

# Development of a Process Model for a Peirce-Smith Converter

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## **Abstract**

Copper was one of the first metals ever extracted and used by mankind. It is used for its unique properties, like corrosion resistance, good workability, high thermal conductivity and attractive appearance. New mines are opened to maintain a supply of primary feedstock to copper smelters. These new deposits are in many instances found to have a more complex mineralogy with several minor elements. Besides treating primary material, copper smelters also show an increasing interest in treating secondary material, such as copper containing scrap from waste electric and electronic equipment, which also have a complex composition.

Waste electric and electronic equipment are first disassembled and upgraded by mechanical processing, generating a product stream called e-scrap, that can be added directly to the smelting processes as cold material or melted in a separate furnace producing a metallic alloy (referred to as black copper) and a slag phase. The black copper can be refined in different ways, whereof one is by using it as a secondary feed material for input to Peirce-Smith converters. Consequently the load of minor elements to the converter can be expected to increase with an increased treatment of e-scrap.

This increased complexity of the raw material can potentially lead to smelter plants having to deal with a feedstock containing several minor elements such as; antimony, bismuth, arsenic, gold, silver, etc. in levels that can influence the ability to, in a cost effective way, maintain the final grade of the copper cathode.

Process simulations can be an important tool for understanding the impact of process parameters on the product quality and for the purpose of process optimisation. In the

present work a dynamic, non-equilibrium model based on thermodynamics over the Peirce-Smith converter has been developed. The non-equilibrium conditions have been simulated by introducing individual but linked segments. The purpose of using segments was to consider different reaction zones which yield different conditions within the converter. The model was validated using plant data and showed good agreement for the major elements. The agreement between plant and calculated data for Pb, and Zn was not as good and more work is required regarding this aspect.

The model was used to investigate the influence on the distribution of Bi and Sb during addition of black copper with or without slag. When black copper is added to a blow, the removal of Bi and Sb becomes lower compared to a blow without addition of black copper. Similar result is obtained during addition of black copper with slag. To maintain a total removal of Bi and Sb in similar levels as a blow without black copper, the black copper should be added as early as possible during the converting operation.

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## List of Papers

- I. **A. Lennartsson**, F. Engström, B. Björkman and C. Samuelsson, “Development of a model for copper converting”, Canadian Metallurgical Quarterly (2013), Vol 52, p 422-429
  
- II. **A. Lennartsson**, F. Engström, B. Björkman and C. Samuelsson, “Thermodynamic process modelling of black copper addition to a Peirce-Smith converter: Effect on the distribution of antimony and bismuth”, Submitted

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Modelling, simulation, result interpretation and writing of Papers I and II. The modelling is based on earlier work by Björkman. The other co-authors have contributed in a supervisory capacity and assisted with revision of the manuscripts.

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**A. Lennartsson**, F. Engström, B. Björkman, C. Samuelsson, “Minor Elements in Copper Converting”, Extended abstract at GTT-Technologies Annual Workshop, Aachen, Germany, 2013

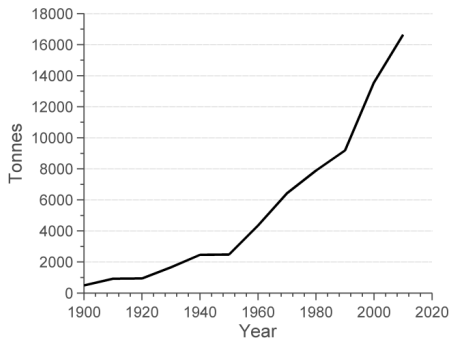
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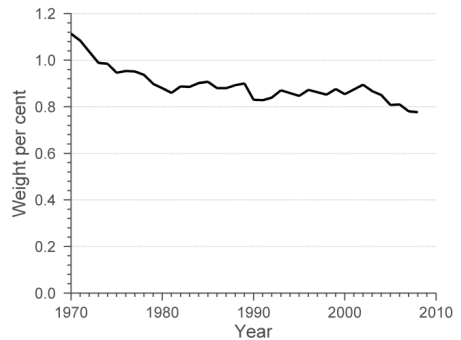
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# 1 Introduction

Copper was one of the first metals ever extracted and used by mankind. It is used for its unique properties, like corrosion resistance, good workability, high thermal conductivity and attractive appearance. Besides its high conductivity, the capability of endless recycling is the most important feature of copper.<sup>1</sup> Despite the possibility to recycle copper from used products there is not enough copper in recirculation to satisfy the demand for copper containing-products. Therefore, new mines are opened to maintain a supply of primary feedstock for copper smelters. Figure 1 shows how the world copper mine production has increased substantially during the last century as a consequence of the increasing demand. The copper ore grades have also declined during the last decades, see Figure 2.



