

Treatment of lead slags

Introduction

The field of the present invention is the recovery of metals from Pb-bearing metallurgical slags.

In the extraction of metals from ores or from secondary materials containing Cu and Pb, a first step is often a smelting operation producing a Cu matte and a Pb-bearing slag. While a major part of the valuable metals reports to the Cu matte, an appreciable part of them also reports to the slag. Such a slag may contain 10% by weight or more of Pb, together with metals such as Cu, Fe, and Zn. Further treatment is required to recover these valuable metals, especially Cu and Zn.

To this end, the slag is typically subjected to reducing conditions in a blast furnace or in an electric arc furnace to produce a metallic alloy containing the valuable metals, and a cleaned slag.

The required reducing conditions are typically obtained by adding carbon, carbohydrates or hydrocarbon to the furnace, often in the form of cokes, or as a liquid or gaseous fuel. The redox reactions lead to the formation of CO, and ultimately to CO₂. It is particularly difficult to capture CO₂ from the furnace off-gas, as the technology is still under development for metallurgical processes. CO₂ therefore ends up in the atmosphere, which is undesirable in view of its recognized greenhouse effect. Such a process is for example described in Vanparys et al. (PbZn 2020: 9th International Symposium on Lead and Zinc Processing. The Minerals, Metals & Materials Series. Springer, Cham.).

A possible alternative to the addition of carbon-based materials is the use of sulfur (S) or sulfur compounds.

CN116024438A describes the introduction of sulfur-containing vulcanizing agents in the form of gypsum, pyrite, or nickel sulfide ore to a molten Ni-rich slag to obtain, among others, a low nickel matte.

Tian et al. (Synergistic recovery of copper, lead and zinc via sulfurization–reduction method from copper smelting slag; Transactions of Nonferrous Metals Society of China 33, 3847-3859, 2023) describes the recovery of Cu, Pb and Zn from copper smelting slag by use of pyrite and cokes to form slag, matte and gas phases. Cokes is used to reduce the high-valent Fe₃O₄ to a low-valent FeO oxide.

CN113046550 describes the reduction of metals in depleted electric furnace slag by using a mixture of pyrite, raw coal and nickel/copper concentrate. Only reducing agent is cokes.

CN113862489 describes a multi-stage process in a reduction furnace, which is divided into two sections: the pre-reduction section and the deep reduction section. A pre-reduction process of lead concentrates uses metal sulfides, such as zinc sulfide, iron sulfide and copper sulfide, or a mixture of metal sulfides and sulfur, to produce liquid metallic lead, high-concentration sulfur dioxide gas, and a lead-depleted slag. At the end of the pre-reduction stage, the liquid lead and the residual slag are

separated. The residual slag containing a small amount of unreduced lead enters the deep reduction stage, demonstrated by several examples using methane or water gas.

Yuan et al. (Powder Technology 230, 63–66, 2012) teaches the addition of sulfur to PbO. Intense co-grinding of the mixture at low temperature results in the partial conversion of Pb to PbS. The sulfides can be separated using flotation. The process may be applied to Pb-bearing wastes such as glasses, wherein Pb is present as an oxide.

Han et al. (Selective Sulfidation of Lead Smelter Slag with Sulfur; Metal Mater Trans B 47, 344–354, 2016) shows sulfidation roasting of slags containing 0.5 to 5 %Pb, some Zn and Fe. Sulfur is used instead of more conventional pyrite to avoid Fe as an impurity. Carbon is added to suppress the generation of SO₂. This results in the formation of CO and CO₂. The initial roasting temperature is limited to about 400 °C to remain below the boiling point of sulfur. A final roasting temperature of up to 1200 °C is applied, while the bulk of the material remains solid. The higher roasting temperatures benefit crystal growth, and result in a more efficient separation of ZnS by flotation in a subsequent process step.

Another possible alternative to the addition of carbon, carbohydrates or of hydrocarbon is based on the use of hydrogen (H₂).

US2022389538A1 describes the recovery of copper from secondary raw materials, where hydrogen is used as combustible to generate heat, not as chemical reductant.

Rukini et al. (Lead Recovery From PbO Using Hydrogen as a Reducing Agent; Metal Mater Trans B 54, 996-1016, 2023) describes the addition of hydrogen to pure PbO pellets at temperatures between 350 to 800 °C, resulting in the formation of metallic lead droplets on the surface of PbO. Only hydrogen was used as reducing agent.

WO2008014538A1 describes the injection of sulphidic material to reduce lead in the slag to metallic lead utilizing a top-submerged lance injection of under reducing conditions. The sulphidic material can be in the form of a concentrate, sulphidic drosses, pyrites, or as combination. The fuel used in the process may be entrained in a carrier gas if it is a solid, such as fine particulate coal, or may be a suitable hydrocarbon gas or liquid.

It appears that most known pyrometallurgical processes make use of carbon, carbohydrates or of hydrocarbon to obtain the reducing conditions leading to clean slags, depleted in heavy metals. This unavoidably also results in the formation of CO₂.

It is an objective of the present invention to offer an alternative scheme for the separation and recovery of metals, in particular Pb, Cu and Ni, from slags, by using a combination of sulfur and hydrogen instead of sources of carbon.

Substituting carbon with a source of sulfur and hydrogen results in the formation of SO_2 and H_2O , respectively, instead of CO_2 . Compared to CO_2 , H_2O is a harmless gas and can be emitted as such, and SO_2 is relatively easy to capture. SO_2 can be converted to SO_3 , and then to sulfuric acid using a standard industrial process. Sulfuric acid is a widely used reactant, for example for manufacturing fertilizers. SO_2 can also be converted to sulfur when the SO_2 concentration in the off-gas is sufficiently high. Environmentally friendly processes, for example using the $\text{CaS} - \text{SO}_2$ reaction (Environ. Sci. Technol. 2002, 36, 13, 3020–3024), have been developed. In this way, a direct effect of the present scheme is the decarbonization of the industrial recovery process.

