Challenges and Opportunities of a Lead Smelting Process for Complex Feed Mixture

Christoph Zschiesche, Mehmet Ayhan and Jürgen Antrekowitsch

Abstract Managing complex material streams within a lead smelting/reduction process has a long history at Aurubis. After modernization of the secondary lead smelter in 1991, Aurubis operates an electric furnace and a Peirce Smith converter to process complex secondary materials. This process links the copper and the lead metallurgy allowing Aurubis to properly combine primary and secondary process lines to optimize the processing of complex raw materials and smelter intermediates. However, combination of copper and lead metallurgy processing requires a continuous evaluation as raw material quality and composition varies. This paper describes Aurubis lead smelter processing and provides some fundamental considerations to optimize the lead processing, in particular with aspects related to speiss formation.

Keywords Lead smelting · Complex feed mixture · Recovery of valuable metals · Lead · Copper · Sulfur

Introduction

Aurubis operations have been associated with the processing of primary and secondary materials for a long time. With the modernization of the copper smelter in 1972 by the adoption of the flash smelting technology, new challenges appeared, mostly related to impurity management. Then, with the acquisition of Hüttenwerke Kayser, in 1999, AG Aurubis extended his portfolio with a flowsheet for processing of secondary copper-lead-tin bearing materials (scrap, shredder material, residues, sludges, e-scrap). Following this step, primary copper business was further strengthen with the acquisition of Cumerio. Both acquisitions enabled Aurubis to become the world largest copper recycler and leading integrated copper producer.

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In addition to the primary and secondary copper assets, the ability to combine copper and lead metallurgy via a dedicated secondary lead smelter in Hamburg, allows Aurubis to have a more efficient processing of copper complex materials, producing other valuable metals such as Au, Ag, Bi, Sb, Sn, Se, Te, etc.).

However, as complexity still growing, Aurubis has developed a new strategy conceptualized in its Vision 2025 to become a multi metal processor in order to ensure its future competitiveness.

The future materialization of this vision imposes challenges to current available metallurgical flowsheets in order to be able to receive and process a broad range of minor element containing raw materials and operate with a high competitive metal recoveries. With the processing of complex feed material the complexity of the refining processes will also increase and require a high awareness for optimum use of the asset. To address the recent developments for the utilization of by-products (e.g. slags) and environmental legislations development of modified or new processes is essential. Flowsheet development also has to take into account the interrelation between of Cu, Pb and Zn metallurgies to optimize valuable metal recoveries and product quality.

Aurubis is therefore committed to continue working in developing flowsheet solutions to combine in a more efficient way the capabilities of copper and lead metallurgy in order to optimize recovery of valuable metals.

The current paper provides a general description of the current lead smelter flowsheet and discuss some key aspects required to optimize the speiss metallurgy.

Process Description

Figure 1 shows the process flowsheet of the lead secondary copper smelter. The electric furnace as the center of the lead smelter links the Cu metallurgy with the Pb/precious metals metallurgy of Aurubis. The electric furnace was commissioned in 1991; this was the replacement for the existing blast furnaces to improve the environmental aspect and reduce the off-gas volume due to heat generation by electricity instead of burning primary or secondary energy sources. That was the base to connect the process gas stream with the scrubber and cooling unit of the acid plant without influencing the quality of sulfuric acid production. The material preparation (sintering) was replaced by a crushing and pelletizing step. Since the commissioning, several modifications have been implemented to meet different requirements such as throughput increase, product quality improvement, improved emission management, life-cycle times and furnace availability [1, 2].

