Experimental investigation and modelling of microstructure and phase composition of the copper smelting slags

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EXPERIMENTAL INVESTIGATION AND MODELLING OF THE MICROSTRUCTURE AND PHASE COMPOSITION OF COPPER SMELTING SLAGS

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ABSTRACT

Effective extraction of copper from sulphide ores requires careful operation of a copper smelter, which in turn depends very much on the chemistry of the feed and the resulting slag and matte. For example, the chemical composition of copper smelting slags has to be within a certain range to ensure that their properties are within specific limits. Disobeying these rules may lead to complications in smelting operation, poor quality of the copper products, and premature shutdown of the copper smelter.

In the present paper the microstructure and phase composition of slags from the Almalyk copper flash smelter were investigated experimentally and then modelled to evaluate potential ways of improvement and optimisation of the copper smelting process and its products. The slag samples were taken at different stages of the copper smelting process. Experimental investigation included the XRD, XRF and SEM techniques, which were also confirmed by the traditional wet chemistry analysis. Modelling was carried out using thermochemical software package MTDATA, which enables thermodynamic and physical properties of the matte, slag and gas phases to be calculated in a wide range of temperatures, pressures and chemical compositions.

It was found that the copper content in the slags may vary significantly depending on the location of slag sampling. Analysis of the microstructure and phase composition showed that major phase found in the samples is fayalite, while other phases are complex spinels, different sulphides and an amorphous phase. Thermodynamic calculations demonstrated the presence of these phases, their compositions and optimal ranges of operating conditions. Potential ways for improving the matte grade and optimising the smelting process were suggested on the basis of the calculations.

INTRODUCTION

A number of metallurgical plants utilise a flash smelting process (Outotec or Inco) in the extraction of copper from sulphide ores. In this continuous process fine particles of the Cu-Fe-S concentrate, SiO₂ flux and O₂ (or air) are fed into a hot (1200-1300°C) smelting furnace, where the sulphide particles react rapidly with oxygen, thereby converting sulphur into SO₂ gas and producing molten matte and slag.

The matte phase consists mostly of Cu-Fe sulphides, while the major components of the slag phase are FeO, Fe₂O₃, and SiO₂, with small additions of other oxides like Al₂O₃, CaO etc. Furthermore, the percentage of ferrous oxide in slag is much greater than that of ferric oxide, because the oxygen potential in the slag is normally very low. The copper smelting slags are
usually referred to as the fayalite slags, since fayalite (Fe₂SiO₄) is one of the main phases crystallised on cooling. However, as found in the present paper, even within a single smelter the slag composition can change significantly during its operation depending on the feed quality, and composition and smelting conditions.

The essential goal of a matte smelting process (such as flash smelting) is to recover as much Cu from the concentrate into the molten matte as possible. The matte grades (the Cu percentage) can vary depending on the Cu content in the original ore and on the type and operating conditions of the smelting furnace. Poor extraction of copper from the concentrate leads to significant copper losses with slag wastes (e.g. 2). To reduce copper losses a detailed understanding of the matte-slag chemistry is necessary.

In the present work a number of slag samples taken from different stages of an Inco flash smelting process located at Almalyk (Republic Uzbekistan) were investigated experimentally by conventional microstructure and analytical techniques and theoretically by the computational thermodynamics method to achieve better understanding of the process and to evaluate possible ways for process improvement and reduction of copper losses.

Ten slag samples were taken from different steps of the Almalyk flash smelter process: at the slag deposition site, during the slag tapping and from the crust formed at the bottom of a slag ladle while being transported to a deposition site. These slag samples were analysed by the X-ray diffraction (XRD), light and scanning electron microscopy (LM and SEM), X-ray fluorescence (XRF) and wet chemistry methods and were modelled using the thermodynamic software MTDATA 3. In the present paper the results of the experimental study and modelling are presented and discussed.

**EXPERIMENTAL**

**X-ray diffraction**

The XRD analysis was carried out on a D8 Discover X-ray diffractometer (Bruker-AXS, Germany). The X-ray 1.6kWt tube with a copper anode was taken as an X-ray source. Parallel beam with a divergence 0.03° was formed by a Goebel mirror. The width of an X-ray beam was 0.2 mm. Reflected beam intensity was measured with a position sensitive detector LynxEye (angular resolution 0.015°). In front of the detector a Ni filter was installed. In order to reduce the X-ray fluorescence influence (samples contain significant amounts of iron) the detector's discriminator window was narrowed, thus improving the signal-to-noise ratio. The measurements were carried out using the 2θ-ω scheme.

