can combine with the sulphur entering the hot drossing kettle will combine with arsenic which is present to form copper arsenide (Cu_3As), which separates out in the mixed dross. The mixed dross is recycled to the rotary furnace where the copper arsenide is decomposed in the presence of an excess of lead sulphide and the liberated arsenic dissolves in the partially de-copperised bullion. This arsenic-containing partially de-copperised bullion is tapped from the rotary furnace and run into shallow ladles and most of its arsenic remains dissolved in the further partially de-copperised bullion which is fed from the shallow ladles to the hot drossing kettle. The arsenic content of the further partially de-copperised bullion is such as to ensure an excess of arsenic in the mixed bullion in the hot drossing kettle, prior to separation of dross, over that required to form copper arsenide with the free copper in the mixed bullion.

Quantity and composition figures for the various materials specified in the flow diagram are given in the following table. The quantities are in tonnes and relate to the treatment of 36 tonnes of raw lead bullion in a 12 hour period.

TABLE III

Raw bullion

	(a) To short rotary furnace	(b) To hot drossing kettle
Lead	19.571	13.980
Copper	1.174	0.839
Arsenic	0.039	0.028
Iron	0.039	0.028
Sulphur	0.039	0.028
Antimony	0.079	0.056
"Others"	0.059	0.041
Total	21.000	15.000

Concentrates

Lead	4.016
Copper	0.191
Zinc	0.223
Iron	0.542
Sulphur	1.275
"Others"	0.128
	6.315

"Other additions"

Coke:

FC	0.158
Ash	0.037
H_2O+VM	0.023
	0.218

Iron	0.396
Sand	As necessary
Lime	As necessary

Slag

Lead	0.017
Copper	0.017
Arsenic	0.013
Iron	0.067
"Others"	0.396
	0.510

Mixed dross

Lead	8.168
Copper	0.945
Arsenic	0.298
Iron	0.028
Sulphur	0.063
Antimony	0.033
"Others"	0.050
	9.585

Matte

Lead	0.530
Copper	2.174
Zinc	0.211
Arsenic	0.014
Iron	0.909
Sulphur	1.215
	5.053

Recycle matte

Lead	0.572
Copper	0.508
Arsenic	0.011
Iron	0.022
Sulphur	0.174
Antimony	0.001
"Others"	0.111
	1.399

Sulphur dross

Lead	1.208
Copper	0.017
Sulphur	0.024
	1.249

Sulphur

To sulphur drossing kettle	0.034
To atmosphere	0.010

Fume

Lead	1.184
Copper	0.010
Zinc	0.012
Iron	0.029
Sulphur	0.151
"Others"	0.436
	1.822

Partially decopperized bullion

	(a) From rotary furnace	(b) From shallow ladle	(c) From hot drossing kettle
Lead	30.596	30.024	37.044
Copper	0.617	0.109	0.020
Arsenic	0.321	0.310	0.040
Iron	0.022	trace	trace
Sulphur	0.185	0.011	0.000
Antimony	0.113	0.112	0.135
"Others"	0.120	0.009	trace
Total	31.974	30.575	37.239

Decopperized bullion

Lead	35.836
Copper	0.003
Arsenic	0.040
Antimony	0.135
	36.014

The sulphur entering the hot drossing kettle $=0.011+0.028+0.024=0.063$ tonne

The copper entering the hot drossing kettle $=0.109+0.839+0.017=0.965$ tonne

The arsenic entering the hot drossing kettle $=0.310+0.028=0.338$ tonne

The copper which can combine with 0.063 tonne S to form $Cu_2S=0.250$ tonne, leaving $0.965-0.250=0.715$ tonne of free copper. This free copper can combine with 0.281 tonne of arsenic to form copper arsenide (Cu_3As), leaving $0.338-0.281=0.057$ tonne of excess arsenic. This excess arsenic is dissolved in $30.575+15.0+1.249=46.824$ tonne of mixed bullion, prior to separation of dross. Whence

the excess arsenic dissolved in the mixed bullion

$$=\frac{0.057\times 100}{46.824}=0.122$$

percent by weight of the bullion

I claim:

1. In a process for decopperizing lead bullion which contains more than 2% by weight of copper and wherein the total quantity of sulphur, arsenic and antimony is not sufficient to combine with all of the copper, the improvement comprising the steps of maintaining the lead bullion in a molten state, adding to the molten lead bullion a material containing compounded sulphur which can react with the copper in the lead bullion to yield cuprous sulphide, maintaining said material mixed with the molten lead bullion at a temperature of at least 540° C. until the reaction with the copper is substantially completed, thereafter allowing the resultant mixture to settle into a first lower layer of molten lead bullion of reduced copper content and a first upper layer of matte containing cuprous sulphide and lead sulphide, isolating molten lead bullion from the lower layer, cooling the isolated molten lead bullion to form a further upper layer of matte containing cuprous sulphide and lead sulphide and a further lower layer of molten lead bullion of further reduced copper content and isolating lead bullion from the further lower layer.