With its capability to process various secondary raw materials and intermediates the secondary smelting process is a key pillar of Aurubis recycling business on the market of Cu-, Pb- and precious metals-bearing materials [1]. The secondary smelter flowsheet allows recovery of precious metals by the combination of Cu and Pb smelting and refining processes. In this process Cu is recovered in a CuPb matte which is converted and recycled within the primary copper operations. The Pb

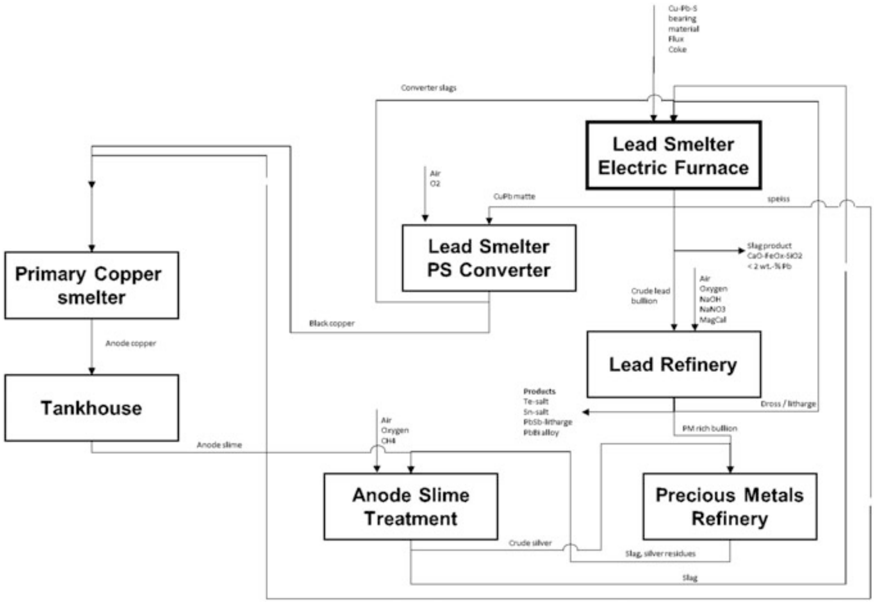

Fig. 1 Aurubis lead smelting operations

phase captures Bi, Sb and Sn for recovery within the lead refining process. The speiss phase as As–Ni bearing material will be refined within the Primary Copper Smelter. The produced slag is utilized as construction material. Various intermediates of the lead refinery (dross), of the secondary smelting operations (converter slag, flue dust) and of the primary copper smelter/anode slime treatment process (flue dust, slag) will be treated within the electric furnace.

Depending on the feed material the off-gas cleaning system is designed to manage fluctuating SO_2 concentrations, Hg and halogen contents [2].

The new lead refinery was commissioned in 2014 and uses the well-known processes to extract the valuables into products like Te–salt, Sn–salt, PbSb–litharge and PbBi alloy. The precious metals will be extracted by adding Zn to produce in a rich bullion which is forwarded to the precious metals plant where also the precious metal stream from the primary production will be processed. The Cu-containing speiss has a high load of As, Sb, Sn and Ni which is processed in the primary smelters to use the existing impurity capacities in the Cu-anode. The produced slag ensures a low valuable metal contents, satisfying physical properties (viscosity, stability, etc) and requirements for utilization. The major intermediate is the produced flue dust which will be recirculated permanently.

As can be noted from the presented process flowsheet, a key aspect of the lead secondary smelter is the processing of complex materials. This type of feed is the main source of different minor valuable metals, such as Ni, Sn, Sb, Bi, among others, important for Aurubis multi metal recovery strategy.

Due to the nature of the lead smelting process, these elements will combine depending on the metallurgical operating conditions of the furnace generating intermetallic compounds, known as speiss. The formation of speiss has been a constant topic for metallurgist operating processes such as the secondary lead process in Hamburg.

Some key aspects observed at Hamburg operations related to the speiss formation process are the following ones:

- As is a key element in the formation of speiss, due to its ability to form intermetallic compounds with base metals such as Cu, Ni and Fe. So the main amounts of As will be within the speiss and blister copper phase.
- Sb has a slightly different behavior as it will distribute between speiss and crude lead. Some Sb is also reporting to the blister copper phase.
- Sn behaves in a similar way to Sb with a weaker tendency to distribute to the lead phase.

Therefore special attention has to be given to understand the fundamental aspects associated to speiss formation.