The new process results in the formation of a so-called matte, i.e. a sulfidic phase formed by metal sulfides, in combination with a so-called alloy, i.e. a mixture of two or more elements, where at least one is a metal, and a Pb-bullion, i.e. also an alloy, but containing a majority of Pb in weight, thereby enabling a better separation of Cu, Pb and Fe in different phases, and excluding the use of traditional carbon-based reductions and the resulting formation of CO_2 .

A first aspect describes a process for the removal of Pb and Cu from a metallurgical slag, comprising the steps of:

- providing a smelting furnace;
- providing a metallurgical slag containing more than 10% by weight of Pb, and further containing Cu, and Fe;
- determining the molar amount of Pb, Cu, Fe, Ni and Zn in the slag;
- smelting the slag or providing the slag already in molten form, thereby obtaining a molten slag in the furnace;
- providing an amount of sulfur (S) and hydrogen (H_2), wherein the sum of (S) divided by the stoichiometric molar amount of Pb, Cu, Fe, Ni and Zn in the slag, and (H_2) divided by the stoichiometric molar amount of Pb, Cu and Ni in the slag, corresponds to a stoichiometric excess of at least 110% and at most 400%;
- feeding said amount of sulfur and H_2 to the molten slag, thereby obtaining a molten bath comprising a slag phase depleted in Pb and Cu, a matte phase, an alloy phase, a Pb-bullion, SO_2 -bearing off-gas, and flue dust; and,
- separating the slag phase, the matte phase, the alloy, and the Pb-bullion.

The metallurgical slags typically originate from industrial smelting and refining operations. The most prominent metal in such slags is Pb. Amounts of between 10 and 50% are common.

Amounts of more than 50% of Pb in such metallurgical slags are less common, as this would make the upstream processes less efficient. Amounts of less than 10% would make the slag viscosity too high and thus require additional fluxing agents.

In another aspect, the metallurgical slag contains 10 to 50% of Pb by weight or 10 to 40% or 20 to 40%.

The metallurgical slags according to the present invention typically originate from other industrial processes, in which the majority of the valuable copper has already been removed. Therefore, in another aspect, the metallurgical slag contains 1 to 15% of Cu by weight. Even dedicated processes for copper removal will typically leave some residual copper in the slag. Having at least 1% of Cu makes a dedicated step for isolating the copper economically worthwhile.

In addition to Pb, Cu and Fe, other metals, such as Ni, As, Bi, Sb, Sn and Zn can be present in the metallurgical slag. Therefore, in another aspect, the metallurgical slag further contains one or more of Ni, As, Bi, Sb, Sn and Zn. Their respective percentages by weight are typically much lower than the above-mentioned amounts for Pb. All except Ni, Fe and Zn are considered as minor impurities with minor or no effect on the present process. The metallurgical slag used at the start of the process can be referred to as “starting slag”.

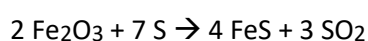
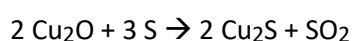
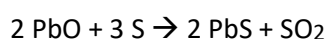
Fe will typically be present in an amount of at least 4% and at most 20% by weight in the starting slag. More common are amounts of 4 to 15%, or even 4 to 10%. Generally, Fe is seen as being uncritical and can report to the slag phase, typically in any of its oxide forms, or to the matte phase, typically as FeS. Amounts of more than 20% of iron are less preferred, as this would make the upstream recovery processes less efficient.

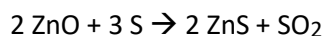
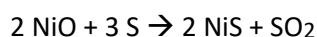
Ni can be present in an amount of at least 0.2% and at most 10% by weight in the starting slag.

Zn can be present in an amount of at least 2% and at most 15% by weight in the starting slag. More common are amounts of 2 to 10%, or even 2 to 7%. High amounts of Zn are less desired, as Zn not only forms sulfides, but can also fume from the slag and report to the flue dust where it can lead to unwanted downstream condensation.

Therefore, in another aspect, the metallurgical slag further contains one or more of Ni and Zn.

Key of the process is the reaction of metals, in particular Pb, in the starting slag with sulfur, thereby forming sulfides. For some selected metals the associated stoichiometric sulfidation reactions are:





It has been found that the stoichiometric amount of sulfur (X_S) according to the present invention is calculated using the following equation:

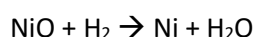
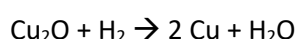
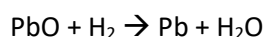
$$(X_S) = 1.5*(\text{Pb}) + 0.75*(\text{Cu}) + 1.5*(\text{Ni}) + 0.75*(\text{Zn}) + 0.875*(\text{Fe})$$

Wherein (Pb), (Cu), (Ni), (Zn) and (Fe) represent the molar amounts of Pb, Cu, Ni, Zn and Fe present in the starting slag, respectively.

Pb, Cu, Ni, Zn and Fe are known to react with sulfur to form sulfides, which typically report to a matte phase. Fe and Zn, if present in significant amounts, should be taken into account when estimating the amount of sulfur to be added to the starting slag. Typically, under the chosen conditions, there is no full conversion and the metals partially stay present in the slag in their oxidic phase. It has been observed that an addition of sulfur corresponding to about 50% of the stoichiometric amount for these two metals is sufficient in the present process.

While As, Bi, Sb and/or Sn can also react with sulfur, they are considered as minor impurities in the present type of slag with very limited or no impact on the overall stoichiometric amount for the process.