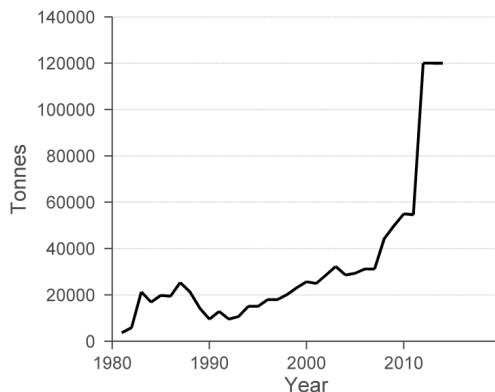
**Figure 1 World copper mine production during the last century. Source: International Copper Study Group**



**Figure 2 Weighted average percentage head grade of copper mines<sup>2</sup>**

This can be explained by the increased demand and higher copper prices, which have made it economically feasible to mine orebodies with a lower copper grade. These new, leaner deposits are also in many instances found to have a more complex mineralogy.<sup>2</sup> A concentrate from a mine with a complex copper ore can also contain elements like: zinc, lead, nickel, antimony, arsenic, bismuth, tin, gold and other precious metals. These elements are commonly referred to as minor elements.

The increased production and utilisation of copper-containing products consequently leads to more used material available for recycling. Waste electric and electronic equipment (WEEE) is one of these copper-containing materials. Primary copper smelters (treating mainly copper concentrates) show an increasing interest in treating secondary and recycled materials. For instance, the Boliden Rönnskär smelter has increased their capacity for treating processed WEEE, electronic scrap (e-scrap), during 2011, see Figure 3.



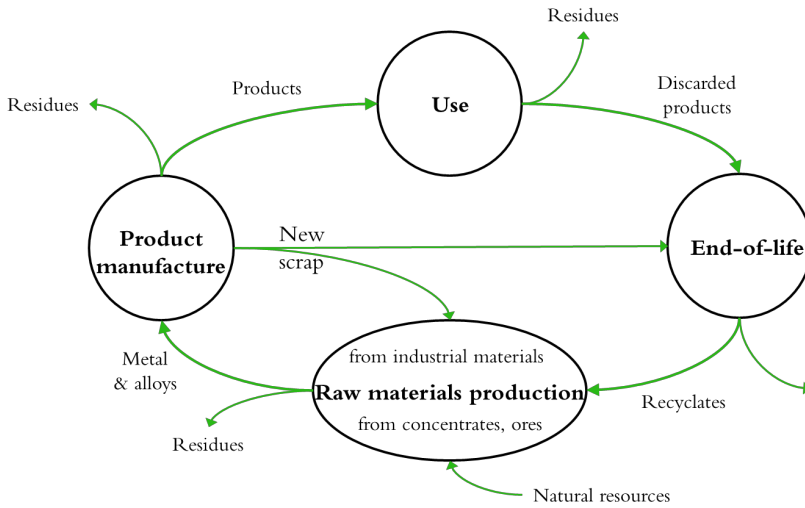
**Figure 3 The increased annual recycling of electronic scraps at the Rönnskär smelter since 1981 (provided by the Rönnskär smelter)**

This situation, together with the increased complexity of the ore, potentially leads to smelter plants having to deal with a feedstock containing several minor elements such as antimony, bismuth, arsenic, gold, silver, etc. in levels that can influence the ability to, in a cost effective way, maintain the final grade of the copper cathode. The accepted levels of minor elements in copper cathodes are controlled by different standards. For a grade 1 cathode the maximum level is usually 65 ppm of minor elements.<sup>3</sup> For a primary copper smelter, the last process for removing unwanted elements from the produced copper is during electrolysis, where copper cathodes are produced from copper anodes. However, there also exist limitations for the amount of minor elements entering the electrolysis. Excessive levels of antimony, bismuth, arsenic and tin in the anodes can lead to the formation of floating slimes in the tanks. These slimes do not settle at the bottom of the electrolysis tank but float on the surface of the electrolyte, leading to short circuits and inclusion of minor elements in the cathode.<sup>1</sup>

The presence of minor elements in the cathode affects the properties of the produced copper. Electrical and thermal conductivity of copper, as in all pure metals, is significantly affected by the presence of other elements. The mechanical properties, like castability and rolling of copper, as well as annealing of rods, are affected by the presence of antimony and bismuth.<sup>4, 5</sup> To avoid these problems, knowledge about the behaviour of minor elements in copper smelting processes, especially about how they can be removed during the processes, is essential.

Since metals are inherently recyclable, knowledge about minor element distribution and removal could also be used to increase the recycling rates for metals. By changing process parameters and operating procedures an element could be enriched into a

certain phase or product stream that later can be refined into a product. Looking at the life-cycle of a metal, Figure 4, an increased extraction of a minor element entering a smelter (part of the raw material production), either from concentrate or secondary material, is beneficial for the recycling and utilisation of that element.