Understanding Speiss Metallurgy

Reviewing the publications during the last decades there is a tendency towards the investigation of fundamental aspects associated to speiss metallurgy. Since the fifty's [3] the miscibility gap between matte and speiss has been discussed. Based on that the ternary or quasi-ternary diagrams e.g. As–X–S, As–X–X–S, As–X–Pb and As–X–Pb–S (X…Cu, Fe, Ni, Pb) were used to define different speiss types [3]. These results were used and linked with industrial applications (e.g. different campaigns within the blast furnace process, imperial smelting process) [4]. With a couple of investigations Gerlach, et.al. described the deportment of Ag between speiss and matte and issued the importance of As, Ni, Sb and Sn for the elemental behavior [5–8]. Following this various publications came from Japan [9–12] where the authors reviewed the recent results and focused on the matte/speiss and lead/speiss equilibrium, especially on the Ag and Au deportment. Additional work was also done on the area of distribution equilibria between speiss and slag [11]. Investigations for minor element deportment between lead and iron speiss indicated that Fe more than As affects the minor element reporting [12].

Regarding the function of the speiss a series of experiments were performed to investigate the treatment of a copper matte under strong reducing conditions with additional metallic Fe to fix As in a FeAs alloy, collect the precious metals in the copper phase and capture e.g. Sb in the lead phase [13–15].

The transition and evaluation of this knowledge to an industrial scale is an aspect which is not covered that often. Nevertheless there are some publications [16–18] which present different approaches to extract speiss forming agents like As, Sb or

Sn from their industrial processes. If these elements are in the feed mixture as sulphides or an excess of sulfur bearing agents will be provided then there is a possibility to extract them via the gas phase [16]. A major share of discussion is about the blast furnace process [17] or electric furnace process [18] and their characteristic speiss. In the scope is the minimization of precious metal losses and the fixation of As within the speiss. Due to the strong reducing conditions some metallic Fe can be present which will lead to a Fe-based alloy with high As amounts.

As the literature indicates, the term speiss is used for a couple of materials differentiate in concentration and characteristic. In the most cases speiss is an undesired phase which collects also valuables like precious metals. Furthermore the control of analysis and quantity can be identified as challenge. Otherwise the speiss can be approached to extract impurities from a process based on the use of affinity differences of Cu, Fe, Pb, Ni and Co to As and S. Based on the compilation of available literature two publications [3, 4] are selected to discuss the relevance of speiss forming agents (As, Sb, Sn) in base metal processes (Cu, Fe, Ni, Pb). Both papers link fundamental work and help to understand the speiss formation with a couple of operational data.

In the first one, Kleinheisterkamp (1948) reported the most relevant fundamental aspects about the miscibility of melts originating from CuPb process within a shaft furnace and delivered hints about how to use these fundamental information for practical work. The difference of a real speiss phase and an alloy is reasoned by the portion of total As + Sb + Sn to Co + Cu + Fe + Ni + Pb. The results showed that the affinity of Fe to As is stronger than it is the case for Cu to As which explain the formation of FeAs speiss (Fig. 2) in strong reducing conditions where metallic Fe is present. The role of Ni is an important one due to its larger affinity to As than for Cu. Following this it seems to be possible to control the Ni deportment within a CuPb process if a certain level of As is in the feed. The solubility of metallic Cu and sulfidic Cu in Ni-arsenides complicates the control of this. The formation of

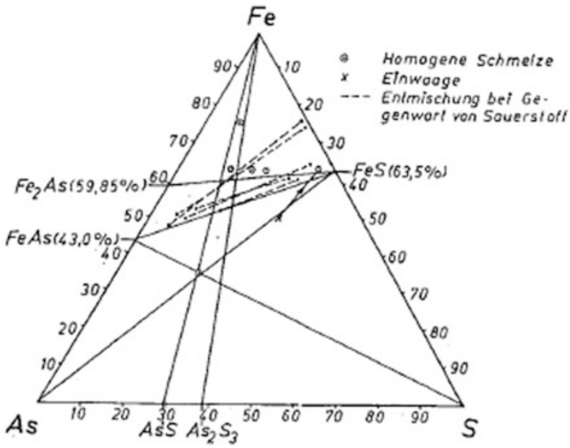

Fig. 2 Ternary phase diagram As–Fe–S (T = 1180–1320 °C) [3]

Ni-arsenides is strongly affected by the As and S content in the feed mixture. The S content in the feed determines the Cu extraction and ensure the formation of matte. The more efficient this take place the less metallic Cu is present to form intermetallic compounds (e.g. Cu antimonides) which will increase the total wt% Cu in the speiss. [3].

