FLUXING OPTIONS IN THE DIRECT-TO-BLISTER COPPER SMELTING

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ABSTRACT

Direct smelting of sulphidic copper concentrates to blister copper involves clear benefits in the smelting operation, in particular if modern flash smelting technologies are used. A simplified process chain and much better environmental as well as occupational performance are among the positive impacts of the technology. Today, two such units are on stream and therefore their fluxing practices will be discussed using multi-component calculated phase diagrams as the tool for a detailed analysis of their characteristic features and properties in use.

The thermodynamic conditions of blister copper making from sulphidic, iron-lean copper concentrates will be presented and linked with the metal value recoveries in the smelting step and its constraints. The impacts of some tricky gangue assays present in the raw materials and the oxidation degree will be discussed using an extensive and well-validated thermodynamic database developed for non-ferrous metals smelting.
INTRODUCTION
It is foreseen, that in the near future more and more copper is produced by using Outotec’s Blister Flash Smelting, i.e. the Flash Converting and the Direct-to-Blister Flash Smelting technologies. In fact, their share in copper production has recently been growing rapidly and the capacity of installed applications by the end of 2008 is about 1.3 million tons of copper annually. Outotec estimates that the annual Blister Flash Smelting capacity will exceed 2 million tons copper before the year 2015.

Flash Converting is a proven, high efficiency and environmentally superior technology, which is currently used in Kennecott Utah Copper Corp. (KUC) in USA and in Yanggu Xiangguang Copper Co. in China. In that process, the blister smelting is carried out using solidified, high-grade copper matte as the raw material, which allows a wide freedom in the flux selection. Due to the nature of the high-grade copper matte containing only a few percent of iron, it will form a small amount of slag in the converting process. Calcium ferrite slag is used in both the existing references, mainly because of its much better ability to remove arsenic as compared to silicate-based slags. In case of the Direct-to-Blister Smelting, the concentrate assay largely determines the quality and composition of the primary slag. Thus it is important to take into account the slag chemistry and physical properties of the slag already in the process design phase, where the fluxing strategy is defined.

This paper first gives a short overview of the Direct-to-Blister Flash Smelting process and the current reference operations and then concentrates more deeply in the slag type selection and chemistry in various Direct-to-Blister processes.

DIRECT-TO-BLISTER FLASH SMELTING
The history of making blister copper in a Flash Smelting Furnace dates back to the late 1960’s, when Outotec’s predecessor Outokumpu first piloted the Direct-to-Blister idea. It was shown, that the Direct-to-Blister concept is technically feasible for almost all sulphidic copper concentrates; the economical feasibility does not allow to use, however, the concept for low grade copper concentrates. The first commercial scale application was commissioned at KGHM Polska Miedź Głogow 2 smelter, Poland in 1978, where the concentrate is lean in iron, but also relatively low in copper [1]. At Olympic Dam smelter (OD), Australia, where the process was commissioned in 1988, the high-grade copper concentrate was an optimal raw material for the Direct-to-Blister smelting [2]. In 1999 the first smelter was replaced with a new line, and the original production capacity was almost quadrupled. The next commissioning of a Direct-to-Blister Flash Smelting line will take place in 2008 at Konkola Copper Mines Plc. (KCM) in Zambia [3], where the concentrate is lean in iron and sulphur, but rich in silica. The raw material also contains a significant amount of cobalt.

The advantages of the Direct-to-Blister smelting are obvious. Being a continuous process in a fully closed vessel, it provides a good basis for the process and emission control, as the ladle transportation of molten matte and a large number of converters are eliminated, and sources for fugitive emissions are minimized and makes it easier to capture the fugitives, too. With direct blister making in a single vessel, the decrease in investment and maintenance costs compared to a two-step processing are also obvious. In addition to that, the investment and operation costs of the acid plant are low, because of the stable and continuous, high-strength SO2 gas flow, from which sulphur dioxide can be captured effectively [4].

