FUNDAMENTAL ANALYSIS FOR AN IMPROVED MULTI METAL RECOVERY BY COMBINING COPPER AND LEAD METALLURGY

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ABSTRACT

Synergies between copper and lead extractive metallurgical processes enable the processing of a broad range of polymetallic materials. However, this complexity also brings some challenges expressed in terms of complex intermediates and final products. For instance, based on the limited solubility of Cu and Ni in crude lead bullion additional phases will appear during the crystallization of the melt. Beyond the need for continuous optimization of metallurgy the control of phase solidification is a further important pillar to achieve a more efficient process by minimizing the amount and cycles of reverts. This paper describes the microscopy study of one of the most relevant intermediate in the Cu and Pb metallurgy, the Cu based alloy and highlights the importance of applying a well-controlled cooling sequence to improve the overall process efficiency.

KEYWORDS

Electric furnace, Intermetallic alloys, Metal processing, Phase separation, Polymetallic, Secondary

INTRODUCTION

One of the key aspects in Aurubis’s 2025 vision is to move towards the implementation of a multi metal recovery strategy. The implementation of this new multi metal vision is supported by the long tradition of the company, founded in 1866 as Norddeutsche Affinerie, and further developed by adopting modern copper smelting and lead smelting technologies for the processing of primary and secondary materials. The combination of these assets have already build the basis for processing of complex materials in the copper and lead circuits implemented in Aurubis’s facilities. The addition of a new smelting facility, will enhance these capabilities. Aurubis current flowsheet combines Cu, Pb and Zn metallurgy. This includes primary smelting of copper concentrate, processing of secondaries (residues, slimes, slags) and recycling materials (scrap, shredder material, e-scrap). These broad range of materials contain not only the mentioned base metals but also a number of minor metals that requires to be properly managed to ensure efficient recoveries and quality of the targeted metals.

The processing of Pb-Cu-S bearing materials is done in Aurubis at the lead smelter, located in Hamburg. A schematic flowsheet of the electric furnace used for the processing of these materials is shown in Figure 1.
Operating a smelter producing a crude lead bullion allows a concentration of a couple of valuables (PM, Bi, Sb, Sn, Te) within this phase and was explained by Bauer (2011). Due to the nature of this process other intermediates will occur, for instance a matte and a speiss phase. The matte has the function to extract the Cu in a sulfide melt which could be processed in primary operation after a converting step. Depending on the adjustment of the lead smelters feed an alloy will be coexisting which can concentrate significant amounts of Cu, Fe and Ni associated with As, Sb and Sn, which is considered as speiss phase. The design and recovery capabilities of downstream processes depend mainly on the composition of the intermediates and will have an impact on the economics of those processes (metal recovery rates, availability, product quality). In contrast to speiss alloys a highly enriched phase of As and Ni is defined by Kleinheisterkamp (1948) as real speiss. The resulting speiss composition depends also on the one hand on the feed arrangement but is also effected by the phase separation process following the metal/matte tap of the key asset, the electric furnace. The flue dust will be recycled within the process and the process gas will be treated in the acid plant.

With the growing complexity in feed material the metallurgy for the electric furnace needs a proper understanding how to utilize the existing phases and the capabilities of all following smelting/refining steps. The operational window is set with controlling the most relevant process criteria such as:

- Copper to sulfur ratio and the selection of suitable sulfur source,
- Adjustment of speiss forming agents (As, Sb, Sn and Ni) in feed,
- Application of the desired reduction potential,
- Process temperature control.

This fundamental knowledge of speiss formation could be applied on various smelting/reduction technologies for instance the well-known process for crude lead production from sinter (Blast furnace) or by smelting of complex materials (electric furnace, KIVCET, QSL) or within a slag reduction process under very strong reducing conditions for Zn fuming (TSL, electric furnace, ISP). However, the metallurgy in the furnace provides the foundation for a highly satisfying metal recovery but need another aspect which often is not discussed and perhaps underestimated. Each technology requires a dedicated technical approach for phase separation after tapping to dismantle slag, matte and metal from each other. Whereas the blast furnace is operating with a forehearth to collect the phases Aurubis secondary smelter tap metal and matte in one large pot. During the cooling an additional phase will occur which contains various intermetallic compounds whereas the proportion of As+Sb+Sn to Co+Cu+Fe+Ni+Pb can lead to a wide range of speiss compositions according the definition of Kleinheisterkamp (1948) and Zschiesche (2018).
Apart from the metallurgical principles there are further important criteria to improve the separation result between the phases to prepare them for downstream refining processes.