In the second one, Fontainas (1978) discussed how to deal with the treatment of complex materials containing lead, copper, nickel, zinc, iron and sulphur. An important part of this is the discussion about various forms of speiss in the system slag, matte, speiss and crude lead. The author agreed on the description of Kleinheisterkamp and also reported about the broad manner of composition (Fig. 3) instead of a particular point for speiss composition. Furthermore the paper took into account that a high enriched metallic copper phase will appear if the activity of Cu is nearly unity but in reality it will be below 0.3. In combination with present impurities like As, Sb or Sn the Cu will form intermetallic compounds which are known as Cu-rich speiss. The formation of an iron-rich alloy (dominated by FeAs or Fe_2As) mainly depends on the amount and form of compound of Fe in the feed mixture, the amount of the other minors and the chosen process atmosphere which is characterized also by final Pb content in the slag. An exemplary reduction process with metallic Fe as reduction agent and decisive amount of minor elements in the feed will produce a low grade CuPb matte with high amounts of Fe and a speiss which can contain up to 60 wt% Fe and 20 wt% As. From a stoichiometric point of view this ratio gives an indication for the dominated phase in the speiss (Fe_2As).

The referred blast furnace process (Fig. 4) will end with 1.5 wt% Pb which means a Fe activity of about 0.1. Under these circumstances the formation of an FeAs main alloy seems to be negligible but this turns when the Fe activity increases due to deeper reduction at least for an activity of 0.5 (Imperial Smelting process) which will promote the formation of a ferrous speiss. Beyond As also Sb and Sn

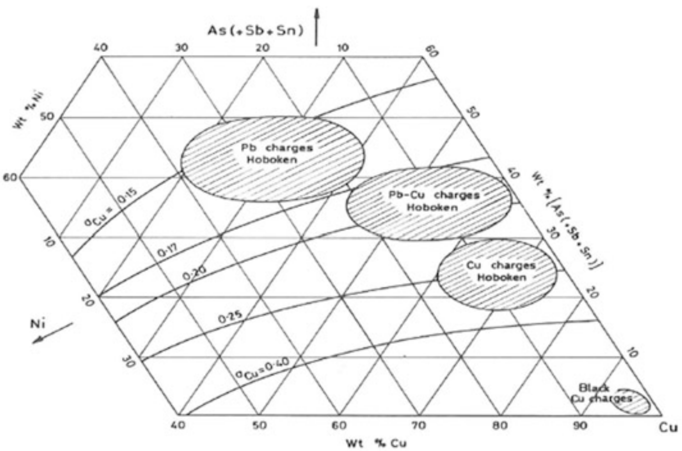

Fig. 3 Cu–Ni–As-based alloys and speiss [4]

will form intermetallic compounds and become a part of the speiss. In Fig. 6 three different operations with speiss production are highlighted. Starting with a low Cu activity of 0.15 in the processing of Pb-bearing materials these speiss are different from the ones produced during the processing of Pb-Cu complex mixture. Then the activity of Cu is increased and this will lead to an excess of copper in the speiss composition. The current speiss composition of Aurubis lead smelting process in the electric arc furnace is in-line with the so called area Pb–Cu charges. If the Cu activity further increases Cu rich alloys will be formed in Cu-charges and this can continue until the right corner is reached where a black copper composition will be reached.