The average measurement time to obtain one diffraction pattern is about 6-7 hours. The background from a quartz glass substrate (sample holder) was first subtracted from the diffraction pattern. Then the phase analysis was performed with the EVA software and database ICDD PDF-2 2004 4.

**X-Ray Fluorescence and Wet Chemistry Analysis**

The X-Ray fluorescence analysis was carried out with a X50 Mobile spectrometer in order to measure the amount of copper in each sample. At first, small amounts (around 15 grams) of each sample were ground in a ring vibratory Herzog H100 using a tungsten carbide mortar. The analysis was carried out simultaneously with three X-rays: a 50 kV tube (for heavy elements), 35 kV (for transit metals) and 15 kV (for light elements). The instrument provides results between 0
to 1% - up to 4 decimal places, in excess of one percent - up to two. For each sample three parallel measurements were carried out.

The Cu content in the slag samples was also verified by a traditional wet chemistry analysis that was based on titration of iodine by a sodium thiosulphate solution. This method is also called the iodometric titration or iodometry and can be used for a precise determination of the Cu amount from 0.05 to 60 wt pct.

**Light and Scanning Electron Microscopy**

Light microscopy was employed to obtain a general view of the sample structure, porosity and approximate sulphide particle size and distribution using a metallographic Olympus GX71F-5 microscope with the magnification from 12.5 to 1000 times.

Microstructure investigation was carried out with an electron scanning microscope TESCAN VEGA LMH (with LaB$_6$ cathode) equipped with an X-ray EDS microanalysis system “Advanced AZtecEnergy” by Oxford Instruments. Prior to the SEM EDS analysis the slag samples were mould into an epoxy resin, polished and covered with a carbon film to provide electrical conductivity.

**Thermodynamic Calculations**

Chemical equilibrium in the "matte-slag-gas" system was calculated with the elemental chemical compositions obtained by the SEM EDS analysis using the MTDATA software 3 and NPLOX database (National Physical Laboratory, UK). The oxygen content was balanced on the basis of the assumption that all the elements except sulphur are present in the slag phase as most stable oxides.

**RESULTS AND DISCUSSION**

**Chemical analysis of the slag samples**

The average chemical composition of the slag samples was determined by the SEM element mapping and is shown in Table 1 (the oxygen content is balanced to 100 at %). The mapping area was a square typically with a side of 0.5-1 mm, so the investigated area of a sample was about 0.3-1 mm$^2$. All elements of the periodic table heavier than Li were identified in the mapping spectra. Samples 1-8 were taken from the slag deposition site, samples 9 (A, B and D) were from the ladle bottom crust (from different zones), and sample 10 was taken on slag tapping.

The normalised slag chemical compositions plotted on the MeO-FeO-SiO$_2$ pseudo-ternary diagram, where MeO is a sum of all other oxides (Al$_2$O$_3$, CaO, MgO etc), are shown in Figure 1. It was assumed for simplicity that the Fe$_2$O$_3$ content in the slag phase is negligible, so all iron can be represented as ferrous oxide. The ratio of FeO/SiO$_2$ corresponding to the fayalite composition is showed as a dotted blue line. It can be seen from this figure that only 3 slag samples (4, 6 and 9) could be considered as a true fayalite slag (i.e. with the SiO$_2$/FeO ratio around 1/2). Samples 1 and 5 are close enough to the demanded ratio, but samples 2, 7 and 10 contain SiO$_2$ greater than 50 molar pct. Samples 3 and 8 lie in-between.

It should also be noted that the SEM EDS analysis cannot determine the oxidation state of iron in the slag, and other methods should be used to distinguish between ferrous and ferric iron. In the
present work, where it was possible, phase determination by SEM EDS was corrected according to the XRD results.