Hydrogen typically reduces the metal oxides from the starting slag to metallic phases such as an alloy phase or a Pb-bullion phase. For some selected metals the associated stoichiometric reduction reactions are:



It has been found that the stoichiometric amount of hydrogen (X_{H_2}) according to the present invention can be calculated using the following equation: $(X_{H_2}) = (\text{Pb}) + 0.5*(\text{Cu}) + (\text{Ni})$

Wherein (Pb), (Cu) and (Ni) represents the molar amount of Pb, Cu and Ni present in the starting slag, respectively.

The oxides of Pb, Cu and Ni are known to react with hydrogen to form metals, that typically report to an alloy or Pb-bullion phase.

The reaction of Fe (typically in the slag in oxidic form) with hydrogen is low, with very limited or no impact on the overall stoichiometric amount for the process.

Key of the process is the reaction of metal oxides in the starting slag with both sulfur and hydrogen, thereby forming metal sulfides and metals, respectively, allowing for an improved separation of the different metals in different distinct phases. Typically, under the chosen conditions, the Cu preferentially goes to the matte phase as Cu_2S , whereas Pb favors the alloy or the Pb-bullion phase as metallic Pb.

In another aspect the amount of sulfur (S) and hydrogen (H_2) is calculated according to the equations:

$$(S) = A \cdot (X_S), \text{ with } 0.05 < A < 1.0;$$

$$(\text{H}_2) = B \cdot (X_{\text{H}_2}), \text{ with } 0.2 < B < 3.5; \text{ and,}$$

$$1.1 < (A + B) < 4; \text{ and,}$$

wherein (X_S) and (X_{H_2}) are the stoichiometric molar amounts of sulfur and hydrogen according to:

$$(X_S) = 1.5 \cdot (\text{Pb}) + 0.75 \cdot (\text{Cu}) + 1.5 \cdot (\text{Ni}) + 0.75 \cdot (\text{Zn}) + 0.875 \cdot (\text{Fe}) ;$$

$$(X_{\text{H}_2}) = (\text{Pb}) + 0.5 \cdot (\text{Cu}) + (\text{Ni}) ; \text{ and,}$$

wherein (Pb), (Cu), (Ni), (Zn) and (Fe) are the molar amounts of metals Pb, Cu, Ni, Fe and Zn in the slag.

In addition to the above-mentioned metals, metallurgical slags also contain slag formers. Typical slag formers are silica (SiO_2), alumina (Al_2O_3), calcium oxide (CaO) or magnesium oxide (MgO). In the metallurgical slags of the present invention, such slag formers can typically be found in the following ranges:

10 to 50 % by weight of silica;

0 to 20% by weight of alumina;

5 to 60 % by weight of calcium oxide; and,

0 to 10 % by weight of magnesium oxide.

Metallurgical slags according to the present invention may contain a combination of slag formers adding up to 25 to 60% by weight, preferably 25 to 40%. A slag containing 25 to 40% of slag formers allows for a proper reaction with sulfur or hydrogen, and for an easy phase separation between slag, alloy, Pb-bullion and matte phase. Lowering the amount of slag formers to less than 25%, would result in overly concentrated metals, while increasing the amount of slag formers to more than 60%, or even to more than 70%, would result in a diluted overall composition, rendering the recovery of the metals uneconomical.

Metallurgical slags generally contain a rather complex mixture of slag formers and metals, typically in form of oxides. Moreover, other impurities can be present, such as P_2O_5 , Na_2O or BaO , largely depending on differences in the feed materials that have been used to produce the slag, and/or the applied process conditions.

In another aspect, other Pb, Cu and/or Ni-containing materials could be added to the furnace together with the metallurgical slag according to the first aspect. Their respective amounts then have to be similarly taken into account when determining the amount of sulfur and hydrogen for the process.

By sulfur is meant elemental sulfur and sulfur combined with any chemical element other than sulfur itself. The former includes octasulfur (S_8), which is a major industrial form of elemental sulfur. The latter includes metal sulfides, such as iron sulfide, zinc sulfide, copper sulfide, nickel sulfide, lead sulfide, pyrite, and chalcopyrite.

The amounts of the different metals in the Pb-bearing slag are determined upfront by known analytical methods. Based on this, the stoichiometric amount of sulfur and hydrogen can readily be derived from the above sulfidation and reduction reactions, respectively.

The kinetics of the sulfur reacting with metal oxides in the molten starting slag are limited. The kinetics depend, among others, on temperature and the intimacy of the mixing between the introduced sulfur and the metal oxides in the molten slag. Some sulfur may leave the molten slag unreacted, forming SO_2 with any air present above the molten bath or further downstream in the gas cleaning circuit.

The kinetics of hydrogen reacting with metal oxides in the molten starting slag are limited. The high buoyancy of hydrogen gas in a molten slag bath will leave some hydrogen unreacted due to short reaction time, or insufficient mixing between gas and molten slag.

The sum of A + B should represent a stoichiometric excess, such as 110% or more, 120% or more, 130% or more, or 140% or more. "A" or "B" refers to the above mentioned formulae for determining the amounts of sulfur and hydrogen.

It is preferred to limit the sum of A + B to at most 400%, preferably to at most 380%, more preferably to at most 360%, and most preferably to at most 340%. In industrial practice, limiting the excess of sulfur and hydrogen fed to the slag is advised due to the cost of the sulfur and hydrogen itself and also to avoid larger off-gas streams.

The present examples have been on lab-scale only, not under industrial conditions. Optimization of preferred industrial conditions is ongoing to save sulfur and/or hydrogen, and consequently also lower costs.

A preferred range for the sum of A and B is therefore 120 to 200%.

In another aspect, A is between 5% and 100%, preferably between 10% and 90%, more preferably between 10% and 80%.

In another aspect, B is between 20% and 350%, preferably between 40% and 300%, more preferably between 50% and 300%.