**Literature review for phase separation process and its importance for speiss composition**

In a previous paper of Zschiesche (2018) a comprehensive literature review was carried out on the mechanism of speiss formation and the existing type of speiss. This paper reviews the literature with focus on the phase separation process and draw conclusions about the lack of data which is still there. The fundamentals of separating speiss from a crude lead phase are based on solubility limitations for Cu and Ni.

Kleinheisterkamp (1948) reported the decreasing Cu solubility in Pb (Figure 2 left), especially if As is present (from 7.5 to 2.5 wt% Cu). For domeykite (Cu₃As) the Pb solubility was specified with 14 wt%. Very similar to Cu the solubility of Ni in Pb will decrease and based on the presence of As there will be a poor solubility of Ni (0.6 wt% for 3.3 wt% As) in crude lead already slightly below process temperature (Figure 2 right). Therefore it can be stated that both intermetallic compounds (nickelinge-NiAs and Ni₅As₂) will solve a minimum of Pb (up to 6 wt%).

![Figure 2 left: Ternary phase diagram of As-Cu-Pb which shows the miscibility gap governed by addition of As; right: Ternary phase diagram of As-Ni-Pb showing different results published by two authors.](image)

Fontainas (1978) published a sort of equilibrium diagram (Figure 3) for the crude lead bullion produced in a blast furnace during cooling period. The author described the start point of speiss crystallization with 1,050°C and defined a range of speiss getting completely solidified in between 600-800°C. For a speiss with a Pb content of approx. 25 wt% a finalized crystallization was assumed with 650°C.
Hino (1998) noted an increase of matte which can be solved within speiss if the Fe content in the speiss increases. This is shown in Figure 4. The equilibrium between speiss and lead, especially for the lower temperature area was not investigated but indicated that As will support the separation of Pb-Cu already at process temperature (1,200°C).

Ettler et al. (2009) published their multi-method mineralogical investigation of matte and speiss samples coming from a blast furnace. Those were coupled with heating and quenching experiments to deliver data according to the order of crystallization. The main observations were the immiscibility of sulphide and metallic melts and the results of their SEM investigations to identify the major phases of matte and speiss. According to the authors for the formation of high-temperature intermetallic phases mainly three elements are responsible. As, Sb and Sn prefer to form compounds with Cu, Fe and Ni. It is important to know that the solidification process of such complex products is widened above a broad range of temperatures, starting above 1,300°C and is completely finished below < 250°C. That is the reason why each phase (matte, lead
and speiss) shows also contents of the other ones. In the following table (Table 1) the observations are summarized:

<table>
<thead>
<tr>
<th>Classification</th>
<th>Name or Stochiometric compound</th>
<th>Start of crystallization T (°C)</th>
<th>Crystallized at T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-temperature phase</td>
<td>Ni$_3$Sn$_2$ or NiSb NiAs, Fe$_2$As Cu$_3$As$_2$ Cu$_3$Sb$_2$ Cu$_3$Sn Pb+Sb eutectic in speiss</td>
<td>1264 and 1147 970 930 709 683 676</td>
<td>247</td>
</tr>
<tr>
<td>In Sulfide melts</td>
<td>Spinels (e.g. Fe$_2$O$<em>4$) Fe-rich sphalerite (ZnS) Pyrrhotite (Fe$</em>{1-x}$S) PbS+CuS eutectic</td>
<td>1195 1050 1115 (pure PbS)</td>
<td>500 - 600</td>
</tr>
</tbody>
</table>

This compilation shows the complexity of compounds which can be observed for each microstructure of such complex matte and speiss phases. For the speiss the microstructure could be very different depending on the components and conditions applied on the melt. This differentiation is perhaps due to:

- entrained matte particles,
- entrained Pb droplets,
- rims of high temperature phases,
- presence of metallic iron (formation of Fe$_2$As compounds).