A simplified process flow sheet of the references mentioned above is given Figure 1. In the smelter, the concentrate is first dried and then fed into the Flash Smelting furnace with the appropriate flux and oxygen-enriched air. The process temperature is controlled
by the oxygen enrichment degree of process air. In reaction shaft the concentrate particles ignite rapidly and react with oxygen and form blister copper, slag and SO₂-rich gas. The particles are separated from the gas stream in the settler, where they form blister and slag layer thus completing the reactions of sulphides, their oxidation products and the flux. The gas rich in SO₂ is further taken through a waste heat boiler, where the heat content of the gas is recovered. Part of the flue dust is recovered in the waste heat boiler, after which the gas is cleaned in an electrostatic precipitator before it is fed into the gas cleaning section of the sulphuric acid plant and finally into the conversion, where the SO₂ is recovered as sulphuric acid.

Figure 1: Direct-to-Blister Flash Smelting

Blister copper is tapped out of the settler and is taken either directly or transported in ladles into anode furnaces. In all the above-mentioned references the slag is taken via launderers into a slag-cleaning furnace, where at least a part of its copper values is recovered. This is the point, where the above-mentioned reference processes diverge: in Głogow 2 smelter the slag is reduced to a point, where it contains only about 0.5 % Cu and can be discarded. Therefore, metallic product of the slag cleaning furnace contains 5-10 % Fe and 12-18 % Pb, which are removed in a separate iron converting vessel before the copper is fed into anode furnace. In the Olympic Dam smelter, the slag is reduced to a point, where iron content of the blister remains low enough so that it can be fed directly into the anode furnaces via launderers. Here, however, the slag still contains some percentage of copper and it is treated in a slag concentrator, where rest of the copper is recovered as a slag concentrate and fed back into the smelting furnace. In KCM’s Nchanga smelter, the Flash Smelting furnace slag is first reduced in a slag-cleaning furnace to a degree, where iron content of the forming blister is low enough allowing treatment in the anode furnace together with the Flash Smelting blister. The residual copper is recovered in a second electric furnace, where also cobalt contained in the slag is captured as a cobalt-alloy, a valuable by-product. In the future it is possible to increase the cobalt recovery with an additional cobalt recovery furnace, which may be installed parallel to the existing cobalt recovery furnace.

The differences of the slag treatment technologies in the above-mentioned examples are not only due to the differences in the slag chemistry, but also other aspects have to be taken into account in the process route selection. However, the fluxing chemistry must be taken into account in the process design. In the following chapters, the slag fluxing
practices will be discussed using thermodynamics and calculated, multi-component phase diagrams as a tool for a detailed analysis of their characteristic features, as well as their properties in use.

**THERMODYNAMICS OF THE SLAGS**

This paper also describes the status of an extensive thermodynamic database in oxide and sulphide systems, which was initiated 20 years ago [5]. The chemical equilibrium of a system is determined by minimising its Gibbs energy with respect to the amounts and compositions of all phases, which might form.

**Models and Experimental Data**

The liquid oxide (‘slag’) phase in the database is modelled in terms of a series of non-ideally interacting species, either pure oxides, such as CaO and SiO₂, or associated species, such as CaSiO₃ and Ca₂SiO₄, used to take account of sharp changes in the thermodynamic properties of the liquid phase at particular compositions. The *associate* model [6] is conceptually simple, flexible and, unlike other models, which were tested, has no trouble representing amphoteric oxides and no tendency to predict spurious miscibility gaps.