Separating the alloy and matte phase from the slag phase is typically achieved by selective tapping, when both phases are still liquid. The separation of Pb-bullion from the alloy can be done consecutively at a reduced temperature when the Pb-bullion is still liquid, but the alloy has solidified already. This stepwise solidification happens around 800 °C.

In another aspect, the furnace is an electric furnace. With electricity as a heat source, the need for carbon-based fuel is alleviated or eliminated. Assuming access to green electricity, the carbon footprint can thus remain remarkably low.

In another aspect, the furnace is a bath-smelting furnace or horizontal converter. A bath-smelting furnace can be a top submerged lance (TSL) furnace. These types of furnaces are particularly suitable for the injection of sulfur and hydrogen, optionally using a carrier gas.

In another aspect, no carbon-based fuel or carbon-based reducing agent is added to the furnace. It is preferred to avoid the addition of carbon-based fuel or carbon-based reducing agent to the furnace. This would result in the formation of CO₂, which is undesired when aiming at the decarbonization of the industrial recovery process. Moreover, CO₂ is not only more difficult to capture than SO₂, it would also make the recovery and re-use of SO₂ more difficult due to diluting the latter. Avoiding carbon-based fuel or carbon-based reducing agents has thus the clear advantage to reduce to overall carbon footprint of the process, especially in an industrial setup.

Fuel refers to any material that is burned to provide the necessary heat for high-temperature process, rather than taking part in the reactions of the process itself.

Generally, the partial pressure of oxygen, pO₂, in a pyrometallurgical system affects the oxidation state and thermodynamic stability of the metal, slag and gas phases. In this process, the pO₂ is preferably in the range of 10⁻¹⁴ to 10⁻⁸, more preferably in the range of 10⁻¹² to 10⁻⁹.

It is preferred to avoid the injection of large amounts of oxygen-bearing gasses, such as air, into the molten bath as this will result in sulfur and hydrogen reacting directly with oxygen instead of with the metal oxides in the slag. Moreover, this will produce larger amounts of off-gas to deal with.

An excess of sulfur or hydrogen, not needed for the reaction with metals (metal oxides) in the slag, can serve as a heat source in the process.

Non-reactive gasses such as nitrogen can be injected into the slag. Their effect is that more volatile species, such as PbS and ZnS, can report to the flue dust instead of to the matte or alloy phase. This effect can be desired or undesired according to the downstream refining processes available to recover these elements from the flue dust. To accumulate more Pb in the flue dust, a gas stream, for example of nitrogen gas, of 0.1 to 5 Nm³ per kg of Pb is applied.

Therefore, in another aspect, a non-reactive gas is injected into the molten bath during or after the step of feeding sulfur and hydrogen to the molten slag. Thereby, the amount of Pb in the flue dust is increased. Depending on the flow rate, even a majority of Pb can be accumulated in the flue dust.

Any amount of Pb reporting to the flue dust decreases the amount of Pb which can report to the matte, alloy or Pb-bullion phase.

Low operational temperatures around the melting point of a slag are preferred to limit refractory degradation in a furnace as much as possible. Preferably, operational temperatures are selected to avoid overheating of the slag too far above its melting point. Typically, the operation temperature of the furnace is from 1150 to 1450°C, preferably from 1180 to 1230 °C.

In another aspect, the amount of sulfur (S) is provided as elemental sulfur in liquid form. An advantage of using liquid sulfur is the established technology for its manipulation and transport in an industrial environment. The liquid sulfur can be injected directly into the molten slag, having a positive impact on the process kinetics.

In another aspect, the sulfur is fed by injection through one or more lances or tuyeres.

A lance is understood to be a tubular entity dipped from above into the molten bath. A tuyere is understood to be a tubular entity piercing the wall or bottom of the furnace, below or above the level of the molten bath, and equipped with means for the injection of gasses, liquids or solids into the molten bath. This includes also porous plugs or similar constructions.

A disadvantage of adding solid sulfur, as elemental sulfur or sulfur compounds, e.g. in form of granules, is the generation of sulfur dust upon manipulation. Sulfur dust shows a potential explosion hazard. Moreover, it will lead to operational difficulties, like clogging of the transportation system.

A possible solution for these problems is the use of solid pellets or briquettes comprising sulfur. This has the advantage that the pelletized sulfur can be top-fed into the furnace, for example through an overhead belt conveyor, optionally along with other feed materials or fluxes while avoiding the above-mentioned dust generation.

Therefore, in another aspect, the sulfur fed to the molten slag is in the form of solid pellets or briquettes comprising sulfur.

In a preferred embodiment, sulfur is mixed with solid metallurgical slag of the same or similar composition as in the first aspect, then pressed. Pressing increases the relative density of the pellets and improves the mixing of sulfur and metals in the molten bath of the furnace. This enhances the overall reactivity of the sulfur with those metals, making the process more efficient.

Therefore, in another aspect, the solid pellets comprising sulfur further comprise solid slag.

In another aspect, the solid slag used for making pellets has the same composition as the metallurgical slag according to the first aspect.

Variations in the sulfur to slag ratio in this mixture have been tested, namely 4:1, 3:1, 2:1, 1:1, and 1:2. A ratio of 2:1 is preferred.

In another aspect, the sulfur to slag ratio in said pellets is from 4:1 to 1:2, preferably from 3:1 to 1:1, more preferably from 2.5:1 to 1.5:1.

In another aspect, hydrogen in gaseous form is fed to the molten bath by submerged injection through one or more lances or tuyeres.

Using gases, for example hydrogen or increasing amounts of carrier gasses, rather than solids or liquids in the process, may lead to an increasing amount of flue dust.