**Figure 4 The life-cycle of a metal consisting of production, product manufacture, use and end-of-life. After Graedel *et al.*<sup>6</sup>**

Looking at recycling rates, copper has according to Graedel *et al.*<sup>6</sup>, a high (>50%) end-of-life recycling rate. However, this is not the case for metals like antimony, indium, bismuth and gallium, which all have recycling rates below 10%. One explanation for the low recycling rate is that these metals are associated with copper in their use and therefore end up in the copper recycling system, where they are seen as impurities and removed by slagging or vapourisation without recovery, and are therefore lost as metals.

## **1.1 Primary and secondary materials**

The raw material processed in a copper smelter can be classified as either primary or secondary. Primary raw material refers to ores or concentrates, while secondary raw material refers to scrap and other recycled metal-containing materials.

### **1.1.1 Complex primary material**

Typically, copper sulphide ores contain from 0.5 wt-% to 2 wt-% Cu. Most of the copper is present as copper-iron sulphide minerals such as chalcopyrite, bornite and chalcocite. Complex sulphide ores also contain various other metal sulphides (ZnS, PbS, AsS, Bi<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>3</sub> etc.) in the copper-iron sulphide matrix. The ore is mined and concentrated to reach a copper content of ~20-30 wt-%.

### **1.1.2 Waste electric and electronic equipment**

Waste electric and electronic equipment (WEEE) has during the last decade become of increasing interest to the nonferrous industry as a secondary feed material because it contains metals (i.e. Cu, Au, Ag, Pd) of interest for the smelters. Besides these desired elements, WEEE also contains several minor elements that can influence the quality of copper anodes. The study by Oguchi *et al.*<sup>7</sup> on end-of-life electric and electronic equipment exemplifies the complexity of these materials. Table 1 shows the metal content for different circuit boards used in their study and, as can be seen, the complexity is great.

**Table 1 Metal content of printed circuit boards<sup>7</sup>**

Equipment type	Metal content of printed circuit board [mg/kg]														
	Common metal						Precious metal			Less common metal					
	Al	Cu	Fe	Pb	Sn	Zn	Ag	Au	Pd	Ba	Bi	Co	Ga	Sr	Ta
Air conditioner	6900	75000	20000	5800	19000	4900	58	15	-	320	-	29	-	26	-
LCD TV	63000	180000	49000	17000	29000	20000	600	200	-	3000	-	-	-	300	-
Desktop PC	18000	200000	13000	23000	18000	2700	570	240	150	1900	50	48	11	380	7
Notebook PC	18000	190000	37000	9800	16000	16000	1100	630	200	5600	120	80	10	380	5800
Mobile phone	15000	330000	18000	13000	35000	5000	3800	1500	300	19000	440	280	140	430	2600

WEEE is usually first disassembled and upgraded by mechanical processing, generating a product stream called e-scrap. The material is then normally further treated with one of the following methods; either it can be added directly to the smelting processes as a cold secondary material in, for instance, a copper smelter or, treated as a primary material with pyrometallurgical methods, which is the normal route. In the pyrometallurgical route e-scrap is burned in a furnace to remove plastics. The alumina and silica present in the printed circuit boards form a slag phase. The resulting melt consists of a copper-rich metallic alloy (referred to as black copper) and a slag phase. The black copper can be refined in different ways, whereof one is by using it as a secondary feed material for input to a copper converter.<sup>8, 9</sup> Since the upgraded and refined e-scrap contains minor elements that could be harmful for the quality of copper anodes it is important to have knowledge about the influence black copper addition has on the converter operations, especially minor elements distributions.

## 1.2 Rönnskär smelter

The Rönnskär smelter of Boliden Mineral AB is located in the north of Sweden. The smelter has produced base and precious metals since 1930. The main products are copper, zinc clinker, lead, silver and gold, while sulphuric acid and liquid sulphur dioxide are some by-products.<sup>10</sup> The feedstock for the Rönnskär smelter is a complex

mixture including, for instance, concentrate, ashes, slags, metallic scrap, e-scrap and steel-making dust.<sup>11</sup>

The copper route at the Rönnskär smelter is shown in Figure 5 and consists of an electric furnace and a flash furnace that smelt raw material to matte for further treatment in Peirce–Smith converters in the converter aisle. The produced blister copper is transported to the anode furnace and then cast into anodes for the electro refining. As shown in Figure 5, the Rönnskär smelter also operates two Kaldo furnaces; one for e-scrap and another for lead concentrate or e-scrap. The melted e-scrap is further treated in the converters for recovery of valuable metals. Consequently, the load of minor elements in the converters can be expected to increase with an increased treatment of e-scrap. For this reason, the focus in the present work is on the Peirce–Smith converter.