With the help of Fig. 4 also the role of Ni will be explained by applying a ternary Cu–Fe–As diagram in which Ni is lumped together with Cu, Sb, Sn and As and with Co, Fe and Zn. Ni is to consider as a base metal like Cu which will form intermetallic compounds e.g. Ni_5As_2, NiAs, NiSb. The Aurubis lead smelting process is close to the iso-activity curve for a typical blast furnace process (with 1.5 wt% Pb in slag). At this point the formation of Fe-rich alloys is not expected due to the low activity of Fe (0.1) [4].

Figure 5 issues the deportment of As, Sb and Sn between crude lead and speiss phase. To keep it simple the diagram relates on a fixed temperature (T = 600 °C) where the solidifcation of speiss is assumed as completed and the lead is still in liquid state. Based on ternary diagrams of Pb–Cu–As, Pb–Cu–Sb and Pb–Cu–Sn Fig. 4 compile all information for As, Sb and Sn concentration in lead versus the concentration of these elements in the Cu-alloy (speiss). This means for a Cu–As alloy with 30 at.% As the concentration in the lead bullion will be about 0.45 wt% As. For As it can be stated that the As deportment is not that strong related to the As content in the Cu-alloy like it is the case for Sn and Sb. Equal amounts of Sn in

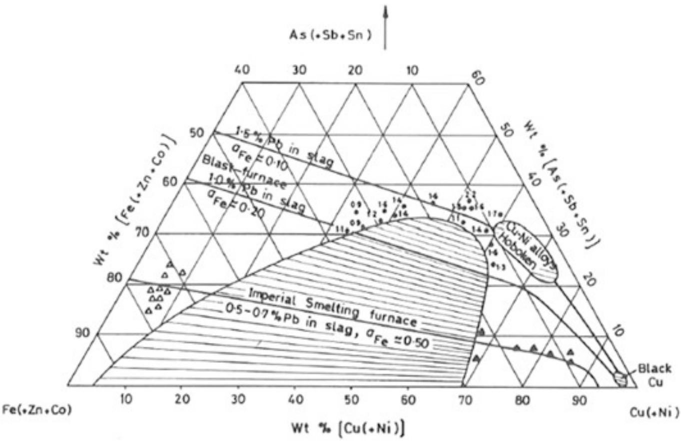

Fig. 4 Cu–Fe–As-based alloys and speiss [4]

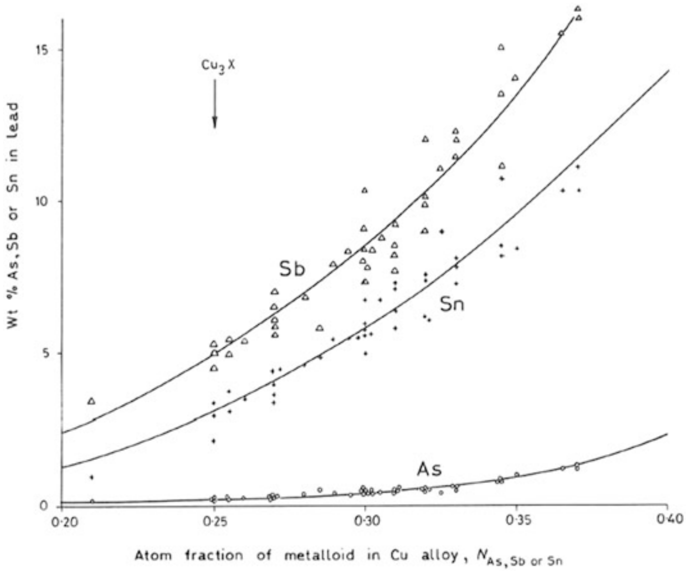

Fig. 5 As, Sb and Sn content of lead bullion as a function of composition of Cu alloy/speiss in equilibrium at 600 °C speiss [4]

Cu-alloy (30 at.% Sn) will lead to 6 wt% Sn in lead (in equilibrium) [4]. Sn and Sb show a similar behavior in terms of element deportment.