Another aspect describes a process, wherein in the step of feeding the amount of sulfur and H₂ is added simultaneously. This triggers the direct formation of the desired liquid phases matte, alloy and Pb-bullion.

In another aspect, hydrogen is added first, followed by sulfur.

In another aspect, sulfur is added first, followed by hydrogen.

The order of addition of hydrogen and sulfur is of minor importance on the output phases, as long as no material is removed irreversibly from the molten bath, e.g. by transferring (significant) amounts of Pb or Zn (as PbS or ZnS) to the flue dust, or by removing (fully or partially) one or more of the output phases, e.g. by tapping.

In the context of the present invention, a simultaneous addition of sulfur and hydrogen is preferred.

In the setup with addition of sulfur first, more Pb and/or Zn can potentially leave the molten bath in

form of their volatile sulfides, especially when working with relatively high amounts of sulfur. This will typically not happen in the setup with addition of hydrogen first, which is therefore also preferred. All liquid phases should preferably be kept together until they have been allowed to react with both sulfur and hydrogen.

Pb remaining in the slag after addition of sulfur and hydrogen may result from insufficient addition of sulfur and hydrogen, ineffective reaction behavior between Pb in the molten slag and sulfur and hydrogen, unfavorable reaction kinetics and/or insufficient decantation in the step of separating the slag from any of the other obtained phases. The latter would result in Pb-containing matte or alloy droplets in the final/depleted slag and thus an overall higher than expected Pb-content in the slag, despite successful conversion to PbS or Pb.

In another aspect, the slag phase depleted in Pb and Cu contains less than 6% of Pb by weight, preferably less than 3%.

It is technically possible to clean the slag further and reach much lower limits of Pb in the slag. However, this requires additional refining operations, which is currently not economical.

In another aspect, the slag phase depleted in Pb- and Cu contains less than 0.5% of Cu by weight. Such a low value of copper indicates an almost quantitative transfer of this valuable metal to one of the other liquid phases, such as the matte phase, from which it can be easier refined and recovered.

In another aspect, the present process is further comprising a step of converting the SO₂ from the SO₂-bearing off-gas to H₂SO₄. Modern industrial plants are often equipped with a conversion unit for the production of sulfuric acid. The H₂SO₄ can for example be valorized or used in acidic leaching operations.

In another aspect, the present process further comprises a step of recovering metals from the matte phase, the alloy and/or the Pb-bullion. The formation of three liquid phases is highly beneficial, as a means to concentrate Pb in the Pb-bullion, Cu in the matte phase and Ni in the alloy.

Target metals are thus selectively sent to a matte phase, an alloy, a Pb-bullion, or kept in a slag phase, this way allowing more efficient refining.

Downstream refining processes of matte phase, alloy and Pb-bullion are known and can be combined with the present scheme.

One possibility for refining a matte phase is to subject it to an oxidative process, such as a converting process. Another, specifically for low grade mattes, is to subject it to copper smelting. These processes produce a high grade matte or a metallic phase, which then can be processed in the traditional way, and SO_2 , which can be captured and/or processed as explained above.

Other refining schemes are possible, e.g. using leaching or flotation. Also SO_2 originating from a further refining of the obtained PbS and Cu_2S -containing matte phase can be recovered and converted to H_2SO_4 .

Downstream refining for a Pb-bullion are traditional lead refining processes, which involves the sequential removal and/or valorization of impurity elements. These can be a combination of pyro- and hydrometallurgical processes. The refining of the Pb-bullion is simplified when having a high percentage of Pb in the Pb-bullion, which illustrates the advantage of prior removal of Ni through formation of an alloy phase, and removal of Cu through formation of a matte phase, in the upstream smelting process.

Downstream refining of the alloy phase can be done via hydro- and/or pyrometallurgical refining steps.

Also the flue dust can be processed via hydrometallurgical processing units or recirculated back as feed, this way recovering metals which escaped from the molten bath or during feeding.

Further definitions of some terms in the context of non-ferrous pyrometallurgy:

Slag: Slag is a byproduct formed during the smelting process. It typically comprises a mixture of metal oxides and silicon dioxide, but it can also contain metal sulfides and elemental metals. Slag is typically less dense than the metal being extracted, allowing it to be separated and removed from the molten metal, for example by tapping.

Matte: Matte is a molten mixture of metal sulfides produced during the smelting. It is typically an intermediate product in the extraction of metals, for example copper. Matte contains the desired metal (or metals) in a sulfide form, which is later converted to a purer form through further processing.

Alloy: An alloy is a mixture of two or more elements, where at least one is a metal. In pyrometallurgy, alloys are often formed during the smelting process when different metals are combined.

Bullion: Bullion refers to precious metals in bulk form, typically gold or silver, that are cast into bars or ingots. In pyrometallurgy, a bullion is the product obtained after refining processes that remove impurities from the metal. A Pb-bullion is specific case of a bullion.

By “major part” of an element is meant at least 50% by weight of the quantity of that element entering the process, preferably 80%.

The following examples illustrate the invention.

Examples

When “(X_S)”, “(X_{H_2})”, “A” or “B” are mentioned in the examples, this refers to the above mentioned formulae for determining the amounts of sulfur and hydrogen.

Example 1

2000 g of starting slag with composition given in Table 1 was provided. The stoichiometric molar amount (X_S) and (X_{H_2}) of this starting slag are 9.6 mol S (308 g sulfur) and 3.8 mol H_2 (7.6 g hydrogen), respectively. 1.9 mol S ($A = 0.2$) and 7 mol H_2 ($B = 1.84$) was added to the starting slag, adding up to a total of 2.04 for the sum of $A + B$. Pellets containing both starting slag and elemental sulfur were prepared. The ratio sulfur to slag in this mixture was 2 to 1. To this end, 30 g of the starting slag was milled and sieved to an average particle size of below 2 mm. The starting slag was mixed with the elemental sulfur to prepare the briquetting mixture. From this mixture pellets were pressed.