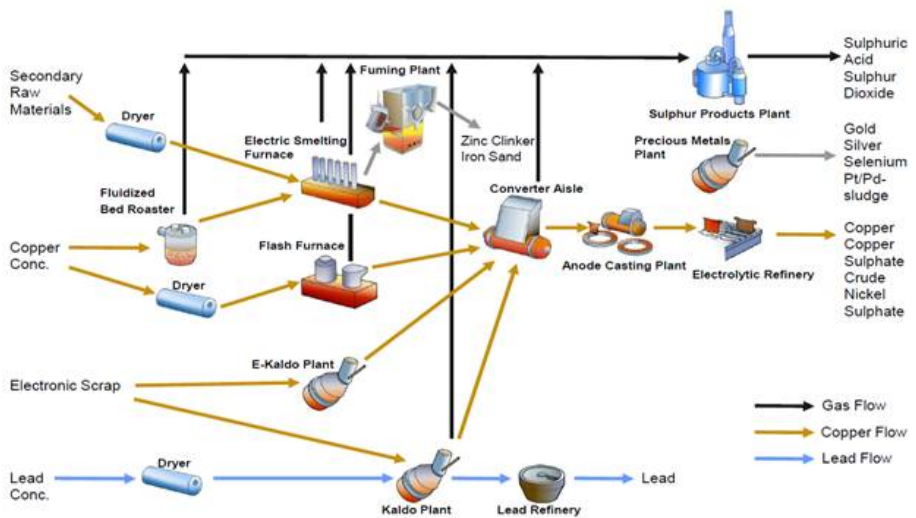


Figure 5 Flow sheet of the Rönnskär smelter (reprinted with permission by Boliden)

### **1.3 Copper converting/Peirce-Smith converter**

The most commonly used process worldwide for converting primary copper matte to blister copper is the Peirce-Smith converter process.<sup>12</sup> The process is normally divided into two main stages: the slag blowing stage and the copper blowing stage. During each stage, air or oxygen-enriched air, is injected through tuyeres into the melt. Depending on the starting matte grade, the slag blowing stage is typically repeated twice, with a slag skimming operation followed by further matte additions. During the slag blowing stage, the injected oxygen reacts with iron sulphide to form iron oxide, which in turn reacts with the added flux, forming a slag phase. After the final slag blow the remaining melt consists mainly of copper sulphide, often referred to as white metal, containing a small amount of iron. The white metal is converted to liquid copper during the copper blowing stage. Solid (cold) material as cooling material, such as copper-containing scrap and reject anodes, is normally added, particular in the copper blow, since the reactions are exothermic. Any unwanted elements present in the feed matte or in other charged materials are removed from the matte and, later, blister copper by either slagging or vaporisation.

### **1.4 Process simulation**

Process simulation can be an important tool for understanding the impact of process parameters on the product quality and for purposes of process optimisation. It can also be used to investigate the possibilities to operate processes in new ways in order to, for instance, increase the recycling rate of minor elements in the metallurgical processes in the copper recycling system.

Since the publication of Gibbs<sup>13</sup> last paper in the series 'On the equilibrium of heterogeneous substances', all terms necessary to describe chemical equilibrium are

defined. Problems related to pyrometallurgy and dealt with via thermodynamic calculations are equilibria in complex systems, i.e. systems with many components and many phases (some or all of which may be non-ideal mixtures) can only be treated safely by minimisation of the total Gibbs energy of the system under some constraints.

The equilibrium condition can be written as:

$$G = \sum_{\Phi} (\sum_i n_i^{\Phi}) G_m^{\Phi} = \text{minimum} \quad (1)$$

Here  $G_m^{\Phi}$  is the molar integral Gibbs energy of phase  $\Phi$ , and  $n_i^{\Phi}$  are the mole number of the phase constituents  $i$  of this phase. From equation (1) it is obvious that for each phase an expression for  $G_m^{\Phi}$  is required. Two cases can occur: either the phase is treated as a pure stoichiometric substance or the phase is a solution with variable content of its phase components. Functions describing  $G_m^{\Phi}$  are normally collected in private or commercial available databases ready for use with software for thermodynamic calculations, i.e. minimisation of Gibbs energy.

For copper smelting processes including converting in Peirce-Smith converters one drawback of assuming equilibrium conditions is that often the copper level in the slag and the degree of magnetite formation can be underestimated.<sup>14</sup> In the case of copper levels in slag, there can be matte entrained in the slag, not included in the equilibrium calculation, thus leading to higher copper levels than estimated thermodynamically. In the case of magnetite formation, in practise, there can be solid magnetite present in the system. It is also possible that the process may not have reached equilibrium.

## 1.5 Aim and Scope

The aim of the current study is to develop a dynamic, non-equilibrium model based on thermodynamics over the Peirce-Smith converter that can be used to predict the effect of changes in process parameters and feed material on the quality of the produced blister copper. The model is validated against process data collected during a sampling campaign performed at the Rönnskär smelter.

The model could also be used to simulate how the process could be changed to increase the recycling rate of the minor elements present in the feed material, for instance, in the melted e-scrap.