The following conclusions can be derived from this literature review:

- Formation of intermetallic compounds will be governed by a feed mixture which contain base metals (Co, Cu, Fe, Ni) and minor metals (As, Sb, Sn).
- Depending on reduction potential, used capability of Cu extraction and ratio of base metals to minor metals will be determining factors which speiss will be formed (quantity and quality).
- Fundamental work deal with ternary and quasi-ternary systems to investigate the miscibility gaps between matte and speiss and the impurity behavior between speiss and lead.
- As minor element the authors mean also Ag and Au whose deportment between speiss and matte and speiss and lead is investigated in a couple of papers. The formation of a Fe/As-bearing speiss will reduce the solubility for Ag which then can be collected in the matte or metallic phase.
- The thermodynamic prediction for Ni is not that easy due to a lack of data in all relevant databases. Further fundamental experiments are required to address the importance of Ni for speiss formation.
- To take Ni into account the phase diagrams (Figs. 3 and 4) can be used to calculate the expected speiss composition for a given copper activity or describe an operational window when the speiss tends to become Fe rich (for higher Fe activity and corresponding low lead content in end slag).

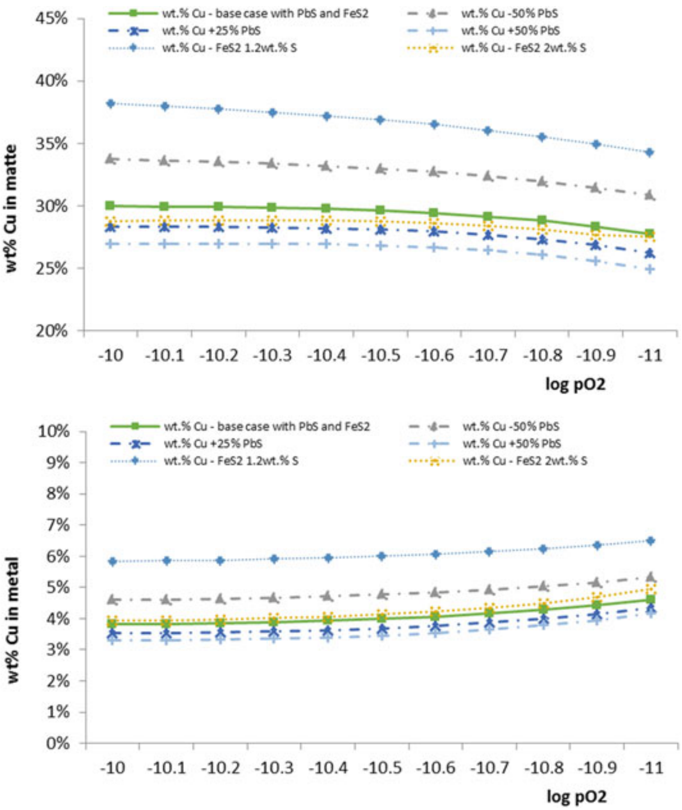

Fig. 6 Dependency of sulfur source addition on the matte grade (top); Dependency of sulfur source on the Cu content in the metal phase (bottom) at T=1150 °C [20]

- Major share of available data is originating from equilibrium tests in lab-scale or bench scale tests. This means the use of synthesized material and the simplification of conditions. Industrial data of various speiss types is quite rare and if present then it will come from a couple of years ago.
- Figure 5 shows a compilation of empiric data which allows the calculation of the As, Sb and Sn content in the crude lead following a complete solidification of speiss.

In addition, the following implifications for industrial lead smelting process can be derived from the above analysis:

- In a couple of literature sources (e.g. Kleinheisterkamp [3]) it is indicated that it is possible to properly determine potential formation of Ni_xAs_y speiss on its different stoichiometry.
- The Fe content of the speiss depends on the presence of metallic Fe which can be minimized by controlling the reduction potential of the process.

- A proper Cu extraction by decreasing the Cu activity will decrease the Cu content in the speiss because of less intermetallic Cu compounds with As, Sb and Sn.
- Although the economic improvement is a main criteria for lead smelting processes, the operation with campaigns would be a serious solution to react on varying feed composition and provide a suitable product quality of lead, matte and speiss.