Ni is associated with As, Sb and Sn and forms intermetallic compounds which can be characterized as a rim between metallic and sulfide melts. Due to the nature of Ni the formation of a couple of such high temperature compounds (Ni$_3$Sn$_2$, NiSb) will have an impact on desired crystallization sequence. At higher As levels the formation of NiAs will be preferred in comparison to Ni$_3$Sn$_2$ or NiSb which will effect the crystallization sequence, too. Cu is bound on As and Sb as Cu$_5$As$_2$ and Cu$_5$Sb or Cu$_3$Sb$_2$ which forms compounds at moderate crystallization temperature. Sn will be with Cu as Cu$_5$Sn$_2$ or Cu$_3$Sn. Based on nearly the same ionic radius Cu could be substituted by Ni.

The following conclusions can be derived from this literature review:

- For primary lead metallurgy but also for smelting of complex feed the formation of speiss will have relevance as long quantitative amounts of As are present and whether the sulfur addition is proper (then major amount of Cu is bound in a CuPb matte phase) or the system is with a sulfur deficite (only an intermetallic phase instead of a matte).
- At process temperature (1,200 to 1,300°C) normally matte and speiss are immiscible and lead phase is settled at the bottom of the furnace.
- With the help of the ternary diagrams it could be shown that the solubility of Cu and Ni in lead is very limited and this will be further promoted by addition of As (in presence of speiss).
- Based on the wide range of cristallization (from 1,300 down to 247°C) a proper separation process is required whereas an insufficient separation processes causes high Pb concentration in CuPb matte and a high amount of entrained metallic droplets (Pb) in the speiss.
- As result of mineralogical investigations a couple of “high temperature” phases could be identified, such as Ni$_3$Sn$_2$ and NiSb and Cu$_3$Sn which will form either individual crystalls or a rim around the metallic droplets. This will block any separation of metal droplets during cooling.
- Literature, describing such processes in an industrial environment is practically not available and make it difficult to translate the findings derived from various fundamental research programs into operations. The right interpretation of the available descriptions together with testwork in industrial scale would significantly improve the situation.
In addition, the following implications for industrial lead smelting process can be derived from the above analysis:

- Adjustment of proper extraction of Cu into matte and right proportion of As will minimize the formation of high temperature intermetallic phases and will enable the sink of Pb droplets during phase separation process.
- The right reduction potential will help to minimize the presence of metallic Fe which will form speiss with a higher solubility for matte particles.
- Tapping temperature has to consider the expected compounds in the speiss to avoid a prior crystallization.
- Prior the optimization of the phase separation for the secondary smelter a fundamental analysis and characterization of the matte and the speiss is essentially needed.

The separation of phases starts already at process temperature within the furnace and continues with the tap of metal and matte

The target slag temperature for the electric furnace is 1,250°C. According to the furnace design there is a certain temperature gradient between the slag and the metal phase at the bottom. The results of various temperature measurements during metal/matte and slag tap are compiled in Figures 5 and 6. The recent results are very close to the data published by Van Negen (1990).

![Figure 5](image)

**Figure 5. Defined temperature gradient between the different layers present in the electric furnace**

The electric furnace operates discontinuously in terms of tapping whereas the feeding is done continuously. The tapping procedure starts with metal tapping for a couple of times per shift and the slag is tapped at the end of the shift into ladles and crushed after the solidification period. The metal and the matte flows into a large pot and during transport to the matte/metal separation area, the melt temperature will drop down from approx. 1,100 to 1,050°C. The measured amount of matte is tilted into a new ladle and the metal (crude lead + speiss) is poured into moulds where the speiss can solidify above the still liquid crude lead. Following the removal of the speiss crust, the liquid lead is poured into ingots that will be transported to the lead refinery after cooling. The described separation process scheme is illustrated in Figure 6.
Characterization of products generated in the phase separation process

In order to characterize the phase separation process, samples were taken at different positions of the molds where the speiss solidifies. Figure 7 shows the elemental composition of speiss samples for three different taps within one shift. After speiss solidification the crust was sampled in the center area (solid line) and at the border to the mould (dotted line). The analysis of 12 samples were measured by using X-ray fluorescence spectroscopy (XRF). Due to different concentration levels the secondary x-axis (top) is linked with the Cu and Pb figures and all the other elements are linked to the primary x-axis (bottom). The boxplot diagram shows the extrema (crosses), the median figure within the box and the lower and higher quartile (box).