Crystalline solution phases, such as those with the spinel, halite, olivine and pyroxene structures are represented using the compound energy model in which ionic species are assumed to mix independently on a series of separate sublattices. The application of this model to solid oxides is discussed in detail elsewhere [7].

| Table 1: Current coverage of the Mtox database |
|---|---|
| **Systems**          | **Current Database (vers. 6.0)** |
| Oxide base system    | Na₂O-K₂O-CaO-Fe-O-MgO-Al₂O₃-SiO₂-S |
| Matte/metal oxide base system | Co-Cu-Fe-Ni-O-S |
| Sub-sets of oxide base system | |
| CaF₂                  | CaF₂-CaO-Al₂O₃-SiO₂ |
| BaO, La₂O₃, SrO, UO₂* | BaO-CaO-SiO₂-La₂O₃-SiO₂-UO₂ |
| Co-O                  | CaO-CoO-Fe-O-MgO-Al₂O₃-SiO₂ |
| Cr-O                  | CaO-Cr-Fe-O-MgO-Al₂O₃-SiO₂ |
| Cu-O                  | CaO-Cu-Fe-O-MgO-Al₂O₃-SiO₂ |
| MnO                   | CaO-Fe-O-MgO-MnO-Al₂O₃-SiO₂ |
| Nb₂O₅*                | CaO-Cr-Fe-O-MgO-Al₂O₃-SiO₂-Nb₂O₅ |
| NiO                   | CaO-Fe-O-MgO-NiO-Al₂O₃-SiO₂ |
| P₂O₅                  | CaO-Fe-O-MgO-Al₂O₃-P₂O₅ |
| PbO and ZnO           | CaO-Fe-O-PbO-ZnO-Al₂O₃-SiO₂ |
| ZrO₂ and V₂O₅         | Na₂O-CaO-MgO-Al₂O₃-SiO₂-ZrO₂-V₂O₅ |
| B₂O₃ and Li₂O         | Li₂O-Na₂O-B₂O₃-SiO₂, Na₂O-CaO-Fe-O-MgO-Al₂O₃-B₂O₃-SiO₂ |
| Pressure dependence   | CaO-Fe-O-MgO-Al₂O₃-SiO₂ |
| Trace anion database  | CaO-Fe-O-MgO-Al₂O₃-SiO₂ and Na₂O-SiO₂ |
| Viscosity of liquid oxide | Na₂O-CaO-Fe-O-MgO-Al₂O₃-SiO₂ |

* Binary systems only completed
Fluxing Options in the Direct to Blister Copper Smelting

Thermodynamic Solver and the Database

The phase equilibrium calculations were carried out using thermo-chemical modelling package MTDATA [8], written at the National Physical Laboratory (NPL). MTDATA is a stand-alone package able to perform calculations appropriate to large multi-component systems containing many different types of phase, such as slags, mattes, alloys, gases and aqueous solutions, with exceptional reliability. Facilities are provided for the generation, manipulation, storage and retrieval of thermodynamic data, for plotting results in a variety of different ways including binary, ternary, multi-component and predominance area diagrams and for linking to other process modelling software. Non-equilibrium calculations can be undertaken by omitting phases or placing restrictions on the distribution of components.

The current content of the extensive oxide and sulphide database Mtox developed particularly for use with MTDATA is described in Table I. As the applications of Mtox are in non-ferrous and ferrous smelting and refining slags, the thermodynamic components of the database are typically slag-forming oxides, such as CaO and SiO₂, and not their elements. In limited cases metallic components are included in the database, thus enabling calculations from a pure metallic composition, an alloy, to a fully oxidic one. Copper is a typical metal in this category, because its oxide systems form a molten state immiscibility area, a miscibility gap, at temperatures where copper smelting is carried out. An exception is the sulphide subset, where the system components are the elements.

DIRECT-TO-BLISTER FLASH SMELTING SLAGS

The basic assay of the copper smelting slags is generated by the components Fe-Cu-O-SiO₂ or Cu₂O-FeO-Fe₂O₃-SiO₂. Gangue components in copper concentrates add some refractory substances into the component list, such as Al₂O₃, CaO and alkali metal oxides. Depending on the raw material basis, the slags may contain significant fractions of lead or zinc oxides, as well as impurities, as As and Sb oxides. In addition the slag assay, an important operational variable as to the copper concentration in the slag is oxidation degree of the smelting charge, or simply sulphur concentration of the blister copper produced, see Table 2.