Approach for a Continuous Improvement of the Secondary Lead Smelting Process

The main purpose of Aurubis Cu/Pb process is the recovery of precious metals in the crude lead phase and the extraction of copper via matte formation. On the other hand, the extraction of minor elements (e.g. As and Ni or Sb and Sn) has to be adjusted to achieve a high efficient process. All in all this will support the recovery of valuables and ensure the use of crude lead which can handle Sb and Sn but also the use of the other intermediates (matte for Cu and the speiss).

In order to optimize this aspect, special attention has to be given to:

- Calculation of feed material and scheduling the operations to address the fluctuating feed composition
- Monitoring of product analysis to evaluate key factors for the feed (e.g. As, Sb, Sn and Ni content)
- Proper sulfur adjustment to capture the copper and keep the matte grade above 30 wt%
- Avoid a limited solubility for Sb and Sn in lead due to an insufficient reduction potential or less metallic Pb amounts

Possibilities to Adjust the Right Metallurgy for Recovery of Cu Within the Secondary Lead Smelting

The Cu/Pb separation depends on the sulfur adjustment in terms of quantity and procedure. Sulfur can be added from different sources (elemental sulfur, pyrite or a lead concentrate), however each one of these sources will have a different efficiency, as discussed later in this section.

- Elemental sulfur addition: Because of the low melting point (115.2 °C) and the low boiling point (444.6 °C) elemental sulfur is not favored due to its low efficiency [19].
- Pyrite/Lead concentrate: This has been industrially proven [3].

Beyond these both additives additional sulfur sources will enter the secondary lead smelting process and support the formation of CuPb matte. The following reactions scheme introduce the principles of the mentioned process. Sulfates will be reduced directly by coke or indirect by carbon monoxide (Eqs. 1 and 2) and will provide PbS which then allows the sulfidation of Cu to form Cu_2S (Eqs. 3 and 4). The advantage of using lead concentrate is the supply of additional metallic lead which is explained in Eq. 5. This additional lead allows the capturing of Bi, Sb and Sn. The major share of metallic lead will be originating from a lead oxide slag which is reduced (Eqs. 6 and 7). Addition of pyrite will enable the reaction with Cu_2O to Cu_2S which is mentioned in Eq. 8. This will also effect the matte grade due to additional amounts of FeS in the matte (Eq. 9).

$$2[C] + \{O_2\} = 2\{CO\} \tag{1}$$

$$[PbSO_4] + 2[C] = [PbS] + 2\{CO_2\} \tag{2}$$

$$[PbSO_4] + 4\{CO\} = [PbS] + 4\{CO_2\} \tag{3}$$

$$[PbS] + (Cu_2O) = [Cu_2S] + (PbO) \tag{4}$$

$$3[PbS] + 2(Cu_2O) = 2[Cu_2S] + 3[Pb] + \{SO_2\} \tag{5}$$

$$2(PbO) + [C] = 2[Pb] + \{CO_2\} \tag{6}$$

$$(PbO) + \{CO\} = [Pb] + \{CO_2\} \tag{7}$$

$$3[FeS_2] + 2(Cu_2O) = 3[FeS] + 2[Cu_2S] + \{SO_2\} \tag{8}$$

$$[FeS] + (Cu_2O) = (FeO) + [Cu_2S] \tag{9}$$

Taken the low efficiency of elemental sulphur into account the use of pyrite is an alternative which provide an improved efficiency of S use due to the smaller reaction surface. For lead concentrate a significant higher amount of material is required due to the low share of S in lead concentrate. For the reaction with one tons of Cu the following amounts are required:

- 800 kg elemental sulphur (assumed efficiency of 25%); disadvantage → a lot of SO_2 emissions
- 1850 kg lead concentrate
- 930 kg pyrite (following the reaction in the scheme—Eq. 8)