![Boxplot diagram showing elemental composition of speiss samples](image)

Figure 7. XRF-analysis of speiss samples which were taken from the solidified moulds in the center (blue coloured) and at the border (red coloured)
From the figures the following observations can be made:

- The deviation of the measured concentrations depends on the sample position (center or border) and is in its extend different for the shown elements. According to the literature review the main characteristic of the investigated speiss is represented by high concentration of Pb and Cu. This would fit into a classification as an alloy.

- Pb is a major player for the total concentrations in the alloy which can be derived from Figure 7, where the Pb-content in the center deviates from 22 to 28 wt% with a mean value of 25 wt%. At the border to the mold, a wider span is represented by the box and shows one extreme at 47 wt%. Based on the figure for S most probably a higher share of metallic Pb droplets are caught in this area which will dilute the concentration of the minors in the alloy.

- According to the Cu and Fe content, a slightly higher concentration of those elements can be noted for the border area which would fit to the hypothesis of an increased amount of entrained matte particles. This is also supported by slightly higher mean value of S.

- For As and Ni a tendency for higher concentrations in the center area could be observed but the span of the box are very similar between center and border area. Due to the very limited solubility in metallic lead this could be expected. In contrast to that the other both speiss forming agents Sn and Sb show a different behavior. Their total concentrations remain on a similar level (center vs. border) which is most probably caused by their given solubility in metallic lead droplets.

- Bi, Se and Te concentrations were measured in a very tight range and seem to be not effected in dependence on sampling position.

Finally, it can be stated that it is not trivial to draw conclusions for an improved phase separation process only with the help of XRF analysis. An improvement in this process would be:

- Minimization of entrained metallic droplets of Pb in speiss will lead to total mass reduction and simplify the speiss crushing afterwards (material will become more brittle).

- Pb droplets will require settling time which is mainly controlled by applied cooling rate.

- Understand main criteria which will block the settlement of Pb droplets during cooling process.

- Optimize ladle/mould geometry to support the aforementioned goal.

In the moulds used, the cooling rate was measured three times by implementing a Type K NiCr-Ni-thermocouple from the top. The cooling curve is plotted in Figure 8 and the average cooling rate between the initial (869°C) and defined end temperature (630°C) was determined with 270 K/h. The maximum measured initial temperature was about 960°C and as the speiss solidification point T=630°C was defined.

![Figure 8. Measured temperature profile for speiss for the cooling procedure within a mould](image)

With the taken samples a scanning electron microscope (SEM) study was done to determine the major components of the speiss (Table 2) and compare it with the observations which were discussed in the
paper of Kleinheisterkamp (1948) and investigated by Ettler (2009). Figure 9 shows the identified phases and presents a mapping of the main elements Cu, Fe, Ni, S and Pb.

Table 2. Comparison of results from SEM investigations with available information derived from literature

<table>
<thead>
<tr>
<th>Author</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ettler 2009 [6]</strong></td>
<td>Cu&lt;sub&gt;5&lt;/sub&gt;As&lt;sub&gt;2&lt;/sub&gt; Cu&lt;sub&gt;4&lt;/sub&gt;Sb&lt;sub&gt;2&lt;/sub&gt; Cu&lt;sub&gt;3&lt;/sub&gt;Sn</td>
<td>Ni&lt;sub&gt;5&lt;/sub&gt;Sn&lt;sub&gt;2&lt;/sub&gt; NiSb NiAs</td>
<td>Pb+Sb eutectic in speiss PbS+CuS eutectic</td>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;As</td>
</tr>
<tr>
<td><strong>Kleinheisterkamp 1948 [2]</strong></td>
<td>Cu&lt;sub&gt;3&lt;/sub&gt;As Cu&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>NiSb NiAs</td>
<td>Pb as metal droplet</td>
<td>FeAs Fe&lt;sub&gt;2&lt;/sub&gt;As</td>
</tr>
<tr>
<td><strong>This study</strong></td>
<td>Cu&lt;sub&gt;5&lt;/sub&gt;As&lt;sub&gt;2&lt;/sub&gt; Cu&lt;sub&gt;2&lt;/sub&gt;Sb or Cu&lt;sub&gt;5&lt;/sub&gt;Sb Cu&lt;sub&gt;3&lt;/sub&gt;Sn Cu&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>NiSb Ni&lt;sub&gt;3&lt;/sub&gt;Sn&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Pb PbTe, PbSe PbS</td>
<td>FeAs Fe&lt;sub&gt;2&lt;/sub&gt;As</td>
</tr>
</tbody>
</table>