Table 1. The chemical composition of the slag samples, at %

<table>
<thead>
<tr>
<th>##</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Ba</th>
<th>Pb</th>
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<td>15.21</td>
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<td>1.60</td>
<td>0.12</td>
<td>0.02</td>
<td>0.17</td>
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<td>0.38</td>
<td>0.44</td>
<td>0.05</td>
<td>0.03</td>
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<td>4.21</td>
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<td>0.47</td>
<td>1.32</td>
<td>1.17</td>
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<td>0.1</td>
<td>12.20</td>
<td>0.74</td>
<td>0.36</td>
<td>0.05</td>
<td>0.11</td>
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<td>4.69</td>
<td>17.00</td>
<td>0.63</td>
<td>1.10</td>
<td>1.32</td>
<td>0.15</td>
<td>0.00</td>
<td>0.13</td>
<td>16.00</td>
<td>0.21</td>
<td>0.87</td>
<td>0.00</td>
<td>0.08</td>
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<td>0.00</td>
<td>2.52</td>
<td>12.30</td>
<td>1.11</td>
<td>1.21</td>
<td>0.89</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>26.25</td>
<td>0.71</td>
<td>0.23</td>
<td>0.00</td>
<td>0.03</td>
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<td>5</td>
<td>0.00</td>
<td>4.84</td>
<td>18.98</td>
<td>1.04</td>
<td>1.33</td>
<td>1.37</td>
<td>0.25</td>
<td>0.00</td>
<td>0.03</td>
<td>14.48</td>
<td>0.22</td>
<td>0.36</td>
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<td>6</td>
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<td>2.18</td>
<td>6.09</td>
<td>11.70</td>
<td>0.36</td>
<td>0.28</td>
<td>0.06</td>
<td>0.00</td>
<td>0.00</td>
<td>29.60</td>
<td>6.23</td>
<td>0.57</td>
<td>0.00</td>
<td>0.18</td>
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<td>7</td>
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<td>30.2</td>
<td>0.70</td>
<td>1.53</td>
<td>0.59</td>
<td>0.07</td>
<td>0.01</td>
<td>0.02</td>
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<td>0.14</td>
<td>0.07</td>
<td>0.02</td>
<td>0.04</td>
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<td>4.12</td>
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<td>0.50</td>
<td>1.57</td>
<td>1.00</td>
<td>0.21</td>
<td>0.10</td>
<td>0.06</td>
<td>15.40</td>
<td>0.26</td>
<td>0.38</td>
<td>0.04</td>
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<td>4.43</td>
<td>30.04</td>
<td>0.4</td>
<td>1.68</td>
<td>1.06</td>
<td>0.18</td>
<td>0.00</td>
<td>0.05</td>
<td>14.07</td>
<td>0.25</td>
<td>0.21</td>
<td>0.00</td>
<td>0.00</td>
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<td>9B</td>
<td>0.00</td>
<td>2.7</td>
<td>20.8</td>
<td>0.7</td>
<td>1.0</td>
<td>0.5</td>
<td>0.1</td>
<td>0.00</td>
<td>0.1</td>
<td>22.5</td>
<td>1.2</td>
<td>0.3</td>
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<tr>
<td>9D</td>
<td>0.00</td>
<td>4.1</td>
<td>27.1</td>
<td>0.9</td>
<td>1.3</td>
<td>2.0</td>
<td>0.2</td>
<td>0.00</td>
<td>0.1</td>
<td>11.3</td>
<td>0.3</td>
<td>0.2</td>
<td>0.00</td>
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<td>3.10</td>
<td>25.4</td>
<td>0.30</td>
<td>1.30</td>
<td>0.70</td>
<td>0.20</td>
<td>0.00</td>
<td>0.00</td>
<td>14.50</td>
<td>0.50</td>
<td>0.30</td>
<td>0.00</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Figure 1 – Pseudo-ternary diagram of the MeO-FeO-SiO₂ (mol %)

The amount of copper determined by the SEM EDS element mapping, XRF and wet chemistry methods is shown on the Figure 2. Since wet chemistry and XRF methods are considered to be more accurate in terms of quantitative analysis, all of the analyses related to Cu content relies on data obtained with these methods, and SEM EDS data is given for comparison. It can be seen from the graph that the Cu amount in the slag samples from the deposition site varies significantly, from 0.45 up to 7.98 wt %. Compared to the amount of copper in the sample from tapping, there are 3 samples with a higher percentage of Cu and 5 with a lower percentage. The average amount of copper in these samples is 1.9 wt %. It should be mentioned that XRF and titrimetric analysis of the sample no. 9 (ladle bottom) was done only for the whole sample (9A + 9B + 9D, in unknown proportions), so the results showed in Figure 2 are average and cannot be compared with the SEM results.
It can also be seen from Figure 2 that the SEM EDS method provides values of the Cu amount comparable with those by the XRF and titrimetric methods for most of the samples.