As a starting point, this work focus on the development of a dynamic, non-equilibrium model describing copper converting in a Peirce-Smith converter and the influence of bismuth and antimony during addition of melted e-scrap.

## 2 Minor elements in copper smelting

During the last century a considerable amount of research with focus on the behaviour of minor elements in copper smelting has been conducted both in academia and in industry. The advancement of scientific knowledge has brought about a better understanding of the key parameters affecting minor element distribution and removal.

### 2.1 Minor elements in copper matte

Little is known about the actual structure of molten copper mattes. The composition of industrial copper matte is close to the  $\text{Cu}_2\text{S}$ - $\text{FeS}$  line across the ternary  $\text{Cu}$ - $\text{Fe}$ - $\text{S}$  system, often leading to the misconception that copper matte is covalently bounded. This is based on the fact that the melt, in such a case, would consist of  $\text{Cu}_2\text{S}$  and  $\text{FeS}$  molecules. The actual structure of molten matte will influence the behaviour of minor elements and their nature in the melt. According to Roine and Jalkanen<sup>15</sup>, the sulphur-to-metal ratio appears to be the most important factor influencing the activity coefficients of minor elements in copper matte. This has been developed further by Lynch *et al.*<sup>16, 17</sup> and Zhong and Lynch<sup>18</sup> by defining the concept of sulphur deficiency. In viewing matte chemistry from a perspective perpendicular to the alkemade line joining the component sulphide, mattes are either metal-rich or sulphur-rich. Either metal atoms are available to interact with solute elements or excess sulphur atoms are an indication of high sulphur potential, which can lead to sulphide formation among minor elements. The extent of the situation can then be represented by the sulphur deficiency, SD, as:

$$\text{SD} = X_{\text{S}} - 1/2 X_{\text{Cu}} - X_{\text{Fe}} \quad (2)$$

where  $X_y$  is the mole fraction of y.

The existence of a sulphur deficiency implies the existence of electronegative sites. The dissolution of minor elements such as Sb in matte therefore also depends on the availability of vacant sites.

## 2.2 Minor elements in copper

When the matte, undergoing oxidation converting, reaches about 1 wt-% Fe, metallic copper starts to precipitate. In the copper melt all minor elements are believed to exist in metallic state. The metallic copper behaves like a sponge for a majority of minor elements. Table 2 shows numerical values of the activity coefficient for As, Sb and Bi in copper matte and copper as presented by Kim and Sohn<sup>19</sup>. The lower the value is, the stronger the bonding forces between the element and the melt are, thus leading to a higher concentration of the element at equilibrium. As can be seen in Table 2, the activity coefficients in copper are lower than for matte.

**Table 2 Raoultian activity coefficients in dilute solutions at 1523 K.  
Calculated from Kim and Sohn<sup>19</sup> with a matte grade of 65% Cu**

Substance	$\gamma_{i(\text{matte})}^{\circ}$	$\gamma_{i(\text{copper})}^{\circ}$
As	1.8	0.0007
Sb	1.6	0.02
Bi	12.3	2.3

## 2.3 Minor elements in slag

The slag phase is normally considered as ionic in its nature, consisting of anions and cations.<sup>20</sup> The slag commonly used in copper smelting and converting has a composition around  $\text{Fe}_2\text{SiO}_4$  and is called fayalite slag after this compound. For continuous converting, calcium ferrite-based slag is usually used instead.

Slag plays an important role in removing unwanted minor elements from the matte during copper converting. The dissolution mechanisms for minor elements in fayalite slag have been discussed by Nagamori and Mackey<sup>21</sup>. The most common dissolution mechanism is oxidic dissolution and occurs when the oxide of an element in the slag is stable under the prevailing conditions. A fayalite slag also has the ability to dissolve sulphur. The dissolved sulphur in the slag can attract elements whose sulphides are stable. This dissolution mechanism is called sulphidic dissolution. When both the oxide and sulphide of an element are unstable under the smelting conditions the element can dissolve in monatomic form, i.e. metallic dissolution. If halogens such as chlorine are present and the halide is stable in the slag there can also be a halidic dissolution.

## 2.4 Distribution of minor elements

The distribution of minor elements between the different phases in copper smelting is of great important. Nagamori and Mackey<sup>21</sup> stated that: “It is often said that steelmaking is a technique of slag-making, meaning that a quality steel results from a good control of the slag. This apparent paradox may be paraphrased for copper smelting by stating that copper-making is a technique of minor element control; a quality copper result from a controlled elimination of minor elements in the course of smelting and electrorefining.”.