<table>
<thead>
<tr>
<th>Slag (%)</th>
<th>OD</th>
<th>KUC</th>
<th>KGHM</th>
<th>KCM(a)</th>
<th>KCM(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>32.5</td>
<td>42</td>
<td>6.4</td>
<td>28.9</td>
<td>17</td>
</tr>
<tr>
<td>SiO₂</td>
<td>17.5</td>
<td>2</td>
<td>31.4</td>
<td>28.2</td>
<td>32</td>
</tr>
<tr>
<td>CaO</td>
<td>-</td>
<td>16</td>
<td>14</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Cu</td>
<td>22.5</td>
<td>20</td>
<td>14.4</td>
<td>17.5</td>
<td>22.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.5</td>
<td>-</td>
<td>9.4</td>
<td>7</td>
<td>4.5</td>
</tr>
<tr>
<td>MgO</td>
<td>-</td>
<td>-</td>
<td>6.2</td>
<td>2.5</td>
<td>7.2</td>
</tr>
<tr>
<td>[reference]</td>
<td>[9]</td>
<td>[10, 11]</td>
<td>[12]</td>
<td>[13]</td>
<td>[14]</td>
</tr>
<tr>
<td>t/°C</td>
<td>1300</td>
<td>1250</td>
<td>1300</td>
<td>1280</td>
<td>1280</td>
</tr>
<tr>
<td>Blister [%]</td>
<td>1.00</td>
<td>0.25</td>
<td>0.50</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>±</td>
<td>0.3</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) MgO-lean feed mixture, b) MgO-rich feed mixture

Copper dissolution in the slag expands the homogenous molten slag domain of the Fe-O-SiO₂ or Fe-O-CaO systems. When a smelter produces blister copper with a single target analysis, typically the dissolved sulphur concentration, the slag chemistry has a simplifying constraint from thermodynamic point of view. It has a fixed oxygen pressure at each temperature, due to the internal equilibrium.
\[ S + 2[O] = SO_2 \ (g, \approx 1 \text{ atm}) \] (1)

The sulphur dioxide pressure in the blister bath or at blister-slag phase boundary must be slightly above the ambient pressure in order to create a gaseous SO\(_2\) bubble. Thus, the compositional variation of molten blister copper in a DB furnace has one degree of freedom less than otherwise would be the case.

**Iron Silicate System**

Olympic Dam smelter uses silica flux for the smelting. The high-copper low-iron concentrate of chalcosite type has a relatively high alumina content in the gangue, increasing the alumina level of the smelting slag to 3-4%. The iron-silicate slags dissolve much copper at high oxygen activities, as demonstrated in Figure 2 for the Olympic Dam slag assay of 17.5 and 22.5% (SiO\(_2\)) at 1% [S] in molten blister copper.

![Figure 2](image.png)

Figure 2: Dissolution of copper in alumina-bearing iron silicate slags in equilibrium with blister copper at 1300°C and \(P_{SO_2} = 1\) atm; at 1% [S] alumina concentration is 3.5% (Al\(_2\)O\(_3\)).

Figure 2 shows the effect of oxidation degree, here expressed as the sulphur concentration of the blister copper under constraint (1), on the copper solubility in the slag. The slag assay at 1% [S] is similar to the Olympic Dam slag in Table 1, with the equilibrium copper solubility of 16-18% at 17.5-22.5% (SiO\(_2\)). At smaller sulphur concentrations, the slag will be diluted by copper oxides dissolving in the slag. One can see that at 0.5% sulphur in blister copper, the equilibrium solubility of copper in the slag would be≈23% (Cu), depending on silica concentration of the slag.