2. In a process for decopperizing lead bullion which contains more than 2% by weight of copper and wherein the total quantity of sulphur, arsenic and antimony is not sufficient to combine with all of the copper, the improvement comprising the steps of maintaining the lead bullion in a molten state, adding to the molten lead bullion a material containing a sulphur compound, said material being added in amount in excess of that required to react with the copper in the lead bullion to yield cuprous sulphide, maintaining said material mixed with the molten lead bullion at a temperature of at least 540° C. until the reaction of the sulphur compound with the copper to yield cuprous sulphide is substantially completed, thereafter allowing the resultant mixture to settle into a first lower layer of molten lead bullion of reduced copper content and a first upper layer of matte containing cuprous sulphide and lead sulphide, isolating molten lead bullion from the lower layer, cooling the isolated molten lead bullion to form a further upper layer of matte containing cuprous sulphide and lead sulphide and a further lower layer of molten lead bullion of further reduced copper content and isolating lead bullion from the further lower layer.

3. In a process for decopperizing lead bullion which contains more than 2% by weight of copper and wherein the total quantity of sulphur, arsenic and antimony is not sufficient to combine with all of the copper, the improvement comprising the steps of maintaining the lead bullion in a molten state, adding to the molten lead bullion a sulphur compound in amount in excess of that required to react with the copper in the lead bullion to yield cuprous sulphide, maintaining said sulphur compound mixed with the molten lead bullion at a temperature of at least 540° C. until the reaction with the copper is substantially completed, thereafter allowing the resultant mixture to settle into a first lower layer of molten lead bullion of reduced copper content and a first upper layer of matte containing cuprous sulphide and lead sulphide, isolating molten lead bullion from the lower layer, cooling the isolated molten lead bullion to form a further upper layer of matte containing cuprous sulphide and lead sulphide and a further lower layer of molten lead bullion of further reduced copper content and isolating lead bullion from the further lower layer, the lead bullion from the first lower layer being isolated by tapping the first lower layer and the lead bullion from the further lower layer being isolated by solidifying the further upper layer of matte and skimming the solidified matte off the surface of the molten lead bullion.

4. In a process for decopperizing lead bullion which contains more than 2% by weight of copper and wherein the total quantity of sulphur, arsenic and antimony is not sufficient to combine with all of the copper, the improvement comprising the steps of maintaining the lead bullion in a molten state in a reaction vessel, adding to the molten lead bullion a material containing compounded sulphur which can react with the copper in the lead bullion to yield cuprous sulphide, maintaining said material mixed with the molten lead bullion at a temperature of at least 540° C. until the reaction with the copper is substantially completed, thereafter allowing the resultant mixture to settle into a lower layer of molten lead bullion of reduced copper content and an upper layer of matte containing cuprous sulphide and lead sulphide, isolating molten lead bullion of reduced copper content from the lower layer, converting the lead sulphide in the upper layer of matte to lead after removal of the molten lead bullion from the lower layer, thereafter removing the residue of said upper layer of matte from the reaction vessel to leave the lead obtained from said lead sulphide in the reaction vessel, adding more lead bullion to be decopperized to said lead in said reaction vessel, and repeating said sequential steps.

5. In a process for decopperizing lead bullion which contains more than 2% by weight of copper and wherein the total quantity of sulphur, arsenic and antimony is not sufficient to combine with all of the copper, the improvement comprising the steps of maintaining the lead bullion in a molten state in a reaction vessel, adding to the molten lead bullion a material containing compounded sulphur which can react with the copper in the lead bullion to yield cuprous sulphide, maintaining said material mixed with the molten lead bullion at a temperature of at least 540° C. until the reaction with the copper is substantially completed, thereafter allowing the resultant mixture to settle into a lower layer of molten lead bullion of reduced copper content and an upper layer of matte containing cuprous sulphide and lead sulphide, isolating molten lead bullion of reduced copper content from the lower layer, thereafter treating the matte in the upper layer with a flux, removing said matte so treated from the reaction vessel, adding more lead bullion to be decopperized to said reaction vessel and repeating said sequential steps.