During recent decades, distribution of minor elements in copper smelting has been the subject of extensive research. To be able to compare data from different plants and experiments the distribution coefficient  $L_{Me}^{i/j}$  is often used and is defined as:

$$L_{Me}^{i/j} = \frac{(\text{wt-\% Me})_{\text{phase i}}}{(\text{wt-\% Me})_{\text{phase j}}} \quad (3)$$

The distribution coefficient can be deduced from equilibrium thermodynamics. Consider an exchange equilibrium between copper and slag for the minor element Me:



The equilibrium constant, K, is given by:

$$K = \frac{a_{\text{MeO}_y}}{a_{\text{Me}} p_{\text{O}_2}^{y/2}} \quad (5)$$

Considering that the impurity is present in a small amount the activities can be described using Henryan dilute solution activity coefficients. Using the one weight per cent dilute solution standard state, equation (5) can be rewritten as:

$$K = \frac{\gamma_{\text{MeO}_y}^{\circ} (\% \text{Me})}{\gamma_{\text{Me}}^{\circ} [\text{Me}] p_{\text{O}_2}^{y/2}} \quad (6)$$

where parenthesis ( ) are used to designate a concentration in the slag and square brackets [ ] are used for concentration in the metal phase.

Assuming the activity coefficients constant and taking the logarithm of (6):

$$\log L_{\text{Me}}^{S/\text{Cu}} = \log \frac{(\% \text{Me})}{[\% \text{Me}]} = \log K' + \frac{y}{2} \log p(\text{O}_2) \quad (7)$$

A plot of  $\log L_{\text{Me}}^{S/\text{Cu}}$  versus  $\log p(\text{O}_2)$ , should give a straight line and the slope contains information about the nature of the minor element Me in the slag, e.g. the value of y in (4). If the gradient is found to be 0.25 then the metal oxide must be  $\text{MeO}_{0.5}$  and the metal must be  $\text{Me}^+$ . The distribution coefficients of an element Me between matte and metal or matte and slag can be deduced in similar fashion.



## 3 Model development

### 3.1 Previous work

A number of previous successful models have been developed with the objective of using thermodynamics to understand the impact of process parameters on the quality of blister copper and for the purpose of process optimisation. Niemi and Koskinen<sup>22</sup> in 1968 and Goto<sup>23, 24</sup> in the early 1970s used mass and heat balances together with predefined equilibrium reactions to model the Peirce-Smith converter. In these studies, the equations are solved simultaneously with the assumption that the converter system is in thermodynamic equilibrium. While adequate for the period, the Niemi and Koskinen model took into account the main elements in the system being, Cu, Fe, S, O and N with the liquid phases being matte, slag and copper, together with a gas phase. On the other hand, Goto extended the range of elements and in addition, by using the model, was able to indicate the optimum fluxing amounts and times. The work by Goto also included the elements Pb, Zn, H and C and the solid phases silica and magnetite. Tan and Zhang<sup>25</sup> have extended the converter modelling capability with the inclusion of a number of minor elements. The most recent version by Tan<sup>26</sup> provided information of a practical nature for operator use, such as melt temperature. A kinetic model of the Peirce-Smith converter has been developed by Kyllö and Richards<sup>27, 28</sup>. In the model it was assumed that each phase is in internal equilibrium, and the mass transfer between gas and liquid and between the liquids is included to describe kinetic behaviour. The model was used to optimise the conditions for a converter, for instance, the tuyere submergence and tuyere diameter. Nagamori *et al.*<sup>21, 29-31</sup> have in a series of papers presented a method for thermodynamically analysing the Noranda Process for copper matte smelting and converting. The model calculated the equilibrium phase composition for ten minor elements, for a given temperature and

level of oxygen enrichment (from which the partial pressures of oxygen is derived) and some additional process parameters. By varying the matte grade, the volatilisation behaviour of key minor elements was studied. The results, including those for minor elements, were in good agreement with plant data. The above-mentioned models have in common the feature that they included a pre-defined set of equations describing the equilibrium reactions.

Björkman and Eriksson<sup>14</sup> used the program SOLGASMIX to carry out a quantitative equilibrium calculation approach to simulate smelting and converting. In this work, the smelting and converting of chalcopyrite to copper was examined. The calculations were performed isothermally and showed that in order to minimise copper losses to the slag, the silica content and temperature of the slag should be kept as low as possible.

To help overcome the limitations of equilibrium thermochemical computations in systems relevant for process metallurgy, Modigell *et al.*<sup>32</sup> modelled the LD converter used for steel production using a combination of thermochemical computations and momentum transport. The thermochemical equilibrium is first calculated using a global Gibbs minimisation routine which can handle non-ideal behaviour within phases. Following this, the momentum transport is calculated outside the Gibbs minimisation routine. Non-equilibrium conditions within the LD converter were simulated satisfactorily with this approach. The decarburisation reaction and the silica content of the metal phase were simulated quite well. Björkman<sup>33</sup> used the program SOLGASMIX-REACTOR to include non-equilibrium conditions when simulating the Peirce-Smith converter. In the program, the converter vessel is conceptually

divided into a number of segments in which equilibrium conditions are assumed to be reached, yielding a model with concentration and or temperature gradients.