The following sections provide results of the microstructure analysis divided into three groups, depending on the sampling location: on slag tapping (sample no. 10), at the deposition site (samples nos. 1-8) and from the ladle bottom (sample no. 9).

**Slag sample from tapping**

Slag samples taken during slag tapping are usually quenched into water right after they have been collected; therefore these samples are likely to be the closest to the original state, in which the molten slag phase is inside the smelting furnace. Figure 3 represents a typical picture of a slag sample (no. 10) taken during slag tapping and quenched thereafter.
Figure 4 shows a light optical microscopy image of slag no. 10. Fine sulphide particles formed apparently during rapid cooling can be seen as bright dots.

![Slag sample no. 10](image)

**Figure 4 – Light optical microscopy image of the slag sample no. 10**

Despite a lot of noise the XRD pattern (Figure 5) showed strong, distinctive peaks (marked in blue) that can clearly be identified as the fayalite ($\text{Fe}_2\text{SiO}_4$) phase. Other peaks are less distinctive, rather broad and small, and cannot conclusively be analysed. Some of these peaks (marked in red) may be attributed to a magnetite-like phase (e.g. $\text{Fe}_3\text{O}_4$) with other atoms (e.g. Al, Mg, etc) introduced into the structure. Formation of the magnetite phase is typical for copper smelting slags (e.g. 1, 5).

![XRD graph for the slag sample no. 10](image)

**Figure 5 – XRD graph for the slag sample no. 10**
The SEM EDS analysis revealed at least two different regions in the slag: a region with the average Fe:2Si stoichiometry (probably FeSi$_2$O$_3$) and a copper sulphide phase with the approximate Cu$_2$S stoichiometry. The former phase appears to be a mixture of two regions differing by the backscattered electron contrast (one is brighter, other is darker), although the EDS spectra of each of these regions are nearly identical. The latter phase consists of scattered spherical particles with the diameter varying from 0.1 to 200 μm. It can be assumed based on the XRD results that the fayalite crystals are very small and scattered in a matrix (a glassy phase) and cannot be detected with the SEM EDS analyser.

It can be seen from the light optical microscopy image (Figure 4) that most of the Cu sulphide particles are very fine (<1 μm). These particles were likely to be dissolved in the slag and precipitated during rapid cooling. However, bigger particles, which are also present in the sample, are likely to be entrained matte droplets.

![SEM EDS image and element mapping](Figure 6 - Sample from tapping phase composition)

Figures 6-7 depicts the SEM EDS image and element mapping of an area about 0.4 mm$^2$ for the slag sample no. 10. It could be seen that the sample looks fairly uniform, which may indicate that crystals are very fine or the sample is in the amorphous state.

Equilibrium crystallisation calculated by MTDATA is shown on Figure 8. It can be seen that at high temperatures the sample consists only of one liquid (slag) phase with dissolved Cu. A small amount of the other liquid (sulphide) phase appears at ~1500°C and crystallises at ~1160°C. The liquidus temperature of the slag phase is around 1300°C; at this temperature the tridymite (SiO$_2$) phase starts to form. The second phase to crystallise out of the liquid slag is fayalite (Fe$_2$SiO$_4$). However, since the actual slag sample was rapidly quenched, the tridymite phase has not been formed and a glassy phase may have been formed instead. As indicated above fine crystals of the fayalite phase may have still been precipitated out of the slag or glass phase.
As indicated above the liquid sulphide (or matte) phase is stable down to ~1160°C, which implies that Cu sulphide particles were liquid during the rapid solidification. The amount of the Cu sulphide phase is rather small and apparently cannot be detected by XRD.
Slag samples from the deposition site

Eight slag samples were taken from the slag deposition site. The samples were picked up at random from the surface of the recent slag deposit over the area of several square metres. Figure 9 represents a typical picture of these samples. All the samples are porous, have different colour of the surface depending on the average composition (red for iron oxide, blue spots for copper oxide, etc.)

![Sample 1, Sample 2, Sample 5](image)

Figure 9 - Some of the slag samples taken from the deposition site

The light optical microscopy image of sample 3 is shown in Figure 10 as an example of typical slag microstructure. Big irregular pores as well as bright sulphide particles can be observed in the sample.