Figure 9. Result of SEM analysis and mapping of Cu, Fe, Ni and Pb in a selected speiss sample of the aforementioned sampling campaign (center area)

The speiss samples showed a couple of intermetallic compounds and sulfides of Cu, Fe and Pb. Align with the statements of Kleinheisterkamp [2] Cu, Ni and Fe are the main metals which are present as intermetallic compounds with As, Sb and Sn. Nevertheless the Aurubis speiss is not a Fe-As-rich speiss which would be characterized by a needle-like microstructure. According to the definition of Kleinheisterkamp [2] it is more a kind of an alloy with significant amounts of Cu and Pb. Important for the solidification is the presence of high melting phases like NiSb (1147°C) and Ni<sub>5</sub>Sn<sub>2</sub> (1264°C). Further important compounds for the crystallization sequence are Cu<sub>2</sub>S and FeS. All the other shown compounds of Cu, Ni and Fe with As and Sb (Cu, Fe) will have lower crystallization temperatures. According to the microstructure in Figure 9 large areas of Pb can be seen which are crossed by intermetallic phases or separate matte phases beyond the metallic droplets. All of those components will solidify earlier as the Pb which will result in a not satisfying settling.
For an optimization of the cooling rate the softening temperature of the speiss is important. This temperature range was examined by conducting melting experiments under argon atmosphere in a high temperature microscope where all characteristic melting stages (Figure 10) were determined. Starting with a defined “block” the shape changed with increasing temperature and the sample started to soften at 797°C. The characteristic hemispherical point was reached at 930°C.

![Figure 10. Result of high temperature microscope analysis for smelting range of the selected speiss sample performed under Ar atmosphere](image)

Based on all of these facts the following hypothesis could be drawn:

- The softening range and nevertheless the solidification range of speiss mainly depends on the composition, more precisely on the formation of high melting phases like Ni₃Sn₂, NiSb, ZnS, Cu₂S and FeS.
- The initial temperature for start of cooling period could not be increased unlimited due to the design of the electric furnace (water cooled bottom). During the metal/matte handling and the required time for logistic, the temperature drops a bit and meanwhile first crystallization occur already.
- Based on available data from the literature (Kleinheisterkamp and Ettler) Pb will not form intermetallic compounds and is not a typical component of the so called speiss phase.
- Present Pb droplets could be shown in the microstructure. A couple of intermetallic phases cross those droplets or form a cover around. This means a blockage for a successful settlement and avoid the theoretical reachable low Pb contents in speiss.
- The right adjustment of furnace feed can support the phase separation by providing a sufficient amount of As to capture the free Cu (S deficit) and Ni which will lead to intermetallic compounds with lower melting points than the one formed out of free Sb or Sn.

**Investigation of the phase separation process to validate the multi metal recovery potential from the molten phases**

Independent from the feed a proper design for phase separation can contribute to the ultimate goal of multi metal recovery. Therefore the following principles were set for the done testwork:

- Separate matte from metal at highest possible temperature (holding furnace was used for testwork).
- T-controlled heating of matte/metal mixture to T>1,150°C
- Pouring the matte into separate ladles
- Pouring the metal into the next ladles
- Avoid additional matte floating on top of the metal (overflow launder Figure 11)
- Solidify the speiss crust directly above the still liquid crude lead
For the test work a rotary holding furnace (Figure 11) was used to buffer the matte / metal taps coming from the electric furnace. The set temperature was 1,150°C to provide suitable conditions to separate the matte before pouring the metal into ladles where the formation of the speiss crust occurred. The crude lead phase is still liquid during this cooling.