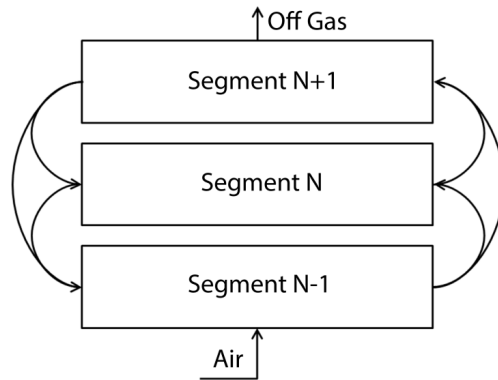
### **3.2 Model basics**

The modelling concept is based on the fact that, at high temperature, chemical reaction rates in liquid melts are usually quite fast. Therefore, on this basis, it can be assumed that thermochemical equilibrium exists locally within the system. Deviations from equilibrium can be caused by limitations in mass and heat transfer between different parts of the system. In fluid systems, mass and heat transfer are dominated by macroscopic momentum transport, i.e. the flow conditions in the system. In solid phases, molecular transport, i.e. diffusive mass and heat transfer, would have the most important influence. As noted, this approach has been used successfully by Modigell *et al.*<sup>32</sup> in the modelling of the LD converter for steel production and Björkman<sup>33</sup> for the Peirce-Smith converter.

The model concept in the present work was realised using the software SimuSage<sup>34</sup>, which is a software tool for process simulation and flowsheeting based on ChemApp and its rigorous Gibbs minimisation technique. Using the above assumptions, the basic structure of the modelling concept was deduced. The Peirce-Smith converter vessel was divided into an arbitrary number of horizontally-aligned segments. Between the segments, concentration and/or temperature gradients were considered to exist. Each segment was modelled as an ideal reactor where equilibrium is reached, i.e. kinetic limitations are neglected. Kyllö and Richards<sup>27</sup> suggested that there is a high degree of oxygen efficiency in the industrial Peirce-Smith converter. Related findings show that the reactions in both the slag and copper blows are under gas phase mass transfer

control, and that the gas residence time in the bath is sufficient to allow the reactions to come close to or reach equilibrium.

The segments are connected by defined mass and energy flows, called streams within SimuSage, see Figure 6.



**Figure 6 Illustration of the assumed general mass flow. The arrows symbolise streams between the segments. Gaseous and oxide species flow upwards, whereas sulphide, silica and liquid metal species flow downwards**

The mass flow is controlled by predefined distribution coefficients, simulating the main mass flows in the converter. Since SimuSage uses thermochemical calculation, the enthalpy of a given stream is calculated, yielding a description of the energy exchange between the segments based on the mass exchange. The procedure is an iterative calculation wherein an increment of air is added to each iteration step, yielding a time dynamic model. Energy losses from the converter resulting from heat transfer by conduction through the refractory, by convection from the vessel shell and by radiation from the converter mouth are taken into account. In addition, the energy

needed to heat up the converter mass from the cold state is included in the model. The bath temperature is assumed to be an average of the temperatures in the segments. In this case, a weighted average is obtained based on the mass of condensed phases in each segment. Implicitly, this means that the average  $c_p$  of each segment per mass is assumed to be equal.

### 3.2.1 Heat Balance

In addition to calculating the equilibrium composition of a system for a given temperature, the Gibbs minimisation routine within SimuSage can also calculate the equilibrium composition and temperature for a given heat duty. Using the latter, a temperature profile for the Peirce-Smith converter throughout the blow can then be obtained. The heat duty for each iteration is obtained from a simple heat balance according to:

$$\text{Heat accumulation} = \text{Heat in} - \text{Heat out} + \text{Heat generation} - \text{Heat consumption} \quad (8)$$

The accumulation term in equation (8) corresponds to the temperature change in the converter during the blow and is calculated for each segment by the minimisation routine for a specific heat duty corresponding to the heat losses.

The ‘heat in’ term is the latent heat of the material charged to the converter, whereas the term ‘heat out’ is both the calculated heat losses, as well as the latent heat of material leaving the converter. As noted, the heat losses arise from two sources: losses through the walls of the converter and convection to the atmosphere and radiation losses through the mouth and hood. The losses by conduction through the refractory walls were, however, neglected in the present calculation. This assumption is based on the result from Goto<sup>24</sup> that the heat losses through the converter wall were in that

particular case approximately 1% of the total heat loss. Radiation losses are calculated by:

$$\dot{q}_{\text{rad}} = \sigma \epsilon_B A_m (T_B^4 - T_H^4) \quad (9)$$

Bath emissivity,  $\epsilon_B$ , and the hood temperature,  $T_H$  were assumed to be 0.8 and 873K, respectively, based in the work of Kyllö and Richards<sup>35</sup>. The converter mouth area,  $A_m$ , depends on the size and geometry of the particular converter vessel; in the present case, the mouth area was 5.2 m<sup>2</sup>.