![Typical slag structure (sample no. 3)](image)

Figure 10 - Typical slag structure (sample no. 3)

A typical XRD pattern for the deposition slag (sample no. 5) is shown in Figure 11. It reveals mainly the fayalite (blue) and magnetite (red) phases. It can be seen from Figure 11 that other
phases are also like to be present, but their exact composition cannot be detected because peaks are very small and indistinctive.

![Figure 11](image.png)

**Figure 11** – A typical XRD pattern (sample no. 5)

A summary of the phases found in the samples using the SEM EDS analysis is given in Table 2. Most of them consist mainly of fayalite, copper and iron sulphides and iron oxides; the latter was assumed to be a magnetite-like phase. The field “Other” represents complex oxide and sulphide phases found only in one of these samples (sample 1 - Fe₂Al₂(SiO₄)₃, sample 6 - KAlSiO₆, FeSiO₂, Fe₃Zn₂PbS₆, sample 7 - SiO₂, FeSO₄, sample 8 - (Cu,Fe)₄S₄).

**Table 2** - The phases found in the samples 1-8 by SEM EDS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe₂SiO₄</th>
<th>CuS/Cu₂S</th>
<th>FeO/Fe₂O₃/Fe₃O₄</th>
<th>FeS/FeS₂</th>
<th>Other</th>
</tr>
</thead>
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<td></td>
<td></td>
<td></td>
<td>*</td>
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<td>8</td>
<td>*</td>
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</tbody>
</table>

An example of evaluation of the phase composition using the SEM EDS phase mapping is given in Figures 12 (a-b). Different phases are marked by different colours, and their average spectra determined by SEM EDS are listed in Table 3. The amount of fayalite (denoted in Table 2 as “FeO-Si”) is found to be 75.2 % of the picture area. Also, a phase called “glass” (denoted as “FeSiO”) was observed in between big fayalite crystals (dark areas in Figure 12 (b)). Its composition is rich in SiO₂, and it contains substantial amounts of other elements (Fe, K, Al, Ca). Since this phase was not detected in the XRD spectrum, despite its significant amount (12.4 % of the sample area), it was assumed to be a glassy phase. The next phase called “Complex Sulphides” represents different sulphides observed in the sample. It can be seen that determination of the magnetite phase (denoted as “FeO”) is most difficult (it can be seen only in
Figure 12 (a) as bright scattered crystals of irregular shape, but sulphide phases are clearly visible on both Figures 12 (a) and (b).

![Figure 12](image)

Table 3 – The phase composition by SEM EDS for sample 4

<table>
<thead>
<tr>
<th>Phase</th>
<th>Marked</th>
<th>%</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fayalite</td>
<td>FeOSi</td>
<td>75.2</td>
<td>Bal.</td>
<td>1.16</td>
<td>13.87</td>
<td>0.25</td>
<td>0.48</td>
<td>0.49</td>
<td>27.8</td>
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<td>0.2</td>
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<tr>
<td>Glass</td>
<td>FeSiO</td>
<td>12.4</td>
<td>Bal.</td>
<td>5.9</td>
<td>16.56</td>
<td>0.86</td>
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<td>2.17</td>
<td>12.6</td>
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<td>0.21</td>
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<td>0.33</td>
<td>16.5</td>
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<td>Bal.</td>
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<td>0.36</td>
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</tbody>
</table>
Elemental mapping done for the same sample area is given in Figures 13. The magnetite phase can be evaluated by comparison the Si and Fe maps. On the Si map the magnetite crystals are dark, while on the Fe map these areas are brighter than the rest of the map. It can be seen that the percentage of the magnetite phase is much greater than that determined by the phase mapping (Table 3). As a result, the fayalite percentage should be less than determined in Table 3.

Figure 13 – Element mapping of the same area of sample 4

Figure 14 represents a typical microstructure found in the sample no. 7. This sample contains significant amount of SiO₂, most likely undissolved flux particles, which can be seen in Figure 14. Phases marked as A and B are complex silicate phases with the following approximate compositions (determined by SEM EDS): \( \text{Si}_{23}\text{Fe}_{13}\text{Al}_6\text{Ca}_2\text{MgKO}_{69} \) and \( \text{Si}_{25}\text{Fe}_7\text{K}_2\text{Al}_4\text{MgCaO}_{68} \), respectively.
Examples of the equilibrium crystallisation curves calculated for the slag samples 2 and 4 are shown in Figures 15 and 16, respectively.