6. A process for decopperizing lead which contains copper and wherein the total quantity of sulphur, arsenic and antimony is not sufficient to combine with all of the copper, said process comprising the steps of obtaining said lead in a molten state from a primary producer, providing a heated holding vessel for storing molten lead from said primary producer at a temperature above that at which copper in the lead can separate as a copper compound, providing a reaction vessel, maintaining said lead in a molten state in said reaction vessel, adding to the molten lead in the reaction vessel a material containing compounded sulphur which can react with the copper in the lead to yield cuprous sulphide. maintaining said material mixed with the molten lead at a temperature of at least 540° C. until the reaction with the copper is substantially completed, thereafter allowing the resultant mixture to settle into a lower layer of molten lead of reduced copper content and an upper layer of matte containing cuprous sulphide and lead sulphide, removing at least a portion of said lower layer from said reaction vessel, treating said matte, feeding molten lead from said primary producer to said holding vessel during the treatment of said matte, removing said matte from said reaction vessel, thereafter feeding molten lead from said primary producer and from said holding vessel to said reaction vessel and repeating said sequential steps in said reaction vessel.

7. In a process for decopperizing raw lead bullion which contains copper and arsenic and wherein the total quantity of sulphur, arsenic and antimony is not sufficient to combine with all of the copper, the improvement comprising the steps of dividing said raw lead bullion into two parts, maintaining the first part of said raw lead bullion in a molten state in a reaction vessel, adding to the molten

lead bullion in the reaction vessel a material containing compounded sulphur which can react with the copper in the lead bullion to yield cuprous sulphide, maintaining said material mixed with the molten lead bullion until the reaction with the copper is substantially completed, thereafter allowing the resultant mixture to settle into a lower layer of molten lead bullion of reduced copper content and an upper layer of matte containing cuprous sulphide and lead sulphide, passing said molten lead bullion of reduced copper content and the remaining part of molten raw lead bullion to a drossing vessel, cooling the mixed molten lead bullion in the drossing vessel to form a dross at the surface, removing said dross to yield a lead bullion of further reduced copper content, recycling said dross as feed material to said reaction vessel and repeating said sequential steps whereby said molten bullion of reduced copper content produced thereby contains arsenic in solution.

8. In a process for decopperizing raw lead bullion which contains copper and arsenic and wherein the total quantity of sulphur, arsenic and antimony is not sufficient to combine with all of the copper, the improvement comprising the steps of dividing said raw lead bullion into two parts, maintaining the first part of said raw lead bullion in a molten state in a reaction vessel, adding to the molten lead bullion in the reaction vessel a lead concentrate containing lead sulphide and iron sulphide which can react with the copper in the lead bullion to yield cuprous sulphide, maintaining said material mixed with the molten lead bullion until the reaction with the copper is substantially completed, thereafter allowing the resultant mixture to settle into a lower layer of molten lead bullion of reduced copper content and an upper layer of matte containing cuprous sulphide and lead sulphide, passing said molten lead bullion of reduced copper content and the remaining part of molten raw lead bullion to a drossing vessel, cooling the mixed molten lead bullion in the drossing vessel to form a dross at the surface, removing said dross to yield a lead bullion of further reduced copper content, recycling said dross as feed material to said reaction vessel and repeating said sequential steps whereby said molten bullion of reduced copper content produced thereby contains arsenic in solution.

9. In a process for decopperizing raw lead bullion which contains copper and arsenic and wherein the total quantity of sulphur, arsenic and antimony is not sufficient to combine with all of the copper, the improvement comprising the steps of dividing said raw lead bullion into two parts, maintaining the first part of said raw lead bullion in a molten state in a reaction vessel, adding to the molten lead bullion in the reaction vessel a material containing compounded sulphur which can react with the copper in the lead bullion to yield cuprous sulphide, maintaining said material mixed with the molten lead bullion until the reaction with the copper is substantially completed, thereafter allowing the resultant mixture to settle into a lower layer of molten lead bullion of reduced copper content and an upper layer of matte containing cuprous sulphide and lead sulphide, passing said molten lead bullion of reduced copper content and the remaining part of molten raw lead bullion to a drossing vessel, cooling the mixed molten lead bullion in the drossing vessel to form a dross at the surface, removing said dross to yield a lead bullion of further reduced copper content, recycling said dross as feed material to said reaction vessel and repeating said sequential steps whereby said molten bullion of reduced copper content produced thereby contains arsenic in solution, the arsenic in solution in the molten bullion of reduced copper content being in excess of that required to form copper arsenide with the free copper in the mixed bullion prior to separation of dross, and the arsenic in the mixed bullion being in excess of the amount required to combine with the free copper by at least 0.07 percent by weight of the bullion.