A 1.5 l alumina crucible with 1970 g of starting slag was placed in an induction furnace and heated under nitrogen atmosphere at 650 °C/h to a temperature of 1250 °C. Then, the sulfur pellets were added. H_2 was blown at 60 l/h flow rate into the slag. Samples were taken periodically to monitor the content of Pb % in the slag. At the end of the process, 1191 g of final slag, 108 g of matte, 88 g of alloy and 265 g of Pb-bullion were present. Periodic samples were taken to monitor the evolution of the slag composition. This is necessary to determine the end point of the process. 6 intermediate samples were taken during the experiment, accounting for a total of 150.9 g of samples. For a lab-scale process, working with only 2000 g of starting slag, the sample amount accounts for significant metal losses. These losses will not be present at industrial scale. In this example flue dust is not captured. The flue dust will contain mostly Pb, Zn and S. The composition of the phases is given in Table 1. Only selected metals are listed in Table 1. The alloy typically further contains As, Sb and Sn in differing amounts. All other metals are considered minor impurities with minor or no effect on the present process. The composition of the slag typically does not sum to 100% because the metals are present in their oxidized forms, and the oxygen content is not included in the calculation.

Table 1: Mass and composition of slags, matte, alloy and Pb-bullion

	Mass	Pb	Cu	Ni	Fe	Zn	Al ₂ O ₃	CaO	SiO ₂	S
	g	%	%	%	%	%	%	%	%	%
Starting slag	2000	27.6	4	1.5	9.5	4.1	5.1	7.5	18.2	0.24
Final slag	1191	2.6	0.08	0.1	20.5	5.8	7.3	13.3	27	0.07
Matte	108	26.3	51.3	0.6	0.4	-	-	-	-	20.3
Alloy	88	17.1	30.9	19.2	0.03	0.03	-	-	-	3.2
Pb-bullion	265	90.5	5.4	-	-	0.03	-	-	-	-

Conclusion: The example shows that after addition of 1.9 mol S and 7 mol H₂, the Pb content of the final slag was 2.6%. Next to slag and matte, also an alloy and a Pb-bullion was formed due to the presence of H₂ as reductant. 5.6% of the Pb present in the starting slag remained in the slag phase, 5.1% was transferred to the matte phase, 2.7% was transferred to the alloy phase and 43.5% was transferred to the Pb-bullion phase. 69% of the Cu present in the starting slag was transferred to the matte, and 56% of Ni present in the starting slag was transferred to the alloy. The remainder of Pb, Cu and Ni can be found in the periodic samples and in the flue dust.

Example 2

2000 g of starting slag with composition given in Table 2 was provided. The stoichiometric molar amount (X_S) and (X_{H_2}) of this starting slag are 9.6 mol S (308 g sulfur) and 3.6 mol H₂ (7.2 g hydrogen), respectively. 7.5 mol S ($A = 0.78$) and 9.5 mol H₂ ($B = 2.62$) was added to the starting slag, adding up to a total of 3.4 for the sum of $A + B$.

Pellets containing both starting slag and elemental sulfur were prepared. The ratio sulfur to slag in this mixture was 2 to 1. To this end, 120 g of the starting slag was milled and sieved to an average particle size of below 2 mm. The starting slag was mixed with the elemental sulfur to prepare the briquetting mixture. From this mixture pellets were pressed.

A 1.5 l alumina crucible with 1880 g of starting slag was placed in an induction furnace and heated under nitrogen atmosphere at 650 °C/h to a temperature of 1250 °C. Then, the sulfur pellets were added. H₂ was blown at 60 l/h flow rate into the slag. Samples were taken periodically to monitor the content of Pb % in the slag. At the end of the process, 1077 g of final slag, 60 g of matte, 81 g of alloy and 425 g of Pb-bullion were present. Periodic samples were taken to monitor the evolution of the slag composition. This is necessary to determine the end point of the process. 7 intermediate samples were taken during the experiment, accounting for a total of 152.8 g of samples. For a lab-scale process, working with only 2000 g of starting slag, the sample amount accounts for significant metal losses. These losses will not be present at industrial scale. In this example flue dust is not captured. The flue

dust will contain mostly Pb, Zn and S. The composition of the phases is given in Table 2. Only selected metals are listed in Table 2. The alloy typically further contains As, Sb and Sn in differing amounts. The composition of the slag typically does not sum to 100% because the metals are present in their oxidized forms, and the oxygen content is not included in the calculation. All other metals are considered as minor impurities with minor or no effect on the present process.

Table 2: Mass and composition of slags, matte, alloy and Pb-bullion

	Mass	Pb	Cu	Ni	Fe	Zn	Al ₂ O ₃	CaO	SiO ₂	S
	g	%	%	%	%	%	%	%	%	%
Starting slag	2000	27.3	3	1.5	10.32	4.2	5.6	7.8	20	0.29
Final slag	1077	1.9	0.27	0.1	20.26	6.6	7.5	12.4	26.4	0.22
Matte	60	18.7	49	0.8	5.5	1.7	-	-	-	15.4
Alloy	81	19.1	33	13.1	2.3	0.42	-	-	-	4.8
Pb-bullion	425	87.8	6.3	-	-	0.03	-	-	-	-

Conclusion: The example shows that after addition of 7.5 mol S and 9.5 mol H₂, the Pb content of the final slag was 1.9%. Next to slag and matte, also alloy and Pb-bullion was formed due to the presence of H₂ as reductant. 3.7% of the Pb present in the starting slag remained in the slag phase, 2% was transferred to the matte phase, 2.8% was transferred to the alloy phase, 68% was transferred to the Pb-bullion phase. 35% Ni present in the starting slag was transferred to the alloy, with only 3.6% found in the final slag and 1.6% in the matte. Cu present in the starting slag was transferred to the matte, alloy and Pb-bullion in almost equal amounts. The increased H₂ addition likely causes a shift of Cu in favor of the alloy and Pb-bullion phase. The remainder of Pb, Cu and Ni can be found in the periodic samples and in the flue dust.