Figure 14 – Example of microstructure for sample 7

Figure 15 - Equilibrium crystallisation of sample no. 2
Sample no. 4 represents a “true fayalite” slag and the sample no. 2 is richer in SiO$_2$ content (see Figure 1). It can be seen that during equilibrium crystallisation the first phase that precipitates out for the sample 2 is the SiO$_2$ phase (tridymite). Fayalite is present in both samples, but sample 4 consists of more than 60 wt % fayalite at room temperature. Other predicted phases include two spinel-like phases: first with Zn, second with Ti. For both samples 2 and 4 the liquid sulphide phase precipitates out of the liquid slag at high temperatures (ca. 1700 and 1900°C, respectively).

Generally, the equilibrium calculations for the sample no. 4 are in good comparison with the phase composition determined by the SEM EDS method (see Table 3). The calculated amount of fayalite is over 60 wt %, which is close to that determined by SEM EDS. The predicted sulphide phase content (digenite, chalcopyrite and pyrrhotite at low temperatures, and liquid sulphide at high temperatures) is also close to the experimentally determined value (Table 3).

The behaviour of minor elements such as Pb, Zn, Ti, etc in the slag samples was also analysed using the SEM EDS analysis. Pb was found only in a sulphide phase (e.g. Figure 17) in contrast to 1, where it was reported that around 20 % Pb should go into the slag phase, while Zn was found to be present mainly in fayalite and also in sulphide phases (Figure 17). The distribution of Pb and Zn was confirmed by thermodynamic calculations.

Ti and Cr was found to be present only in the magnetite phase, a spinel-type phase; this was also confirmed by thermodynamic calculations. In a number of samples Mo was found to be associated with a sulphide phase, while As, Ba, Mn were found to be present in the slag phases (e.g. fayalite, glassy phase, etc).
Slag from the ladle bottom

The slag sample no. 9 was taken from the crust formed at the slag ladle bottom. This so called bottom crust is formed during slag pouring into the ladle and further transportation of the ladle to the slag deposition site by train.

Four zones can be distinguished on the cross-section (Figure 18) from the bottom to the top: zone “D” is adjacent to the ladle bottom steel wall; two zones marked “B”, identical in chemical composition and microstructure, are highly porous, found to be rich in sulphides and separated by the interface “C”; zone “A” is a part of the bulk slag. Each zone was investigated separately to obtain information on its microstructure, phase composition and amount of copper.

The zone A of the sample 9 is a top area in the cross-section, the most distant from the ladle bottom. Typical microstructure of this zone is given in Figure 19. Between dendrites of fayalite the SiO₂-rich slag (with SiO₂ ~ 80 mol %) can be observed. The magnetite phase with dissolved Al and Ti marked as “FeO” in Figure 19 can typically be seen in this zone as big crystals of fairly geometrical shape. The amount of copper in the zone A detected by SEM EDS is 0.6-0.7 wt %. 

Figure 17 – Example of Pb and Zn sulphides present in the slag sample 3
Figure 18 – Cross-section of sample 9

Figure 19 – Microstructure of A-zone
The interface between zones A and B is shown in Figure 20. It can be seen that the interface is very thin (few \( \mu \text{m} \)) and also was found to be very brittle.

The elemental mapping for Cu, Fe, K, S, and Si is shown in Figure 21. Figures 22 illustrates the distribution of Fe, Cu, Si, Al, and S across the zones A and B scanned along the line marked on the micrograph. Zone A is richer in Si and Al, but depleted in Fe. It can also be seen that there is a sub-zone within the zone B with a higher amount of copper and sulphur.

![Figure 20 – The A-B interface](image1)

![Figure 21 – Elemental mapping of the A and B zones interface](image2)
These figures clearly demonstrate that in zone B (the right-hand side of the pictures) the amount of S, Cu and Fe is greater than in zone A (left-hand side). It can be seen that sulphides are present as small rounded particles.

Figure 22 - Elements distribution in the A-B interface
The B zones are formed in the middle of the bottom crust. These zones are more porous than the A and D zones and have a different colour from the others. As it can be seen in Figures 20-22 the zone is not uniform in the vicinity of the interface. A typical microstructure of this zone far from the interface is given in Figure 23. The average amount of copper in this zone was found to be 2.8 wt %.