10. In a process for decopperizing raw lead bullion which contains copper and arsenic and wherein the total quantity of sulphur, arsenic and antimony is not sufficient to combine with all of the copper, the improvement comprising the steps of dividing said raw lead bullion into two parts, maintaining the first part of said raw lead bullion in a molten state in a reaction vessel, adding to the molten lead bullion in the reaction vessel a material containing compounded sulphur which can react with the copper in the lead bullion to yield cuprous sulphide, maintaining said material mixed with the molten lead bullion until the reaction with the copper is substantially completed, thereafter allowing the resultant mixture to settle into a lower layer of molten lead bullion of reduced copper content and an upper layer of matte containing cuprous sulphide and lead sulphide, passing said molten lead bullion of reduced copper content and the remaining part of molten raw lead bullion to a drossing vessel, cooling the mixed molten lead bullion in the drossing vessel to form a dross at the surface, removing said dross to yield a lead bullion of further reduced copper content, recycling said dross as feed material to said reaction vessel repeating said sequential steps whereby said molten bullion of reduced copper content produced thereby contains arsenic in solution, and initially adding to the molten bullion in the reaction vessel a further amount of a dross comparatively rich in copper arsenide and comparatively poor in a copper-antimony compound to hasten the build up of arsenic content of the molten bullion in the reaction vessel.

11. In a process for decopperizing raw lead bullion which contains copper and arsenic and wherein the total quantity of sulphur, arsenic and antimony is not sufficient to combine with all of the copper, the improvement comprising the steps of dividing said raw lead bullion into two parts, maintaining the first part of said raw lead bullion in a molten state in a reaction vessel, adding to the molten lead bullion in the reaction vessel a material containing compounded sulphur which can react with the copper in the lead bullion to yield cuprous sulphide, maintaining said material mixed with the molten lead bullion until the reaction with the copper is substantially completed, thereafter allowing the resultant mixture to settle into a lower layer of molten lead bullion of reduced copper content and an upper layer of matte containing cuprous sulphide and lead sulphide, passing said molten lead bullion of reduced copper content and the remaining part of molten raw lead bullion to a first drossing vessel, cooling the mixed molten lead bullion in the drossing vessel to form a dross at the surface, removing said dross to yield a lead bullion of further reduced copper content, recycling said dross as feed material to said reaction vessel so that said molten bullion of reduced copper content produced thereby contains arsenic in solution, transferring the bullion of further reduced copper content from the first drossing vessel to a second drossing vessel, cooling said bullion of further reduced copper content, mixing said cooled bullion of further reduced copper content with granular sulphur to form a sulphur dross and yield bullion of low copper content, and repeating said sequential steps.

12. In a process for decopperizing raw lead bullion which contains copper and arsenic and wherein the total quantity of sulphur, arsenic and antimony is not sufficient to combine with all of the copper, the improvement comprising the steps of dividing said raw lead bullion into two parts, maintaining the first part of said raw lead bullion in a molten state in a reaction vessel, adding to the molten lead bullion a lead concentrate containing lead sulphide and iron sulphide which can react with the copper in the lead bullion to yield cuprous sulphide, maintaining said lead concentrate mixed with the molten lead bullion until the reaction with the copper is substantially completed, thereafter allowing the resultant mixture to settle into a lower layer of molten lead bullion of reduced copper content and an upper layer of matte containing cuprous sulphide and lead sulphide, treating said matte, removing said matte from said reaction vessel, passing said molten lead bullion of reduced copper content and the remaining part of molten raw lead bullion to a drossing vessel, cooling the mixed molten lead bullion in the drossing vessel to form a dross at the surface, removing said dross to yield a lead bullion of further reduced copper content and recycling said dross as feed material to said reaction vessel so that said molten bullion of reduced copper content produced thereby contains arsenic in solution the reaction between the raw lead bullion and the lead concentrate in the reaction vessel and the treatment of the matte in the reaction vessel being carried out alternately, the molten lead bullion of reduced copper content being passed to the drossing vessel during a period when said reaction is carried out and said remaining part of molten raw lead bullion being added to the drossing vessel during another period when said treatment of the matte is being carried out.

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