To minimize the floating matte on top a cascade system was applied which consists of two ladles which are linked via an overflow. By pouring metal/matte to the first ladle, the matte with lower density was flushed to the second ladle. The pouring temperature was measured with a temp-tip measurement probe. Following the filling of the ladle with metal one type K (NiCr-Ni) thermocouple was lowered down from the top to measure the temperature in the near of the top and another one was introduced in the bottom area of the ladle to measure the temperature within the crude lead phase. This allows the conclusion when the temperature in the upper part of the ladle drops below 650°C which was defined as end-point for speiss solidification. On the other hand, the temperature within the crude lead phase was measured, as well.

Figure 11. Experimental setup for field test work to measure the cooling curve for a ladle filled with metal with minimized amount of floating matte on top

RESULTS

In Figure 12 the temperature curves measured in the metal ladle are plotted over the period time of cooling. Both zones show a similar trend of the curve starting at approx. 800 to 850°C. This means a decisive drop of temperature in comparison to the pouring temperature (1,150°C). In between there was the pouring of the metal into the larger ladle followed by pouring into “overflow launder” ladle. After the last remaining matte was flushed to the next ladle the pouring was stopped. This whole sequence required approx. 30 min. Furthermore the thermocouples were protected with steel tubes which slows down the initialization of the measurement. Those are the reasons for the gap of pouring temperature and recorded “initial” temperature. However, this means that the cooling rate was calculated for the mentioned initial temperature to the target point of speiss solidification (650°C). A significant decrease of cooling rate by 43% (compared to the example shown above, Figure 8) could be calculated. The defined average cooling rate could only be approached to the given specification of the experimental setup and will be effected by the selected ladle geometry (surface/volume-ratio), initial temperature of the melt, thickness of remaining matte phase floating on top and the position of the thermocouples itself.
From the described test work, the extracted speiss crust was sampled and investigated with the help of a SEM analysis. The two samples are differentiated in a bottom part (means speiss body) and an upper part (means crust above). With the help of this characterization work the success and improvement potential of the phase separation was evaluated.

Figure 13 represents a selected frame of a sample from the speiss body (bottom part) and compares the results of assays given by a SEM investigation (red frame) and a XRF measurement for the whole sample.

Table:

<table>
<thead>
<tr>
<th>Element</th>
<th>SEM Wt%</th>
<th>XRF analysis Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Fe</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Ni</td>
<td>5.9</td>
<td>5.7</td>
</tr>
<tr>
<td>Cu</td>
<td>41.2</td>
<td>42.1</td>
</tr>
<tr>
<td>As</td>
<td>11.8</td>
<td>11.0</td>
</tr>
<tr>
<td>Sn</td>
<td>8.4</td>
<td>7.1</td>
</tr>
<tr>
<td>Sb</td>
<td>7.8</td>
<td>6.1</td>
</tr>
<tr>
<td>Pb</td>
<td>20.5</td>
<td>22.4</td>
</tr>
<tr>
<td>Bi</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Rest</td>
<td>1</td>
<td>0.7</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>99.2</strong></td>
<td><strong>99.3</strong></td>
</tr>
</tbody>
</table>

In comparison to the done XRF analysis the result from the SEM is very close and could be seen as representative for the selected frame on the sample. As already indicated the speiss consists of many phases which show characteristic shape and color. The dominant grey particles (spectrum 172 and 173) represent...
metallic lead which are marked as area 1 in Table 3. The area 2 (spectrum 167-171) shows the composition of the speiss areas without any entrained matte or Pb droplets.

In Figure 13, some dark grey rims could be identified as separate phases. Spectrum 174-177 (area 3) specifies matte with the main compound Cu\(_2\)S with 74.2 wt% Cu and 19.3 wt% S (stoichiometric Cu\(_2\)S with 80% Cu and 20% S).