Zone C is an interface zone in the middle of two B zones. The phase composition from both sides of the interface is similar, but the size of crystals is significantly smaller. The interface itself consists mostly of iron oxide, most probably Fe₂O₃, with inclusions of sulphides. It is not quite clear how this interface line was indeed formed; perhaps the reason lies in the exact procedure and timing of pouring liquid slag in the ladle. A small part of molten slag could have been poured into the ladle, crystallized from being in contact with oxygen from the atmosphere, and then the rest of the slag was poured. This could explain the oxide film layer and the smaller grain size. The width of the iron oxide interface is significantly larger than that of the A-B interface and is about 20 μm.

Figure 23 – Microstructure of the zone B
The zone D of the sample is closest to the ladle steel bottom. Due to a high cooling rate it solidifies very rapidly and is very disperse. It can be seen from Figure 25 that the fayalite crystals are indeed very fine. The amount of copper in the zone D determined by SEM EDS is 0.07 wt %.

Microstructure investigation revealed that the bottom crust is actually formed in several steps. First of all, zone D is formed as the slag starts to be poured into the ladle. Because of the high temperature gradient it is solidified immediately and forms a quenched layer of slag. When the ladle is filled with the rest of slag, sulphides previously dissolved in the slag precipitate out on
cooling. With time sulphide droplets settle down to the ladle bottom, solidify and formed the zone B, rich in copper and sulphur. While the ladle is being transported to the deposition site, the process of sulphide settling is promoted by gravitation and vibrations of the carriages. As the crust formed the slag adjacent to it may remain liquid. The origin of the solid interface between two zones B is not certain.

**Reduction of copper losses**

Analysis of the slag samples collected at the Almalyk copper smelter showed that the copper content in slag samples may vary significantly depending on numerous factors. While the slag samples obtained on tapping may contain an amount of copper that is acceptable for effective smelter operation (e.g. around 1 wt %), the slag from the ladle bottom can have very high copper content (2-3 wt %) due to segregation of the sulphide phase from slag.

Apparently the major source of copper losses lies in the formation of the so called bottom crust during slag tapping and transportation to the deposition site. The bottom crust formed is rich in the sulphide phase (and consequently, copper) and stems from the segregation of sulphides from the liquid slag phase. The matte-slag separation is a core of the copper smelting and is governed generally by the thermodynamic driving force, difference in specific gravity of the slag and sulphide phases and such properties of the liquid slag like viscosity and surface tension. Since the separation process cannot be avoided completely, the only way to reduce copper losses in a slag ladle is essentially to enhance sulphide segregation inside the furnace.

There are not many parameters of the process that can be tuned to enhance the matte-slag separation in the smelter. It can be seen from thermodynamic calculations that the onset temperature of precipitation of the liquid sulphide phase can vary significantly depending on the slag composition. Specific gravity decreases with increasing Fe content in the sulphide phase, which in turn reduces the matte grade and therefore is not desirable. Viscosity and surface tension of the liquid slag can also be adjusted using slag additives like SiO₂, CaO etc.

However, since the segregation process in a slag ladle cannot be stopped entirely, to minimise copper losses the bottom crust should be collected and recycled.

**CONCLUSIONS**

In the present paper the microstructure and phase composition of slags from the Almalyk copper flash smelter were investigated experimentally by different methods (light optical microscopy, XRD, SEM, and XRF) and then modelled to obtain detailed understanding of the copper smelting process and to evaluate potential ways of its improvement. The slag samples were taken at different stages of the Almalyk copper smelting process.

It was found that the copper content in the slags may vary significantly depending on the location of slag sampling. Analysis of microstructure and phase composition by SEM EDS showed that the major phase found in the samples is fayalite, while other phases are complex spinels (including magnetite), different sulphides and an amorphous phase. Thermodynamic calculations demonstrated the presence of these phases, their compositions and optimal ranges of operating conditions. Analysis of the slag samples revealed that some of them are fayalite slags, but the others may differ significantly from the fayalite composition.

Examination of the samples from the ladle bottom showed the presence of segregation in the chemical composition of the sample. The area which contains the highest amount of copper is
close to the bottom of the ladle. It was concluded that segregation is the reason for the discrepancy in amounts of copper in samples taken from tapping and on the slag deposition site.

It was found that Pb is present only in the sulphide phase, while Zn was observed both in the slag and sulphide phases. The behaviour of other minor elements was also analysed and discussed.

Potential ways of reducing copper losses and optimising the smelting process were suggested on the basis of the overall investigation.

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