The effect of using pyrite or lead concentrate will be discussed in the following thermodynamic calculations which were based on a given example by applying a feed mix which is dominated by a high amount of Pb (20–40 wt%). Other base metals like Cu and Fe are also present. Because of the lack of data Ni was not considered. The following fixed parameters (process temperature 1150 °C, closed system without any gas exchange, equilibrium between slag/matte/metal) were set for the calculations. As scenarios the following cases were calculated:

- I—Base case applies the feeding of lead concentrate and pyrite in a ratio of (11:1) by adjusting 2 wt% S in the feed
- II and III—Increase of lead concentrate amount by 25% steps whereas the second steps results in 2.3 wt% S in the feed
- IV—Decrease of lead concentrate amount by 50% in one step results in 1.7 wt% S in the feed
- V Replace the lead concentrate in base case by pyrite to adjust the same 2 wt% S in the feed
- VI Apply case V and reduce the amount of pyrite which means 1.2 wt% S in the feed

The first plot in Fig. 6 shows the dependency of matte grade on the oxygen potential and the second one discusses the corresponding Cu content in the metal phase.

The “worst” case (1.2 wt% S) means an insufficient sulfidation which will lead to an increase of Cu content in the metal phase. Cu which is not bound on sulfur is able to form intermetallic compounds by capturing As, Sb or Sn. On the other site an exceed of sulfur in the feed (pyrite and lead concentrate like in base case +50% more lead concentrate) will lead to a poor Cu content in CuPb matte with contents of 25 wt% Cu. But at the same time the Cu which is present in the metal will also shrink and concludes to a less amount of intermetallic copper compounds, better known as speiss. The dependency of the matte grade on the present oxygen potential can be specified for log p_{O2} from −10 to −11 with 27.5–30 wt% Cu (base case, T = 1150 °C). If lead concentrate is substituted by pyrite which will provide the same amount of introduced sulfur the matte grade will be effected and changes from 29.6 to 28.8 wt% Cu. In contrast to the effect on the matte grade for the metal phase an increase of Cu concentration is associated with increasing reduction potential. An exceed of sulfur will decrease the Cu content in the metal whereas a lack of sulfur increases the Cu content.

The results allow the following interpretation:

- In principle both additives will address the task to deliver sulphur to the system to form a matte for Cu extraction.
- The expected matte grade is influenced by the reduction potential. For a constant log p_{O2} the sulfur adjustment is the main paramter which is changing the matte grade.
- A well-calculated sulfur adjustment will determine the operational window for the matte and will have also an effect on the metal phase composition.
- Contradictory to the matte grade change the Cu content in the metal will increase with higher reduction potential.
- Which sulfur adjustment will be the right one depends on a couple of parameters and has to be defined from one to another operation. The following processing step for the matte has to be considered as well.

Conclusion

In the present paper Aurubis lead smelting process and its main function was presented. For the upcoming challenges operating a flowsheet which is able to link the Cu metallurgy with the complex metallurgy will be a key aspect. Therefore the most relevant criteria is the achievement of high metal recovery rates for a couple of valuables and the precious metals.

The feed of the electric furnace will become more complex and this complexity will be somehow transmitted to the products (CuPb matte, crude lead bullion, speiss and a $CaO–FeO–SiO_2$ based) and the following refining steps. The metallurgy has to be managed actively to react on the feed composition and obtain the right operational windows to provide a proper product composition for their foreseen treatment within Aurubis.

The formation of intermetallic compounds in a separate phase, better known as speiss, is still not well understood. Fundamental work is still required to support proper metallurgical operations. Development of thermodynamic data base will support this goal.

Secondary copper lead metallurgy requires proper understanding of required Cu, Pb and S ratios to optimize the metallurgical process and recovery of valuable metals. The extraction of Cu will be controlled by the addition of a suitable sulfur source which can be lead sulphate rich dusts, lead sulphate based slimes, lead concentrate or pyrite. The last two additives were discussed in the paper.

The transition of the mentioned knowledge will support the aim to improve the impurity management of Aurubis and will provide a great future for the lead smelting activities within the electric furnace. With the right know-how the process will be fit for purpose and deliver it's contribution for increase of metal recovery rates and more intelligent impurity control.

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