Example 3

2000 g of starting slag with composition given in Table 3 was provided. The stoichiometric molar amount (X_S) and (X_{H_2}) of this starting slag are 9.6 mol S (308 g sulfur) and 4.3 mol H₂ (8.6 g hydrogen), respectively. 3.7 mol S ($A = 0.39$) is added to the starting slag as pyrite, and 9.5 mol H₂ ($B = 2.21$), adding up to a total of 2.6 for the sum of $A + B$.

Pellets containing both starting slag and pyrite were prepared. The ratio pyrite to slag in this mixture was 2 to 1. To this end, 120 g of the starting slag was milled and sieved to an average particle size of below 2 mm. The starting slag was mixed with the pyrite to prepare the briquetting mixture. From this mixture pellets were pressed. A 1.5 l alumina crucible with 1880 g of starting slag was placed in an

induction furnace and heated under nitrogen atmosphere at 650 °C/h to a temperature of 1250 °C. Then, the pyrite pellets were added. H₂ was blown at 60 l/h flow rate into the slag. Samples were taken periodically to monitor the content of Pb % in the slag.

Table 3: Mass and composition of slags

	Mass	Pb	Cu	Ni	Fe	Zn	Al ₂ O ₃	CaO	SiO ₂	S
	g	%	%	%	%	%	%	%	%	%
Starting slag	2000	29.3	5.6	1.6	7.7	3.6	4.6	7.3	15.6	1.1
Final slag	634	2.1	0.7	0.1	22.6	4.3	7.21	14.1	24.7	0.2

Conclusion: It could be demonstrated that the following metals were significantly reduced in the slag. Namely, Pb from 29.3% to 2.1%, Cu from 5.6% to 0.7%, Ni from 1.6% to 0.1%. Equally, a matte phase, an alloy and a Pb-bullion were formed, but not analyzed in more detail. This demonstrates that pyrite could potentially replace elemental sulfur in an industrial setup. More experimental work is ongoing to define preferred conditions for such a process on industrial scale.

Example 4 (Comparative Example)

2000 g of starting slag with composition given in Table 4 was provided. The stoichiometric molar amount (X_s) of this starting slag is 9.6 mol S (308 g sulfur). 24.4 mol S ($A = 2.55$) is added to the starting slag.

Pellets containing both starting slag and elemental sulfur were prepared. The ratio of sulfur to slag in this mixture was 2 to 1. To this end, 390 g of the starting slag was milled and sieved to below 2 mm. The starting slag was mixed with the elemental sulfur to prepare the briquetting mixture. From this mixture pellets were pressed.

A 1.5 l alumina crucible with 1610 g of starting slag was placed in an induction furnace and heated under Argon atmosphere at 650 °C/h to a temperature of 1250 °C. Then, the sulfur-slag pellets were added in the course of 3 hours in regular intervals. Samples were taken periodically to monitor the Pb % in the slag. At the end of the process, 1000 g of final slag and 519 g of matte were present. The composition of both phases is given in Table 4. Periodic samples were taken to monitor the evolution of the slag composition. This is necessary to determine the end point of the process. 10 intermediate samples were taken during the experiment, accounting for a total of 251.2 g of samples. For a lab-scale process, working with only 2000 g of starting slag, the sample amount accounts for significant metal losses. These losses will not be present at industrial scale. In this example flue dust is not captured. The flue dust will contain mostly Pb, Zn and S.

Only selected metals are listed in Table 4. All other metals are considered as minor impurities with minor or no effect on the present process. The composition of the slag typically does not sum to 100% because the metals are present in their oxidized forms, and the oxygen content is not included in the calculation.

Table 4: Mass and composition of slags and matte

	Mass	Pb	Cu	Ni	Fe	Zn	Al ₂ O ₃	CaO	SiO ₂	S
	g	%	%	%	%	%	%	%	%	%
Starting slag	2000	27.4	2.8	1.5	10.2	4.2	5.7	8	20.2	0.45
Final slag	1000	5.6	0.7	0.4	16.8	6.2	11.9	19.4	31.6	1.5
Matte	519	50.9	10.5	5.2	6.4	2.8	-	-	-	18.8

Conclusion: The example shows that after addition of 24.4 mol S, the Pb content of the final slag was 5.6%. Next to slag, only matte was formed using S as sole reductant. 10% of the Pb present in the starting slag remained in the slag phase and 48.2% was transferred to the matte phase. The remainder of the Pb can be found in the periodic samples, with a composition ranging from 27.4 to 5.6 wt.% Pb, and in the flue dust. 97% of the Cu present in the starting slag was transferred to the matte phase. 90% of the Ni present in the starting slag was transferred to the matte phase. The remainder of Pb, Cu and Ni can be found in the periodic samples and in the flue dust.

Example 5 (comparative example)

2000 g of starting slag with composition given in Table 5 was provided. The stoichiometric molar amount (X_{H_2}) of this starting slag is 3.7 mol H₂ (7.4 g hydrogen). 11 mol H₂ ($B = 2.99$) is added to the starting slag.