<table>
<thead>
<tr>
<th>Area/Phase</th>
<th>Wt% Cu</th>
<th>Wt%Fe</th>
<th>Wt%Ni</th>
<th>Wt%Pb</th>
<th>Wt%S</th>
<th>Wt%As</th>
<th>Wt%Sb</th>
<th>Wt%Sn</th>
<th>Wt%Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3-0.8</td>
<td>-</td>
<td>-</td>
<td>92-93</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>49.2</td>
<td>0.9</td>
<td>11.5</td>
<td>0.6</td>
<td>18.2</td>
<td>9</td>
<td>10.1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>75.7</td>
<td>0.9</td>
<td>-</td>
<td>0.7</td>
<td>19.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Based on this analysis, the following findings for the bottom part of the speiss crust can be noted:

- The major share of the surface is represented by a phase which could be identified as speiss based on a mixture of Arsenides, Antimonides and Stannides associated with Cu and Ni. The Pb concentration within this phase is negligible what proves the conclusion of the available literature.
- Within the identified lead phase more or less only Bi and Ag could be measured. The limited solubility for Cu is expressed with a measured concentration from 0.3 to 0.8 wt%.
- Furthermore a separate phase could be measured which is very close to a pure Cu\(_2\)S or a white metal composition. This phase crystalizes as rims or as thin stalks. Pure white metal has a melting point of 1,130°C which will mean a prior crystallization during cooling period (phase separation).
- Hypothetically spoken those pure white metal droplets could be a key parameter which blocks the settlement of metallic Pb droplets.

In analogy to this mechanism the entrainment of matte droplets in speiss or vice versa will be discussed with the help of the Figure 14. Therefore the sample from the upper part was characterized in the same way like for the bottom part.

![Elektronenbild 22](image)

Figure 14. SEM recording of a dedicated area of sample – upper area; mean values for the phases: Cu-Fe-S, Cu-Fe-Pb-S and Fe-rich speiss particles

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>CuPb matte particle in white dendrites</th>
<th>2</th>
<th>Fe-rich speiss particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>24.6</td>
<td>15.3</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>12.6</td>
<td>4.8</td>
<td>13.8</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.1</td>
<td>0.3</td>
<td>20.2</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>60.2</td>
<td>23.2</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.3</td>
<td>b.d.</td>
<td>41.9</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>0.4</td>
<td>1.2</td>
<td>b.d.</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>b.d.</td>
<td>b.d.</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>b.d.</td>
<td>b.d.</td>
<td>8.6</td>
<td></td>
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<tr>
<td>Te</td>
<td>0.3</td>
<td>0.8</td>
<td>b.d.</td>
<td></td>
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<tr>
<td>Pb</td>
<td>0.4</td>
<td>54.4</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>1.2</td>
<td>b.d.</td>
<td>b.d.</td>
<td></td>
</tr>
</tbody>
</table>

**Total** 100 99.3 96.4
The microstructure in Figure 14 varies from Figure 14 (speiss crust bottom part). The XRF analysis of the upper layer sample shows a Fe content of approx. 10 wt% which is very high in contrast to the bottom area (0.8 wt% Fe). All in all it can be stated that this kind of structure is a part of the matte which solidifies on top of the speiss.

The SEM investigations show that Fe is reporting to matte and speiss. A low grade matte phase was identified by the spectrum 162 (white phase with dark dendrites) but one has to keep in mind that the SEM show also superimposed structures e.g. a metallic lead phase and a matte droplet which will effect the assay. According to this the Pb amount is with 54 wt% very high and the Cu content comparable low (23.2 wt%). The matrix of the sample is formed by a matte which contains CuS and FeS (spectrum 155, 156 and 163-165). Vice versa also a speiss phase could be identified (spectrum 157 and 158) those composition shows a very high As content of up to 42 wt%. Furthermore significant amounts of Ni and Fe, as well as Sb and Sn are part of the speiss phase.