This slag is typical to many PS-converting operations, but its low silica and relatively high alumina make it non-characteristic to the FSF matte smelting operations, where the silica level is maintained between 30 and 35%. The small mass of slag forming in the smelting ensures high copper recovery in the primary smelting stage, when sulphur concentration of the blister produced is relatively high.
Calcium Ferrite System

Calcium ferrite slags are characterised by their wide homogeneity range, extending essentially from iron saturation to pure oxygen [15]. The basic assay of the slags is generated by the components Fe-Cu-O-CaO or Cu₂O-FeO-Fe₂O₃-CaO. Their activity coefficient of copper oxide is high and thus the solubility of copper is less than in iron silicate slags. They are sensitive to silica and therefore their use in the primary, concentrate smelting step is not possible. The homogeneous slag domain in copper-free systems at P_{O₂} = 1 Pa (≈10⁻⁵ atm) is shown in Figure 3.

Calcium ferrite slags in the Flash Converting have the following assay [10]: 16%CaO, 20% Cu, 42% Fe and 2% SiO₂. Sulphur in blister copper is controled to 0.25%. Temperature in the FCF is 1250°C, and in cases of build-up formation in the settler 1270°C [11]. As the activity of lime is high in typical slag compositions, the slagging of arsenic is effective and it may be further controlled by adjusting lime concentration of the slag.

![Figure 3: An isopleth of the system Fe-O-CaO as a function of the lime concentration under a constant oxygen partial pressure of 1 Pa (≈10⁻⁵ atm); Mtox 6.0 database](image)

The dissolution of oxygen in the blister copper melt is dependent on the smelting temperature at constant sulphur concentration. Figure 4 shows the equilibrium solubility of oxygen at 0.25% [S] in blister copper, in equilibrium with a calcium ferrite slag containing 18% lime. The graph indicates clearly that the smelting product on this sulphur level contains in excess oxygen in order to remove all sulphur as SO₂(g), which is favourable in terms of the subsequent anode furnace treatment. This condition generally requires sulphur concentrations less than 0.4% in blister copper.
Figure 4: Solubility of oxygen in blister copper as a function of the smelting temperature, in equilibrium with a calcium ferrite slag containing 18% lime and the blister copper has 0.25% [S]

**Ferrous-Earth Alkali Silicate Systems**

Another group of smelting slags used in the direct blister smelting is vaguely related to the ferrous calcium silicate slags discussed widely in the literature by Yazawa and his co-workers already some time ago [16, 17]. They and other authors have been proposing the use of a number of compositional areas of the CaO-Fe-O-SiO$_2$ system in non-ferrous smelting processes, and even patents have been applied for carefully selected composition ranges [18, 23], see Figure 5.

Figure 5: Compositional ranges of applied patents on the ferrous calcium silicate slags in copper smelting [18, 23]
Two examples of the application of this fluxing chemistry refer to the KGHM operation in Głogow 2 and the KCM DB smelter. The special feature here is the gangue minerals of the feed mixture, adding significant fractions of alumina as well as magnesia to the smelting slag assay. Very little has been published, however, on the effects of alumina or magnesia on the metal value distributions in the copper smelting [24, 25]. The liquidus contour projection of the system $\text{Al}_2\text{O}_3$-$\text{CaO}$-$\text{Fe}_3\text{O}_4$-$\text{SiO}_2$ at 10% ($\text{Al}_2\text{O}_3$), under oxygen partial pressure of 1 Pa ($\approx 10^{-5}$ atm) is shown in Figure 6.

The basic difference between these DB slags is their iron oxide concentration. The raw materials used in Głogow 2 are very low in iron, resulting in slags with less than 10% iron. In Zambian raw materials iron is much higher than in Poland, and the resulting DB slag contains iron oxides in concentrations similar to conventional copper smelting slags, Table 2.