A 1.5 l alumina crucible with 2000 g of starting slag was placed in an induction furnace and heated under nitrogen atmosphere at 650 °C/h to a temperature of 1250 °C. Then, H₂ was blown at 60 l/h flow rate into the slag. Samples were taken periodically to monitor the content of Pb % in the slag. At the end of the process, 1216 g of final slag, 101 g of alloy and 285 g of Pb-bullion were present. Periodic samples were taken to monitor the evolution of the slag composition. This is necessary to determine the end point of the process. 7 intermediate samples were taken during the experiment, accounting for a total of 159.2 g of samples. For a lab-scale process, working with only 2000 g of starting slag, the sample amount accounts for significant metal losses. These losses will not be present at industrial scale. In this example flue dust is not captured. The flue dust will contain mostly Pb, Zn and S. The composition of the phases is given in Table 5. Only selected metals are listed in Table 5. The alloy

typically further contains As, Sb and Sn in differing amounts. All other metals are considered as minor impurities with minor or no effect on the present process. The composition of the slag typically does not sum to 100% because the metals are present in their oxidized forms, and the oxygen content is not included in the calculation.

Table 5: Mass and composition of slags, alloy and Pb-bullion

	Mass	Pb	Cu	Ni	Fe	Zn	Al ₂ O ₃	CaO	SiO ₂	S
	g	%	%	%	%	%	%	%	%	%
Starting slag	2000	27.1	3.5	1.5	10.6	4.2	5.2	7.7	19.1	0.39
Final slag	1216	2.3	0.38	0.05	20.8	5.3	7.6	12.4	26.9	0.18
Alloy	101	22.8	35.3	15.8	1.2	0.17	-	-	-	2.4
Pb-bullion	285	88.9	6.4	-	-	0.025	-	-	-	-

Conclusion: The example shows that after addition of 11 mol H₂, the Pb content of the final slag was 2.3%. Next to slag, only alloy and Pb-bullion was formed using H₂ as sole reductant. Pb is transferred to the alloy and Pb-bullion phase. 5.2% of the Pb present in the starting slag remained in the slag phase, 4.2% was transferred to the alloy phase, 47% was transferred to the Pb-bullion phase. 51% of the Cu present in the starting slag is transferred to the alloy phase. 54% of the Ni present in the starting slag is transferred to the alloy phase. The remainder of Pb, Cu and Ni can be found in the periodic samples and in the flue dust.

Claims

1. Process for the removal of Pb and Cu from a metallurgical slag, comprising the steps of:

- providing a smelting furnace;
- providing a metallurgical slag containing more than 10% by weight of Pb, and further containing Cu and Fe;
- determining the molar amount of Pb, Cu, Fe, Ni and Zn in the slag;
- smelting the slag or providing the slag already in molten form, thereby obtaining a molten slag in the furnace;
- providing an amount of sulfur (S) and hydrogen (H₂), wherein the sum of (S) divided by the stoichiometric molar amount of Pb, Cu, Fe, Ni and Zn in the slag, and (H₂) divided by the stoichiometric molar amount of Pb, Cu and Ni in the slag, corresponds to a stoichiometric excess of at least 110% and at most 400%;
- feeding said amount of sulfur and H₂ to the molten slag, thereby obtaining a molten bath comprising a slag phase depleted in Pb and Cu, a matte phase, an alloy phase, a Pb-bullion, SO₂-bearing off-gas, and flue dust; and,
- separating the slag phase, the matte phase, the alloy, and the Pb-bullion.

2. Process according to claim 1, wherein the amount of sulfur (S) and hydrogen (H₂) is calculated according to the equations:

$$(S) = A \cdot (X_S), \text{ with } 0.05 < A < 1.0;$$

$$(H_2) = B \cdot (X_{H_2}), \text{ with } 0.2 < B < 3.5; \text{ and,}$$

$$1.1 < (A + B) < 4; \text{ and,}$$

wherein (X_S) and (X_{H₂}) are the stoichiometric molar amounts of sulfur and hydrogen according to:

$$(X_S) = 1.5 \cdot (Pb) + 0.75 \cdot (Cu) + 1.5 \cdot (Ni) + 0.75 \cdot (Zn) + 0.875 \cdot (Fe) ;$$

$$(X_{H_2}) = (Pb) + 0.5 \cdot (Cu) + (Ni) ; \text{ and,}$$

wherein (Pb), (Cu), (Ni), (Zn) and (Fe) are the molar amounts of metals Pb, Cu, Ni, Fe and Zn in the slag.

3. Process according to claim 1 or 2, wherein the furnace is an electric furnace.

4. Process according to any one of claims 1 to 3, wherein no carbon-based fuel or carbon-based reducing agent is added to the furnace.

5. Process according to any one of claims 1 to 4, wherein the sulfur fed to the molten slag is in the form of solid pellets comprising sulfur.
6. Process according to claim 5, wherein the solid pellets comprising sulfur further comprise solid slag.
7. Process according to claim 6, wherein the solid slag has the same composition as the metallurgical slag according to claim 1.
8. Process according to claims 6 or 7, wherein the ratio of sulfur to solid slag is from 4:1 to 1:2.
9. Process according to any one of claims 1 to 8, wherein the slag phase depleted in Pb and Cu contains less than 6% of Pb by weight, preferably less than 3%.
10. Process according to any one of claims 1 to 9, wherein the slag phase depleted in Pb and Cu contains less than 0.5% of Cu by weight.
11. Process according to any one of claims 1 to 10, wherein in the step of feeding the amount of sulfur and H₂ is added simultaneously.
12. Process according to any one of claims 1 to 4, wherein the sulfur is fed by injection through one or more lances or tuyeres.
13. Process according any one of claims 1 to 12, wherein hydrogen in gaseous form is fed to the molten bath by submerged injection through one or more lances or tuyeres.
14. Process according to any one of claims 1 to 13, further comprising a step of converting SO₂ from the SO₂-bearing off-gas to H₂SO₄.
15. Process according any one of claims 1 to 14, further comprising a step of recovering metals from the matte phase, the alloy and/or the Pb-bullion.