Based on this analysis the following findings for the upper part of the speiss crust can be noted:

- On the one hand the speiss phase contains entrained particles of matte but on the other hand also speiss particles are measured in the matte phase.
- The Fe and S content could be used as an indicator, how much matte particles are entrained in the speiss. The matrix of the matte which is present in the electric furnace is dominated by CuS-FeS and PbS as well. This is reflected by the measurement which was discussed with the help of Figure 14. Despite the high effort to be sure that all the matte is removed via an overflow launder, a certain amount of floating matte on top of the speiss could be measured.
- Speiss in matte phase can have a different composition than the one which is crystallized below.

As a criteria for the success of phase separation the amount of entrained matte in speiss was estimated based on the analysis for Cu and Fe and the assumption that the S in the speiss is mainly associated with Cu or Fe. Because of the excess of Cu (which is able to form intermetallic compounds) the calculation was started with the assumption that all the Fe is present in form of FeS. The remaining amount of S was distributed to Cu to form CuS. The data for the following diagrams is generated by analyzing six ladles via XRF and classification into the dedicated areas (top, center, bottom). The left diagram in Figure 15 shows the portion of S bound on Cu and the Cu which remains as “free” Cu, whereas the right diagram explains the distribution of S on Cu, Fe and Pb. It can be noted that in the top layer a higher share of S is bound on Fe than in the other zones and the share of Cu which is associated with S is even higher which supports the made observations that not all of the matte could be separated and the amount of entrained matte particles is higher in the upper layer of the speiss. Taken all S, Fe and Cu (associated with S as CuS) into account, this will lead to a prediction for the mass of entrained matte in speiss. The result of this view is displayed in Figure 16 and shows the dependency between density-based separation of matte particles and speiss due to the cooling process.

![Figure 15. Calculation of Cu and S distribution in speiss crust depending on the selected layer of crust](image-url)
It becomes obvious that not only an increase of metallic Pb droplets (insufficient settling) will lead to a dilution of the speiss, also the increase of entrained matte droplets have an impact on the speiss mass and the concentration level of minor elements. If the ultimate goal is to use the speiss as collector for instance for As and Ni it would be essential to optimize the phase separation process and adjust the feed mix in the furnace to address a minimization of Cu which is not bound on S to avoid that the formation of intermetallic compounds on Cu base is governed. Also the control of the reduction potential within the electric furnace is key to avoid the presence of major amounts of metallic Fe which are also able to form intermetallic compounds, most likely with As.

CONCLUSIONS

In the present paper the phase separation process of Aurubis secondary smelter was explained and it’s importance for the target products. The separation of a complex matte phase and metal phase which will be further separated along the cooling in a crude lead and speiss phase effect the downstream processes in terms of achievable metal recovery, processing time and finally availability.

Because of the broad range of compositions for those complex phases it is hard to interpret the available literature correctly and draw the right conclusions to optimize the current and often tailor made solutions for the existing complex metallurgy smelters. This complexity is further increased by operating with various feed mixes which will end up in different composition of matte and metal and consequently different crystallization behavior.

The phase characterization reflected key pillars of published literature and draw a comparison to the recent one which was issued by Ettler (2009) who constructed a crystallization sequence and the fundamentals reported from Kleinheisterkamp (1948). A high temperature microscopy defined the melting area of a typical production speiss sampled within Aurubis secondary smelter.

The performed testwork showed the potential to minimize the amount of entrained matte in speiss and provided an explanation of the high Pb content of a speiss alloy. For obvious reasons there seems to be a link between a satisfying matte separation prior to the cooling of metal which will lead to a speiss phase with less amount of matte particles (represented by lower amounts of Cu, Fe and S). The Pb content would be decreased due to a suitable cooling time which governs the settling of the droplets. A recommended cooling rate will be < 200 K/hr (depending on initial temperature and the point where the solidification of speiss is reached).

This part of the process is not covered very well by thermodynamic calculations. A continuous improvement of databases will allow to improve the understanding how the speiss solidification is effected by formation of sulfide or intermetallic compounds.
The implementation of the gathered knowledge in the operations will also contribute to the multi metal recovery approach by steering the main metals and minor elements in the right way allowing to concentrate them in the right carrier phases (Cu and Pb). Based on that the connection between the smelter and the refinery could be improved which will govern the multi metal recovery capability and ensure efficient processes.

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REFERENCES