Low-iron silicate slags with alumina and lime at Głogow 2 smelter are typically [12]: 14.4% Cu, 3.4%Pb, 6.4%Fe, 0.05%S, 0.2%As, 31.4% SiO$_2$, 14.0% CaO, 6.2% MgO and 9.4%Al$_2$O$_3$. Tapping temperatures of blister and slag are 1280-1320 °C. The blister produced contains 0.5% S as the target value. EF slag ('waste slag') assay post the slag cleaning is: 0.6%Cu, 1.1%Pb, 0.02%As, 6.3%Fe, 0.01%S, 37.2%SiO$_2$, 23.6%CaO, 8.1%MgO and 10.5%Al$_2$O$_3$ [12]. Limestone is added to EF for improving the slag cleaning. Its essential effect is enhanced mixing of the bath by evolving CO$_2$(g) from decomposing limestone during the reduction period.

The effect of oxidation degree to the copper losses in the KGHM operation is shown in Figure 7, where copper dissolution into the slag is depicted as a function of sulphur concentration of blister copper melt produced at 1300°C. The curve labelled 'base' corresponds to the full slag analysis given above and the corresponding feed mixture with the components given in the legend. The two other curves refer to alternative feed mixtures with 10 or 20% chalcopyrite concentrate added. The operational point of KGHM with 0.5% sulphur in the tapped blister copper ensures copper losses below 15% (Cu) in the slag, whereas the typical blister of KUC would lead to much higher copper concentrations in the slag (see the vertical line and the circle).
The new DB smelter of Vedanta Group in Zambia [13] has unusual slag chemistry in terms of its silica. The raw material basis at KCM smelter has been estimated to result in the smelting the following FSF slag assay: 17.5% Cu, 7.0% Al₂O₃, 5% CaO, 2.5% MgO, 28.2% SiO₂ and 28.9% Fe, when the produced blister copper at 1280°C contains 0.3% S [14]. The high-MgO slag contains up to 7% MgO and its assay is given in Table 2. The slag forming in DB smelting contains about 30% (SiO₂), and its melting point is controlled by lime additions. Alumina in the CaO-Fe-O-SiO₂ system, in equilibrium with blister copper, expands the domain of the molten slag, see Figure 8, and has an impact to copper solubility, too, Figure 9.

The special feature of the KCM operation is that the FSF slag is treated in EF for recovering its cobalt values in two steps; first the dissolved copper will be removed with very low cobalt carry over to the EF-matte and thereafter the slag is treated with a second reduction step for obtaining a CuCoFe-alloy. This discard slag is low in ferric iron and essentially copper-free. Therefore, its melting point is the key point of the FSF slag fluxing, limiting the possible compositions to fully molten slags in the EF only.
DISCUSSION

Currently, direct blister smelters use three different fluxing chemistries. In addition to the calcium ferrite system used in the Flash Converting, KGHM Głogow 2 smelter utilises high alumina slags with a low iron oxide concentration as a natural assay from their gangue minerals [12]. Olympic Dam operation uses the classical iron-silicate chemistry [9], and the most recent application by KCM adds lime in their high-magnesia high-silica slags for enabling sufficiently low melting point and fluidity to the smelting slag and discard slag post the EF slag cleaning steps [14].
Calcium ferrite-type slags allow production of blister copper in the flash converting with a low sulphur concentration of below 0.3% \([S]\), but they are sensitive to gangue components. Mixed earth alkaline silicate slag with alumina provide many similar properties to calcium ferrite slags, but their fluidity may be compromised by the high melting point of the slag and thus proper and accurate fluxing is necessary. Iron silicate slags allow a simple fluxing alternative, which dissolve large amounts of copper and thus may be used at high sulphur levels of the blister copper only.

Predictive properties of the Mtox database can be effectively utilised when designing the slag chemistries in copper smelting for non-conventional raw materials as well as for novel processing conditions. A forthcoming feature of the database will be its extension to transport properties of slags, including viscosity, which is currently under validation.

ACKNOWLEDGEMENTS
The authors wish to express their thanks to MIRO (The Mineral Industry Research Organisation, Birmingham, UK) and NPL for their long-term commitment to the development of the Mtox-group databases.

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