The heat consumption term is made up of the heat required to raise the charged materials and injected gas to the bath temperature and the heat required to raise the internal surface of the refractory to the new bath temperature. All material within a segment is assumed to reach the equilibrium temperature after a given iteration. The internal surface of the refractory is assumed to obtain the new weighted bath temperature after each iteration. The heat required to raise the internal surface of the refractory to the new temperature is given as:

$$\dot{q}_{\text{ref}} = m_{\text{ref}} c_{p,\text{ref}} \Delta T / 2 \quad (10)$$

where  $\Delta T / 2$  is the average temperature of the refractory, assuming a constant outer surface temperature of 473K. The refractory weight,  $m_{\text{ref}}$ , is assumed to correspond to that of a newly rebuilt converter consisting of 240 tonnes of magnesia-chrome refractory bricks with a  $c_{p,\text{ref}}$  of 960 Jkg<sup>-1</sup>K<sup>-1</sup>.

In the calculation the total heat losses are divided between the segments. The radiation losses described above are taken from the top segment only, whereas the heat required

to raise the internal surface of the refractory is divided between the segments based on their respective sizes.

### **3.2.2 Thermodynamic data**

The thermodynamic system in the model consists of 16 elements: Al, As, Bi, Ca, Cr, Cu, Fe, Mg, N, Ni, O, Pb, S, Sb, Si and Zn. The thermodynamic data used in the calculations are taken from the FactSage 5.5 databases.<sup>36</sup> Stoichiometric compounds were taken from Fact53, while the solutions were from FToxide and FTmisc. The solution phases of liquid matte, slag and metal, together with the solid solutions olivine and wustite type metal oxide were used. In addition to gaseous species from Fact53, AsO (g), As<sub>4</sub>S<sub>4</sub> (g), SbO (g), Bi<sub>2</sub>S<sub>2</sub> (g) and Bi<sub>2</sub>S<sub>3</sub> (g) were also incorporated according to the result by Samuelsson and Björkman<sup>37</sup>. The thermodynamic data on these compounds were taken from the same source.

### **3.2.3 Addition of antimony and bismuth**

Neither antimony nor bismuth are included in the description of the phases slag, matte and liquid metal. Antimony and bismuth are therefore included as dilute solutes into respective phase using activity coefficients using the option with dilute solution within FactSage software. The used activity coefficients are shown in Table 3. The activity coefficients from Björkman<sup>38</sup> are used because they are derived from industrial data. The matte phase modelled in FactSage is based on elements as constituents; therefore, Me(l) is used as dilute species, whereas the slag phase has components as constituents<sup>39</sup>.<sup>40</sup> For this reason BiO<sub>1.5</sub> and SbO<sub>1.5</sub> are also used as dilute components in the slag.

**Table 3 Activity coefficients used in the present model**

Component	Activity coefficient	$\gamma_{1523K}$	Ref.
In matte phase			
Bi	$\exp(4440/T-2.03)$	7.68	<sup>18</sup>
Sb	$\exp(-955.9/T)$	0.24	<sup>38</sup>
In metal phase			
Bi	$\exp(1900/T-0.885)$	2.30	<sup>41</sup>
Sb	$\exp(-4977.9/T+1.24)$	0.009	<sup>38</sup>
In slag phase			
Bi	$\exp(4230.9/T)$	600	<sup>38</sup>
BiO <sub>1.5</sub>	$\exp(-443.979)$	0.51	<sup>38</sup>
Sb	$\exp(626.7/T)$	2.58	<sup>38</sup>
SbO <sub>1.5</sub>	$\exp(417.9/T)$	1.88	<sup>38</sup>

### 3.3 Calculation procedure

Consider a Peirce-Smith converter, arbitrarily divided into a number of segments according to the description above and Figure 6. Initially, matte, flux and cold charge material are added before the start of a simulation and are assumed to be equally distributed between the segments. The calculation technique is one of repetitive substitution and a calculation that moves from bottom to top throughout the segments of the vessel model. Flows in the direction of the calculation are used as input to the calculation of the subsequent segment, whereas flows in the opposite direction are used as input to the segments in the next iteration step. Taking segment N as an example, in the first iteration step the products from the equilibrium calculation flowing with the calculation direction are used as input to segment N+1 in the current

iteration step, whereas equilibrium products flowing opposite to the calculation order are used as reactants in segment N-1 in the next iteration step. During each iteration step an increment of air and/or oxygen is added. The iteration stops when the copper content of the matte phase has reached the chosen value. Instead of the matte copper content, the iron content of the matte can be used, or alternatively, a fixed number of iterations can be used as the stop value.

Flows or streams in SimuSage are defined by stream types and are managed by the user. In the current model, the following stream types were defined: slag consisting of liquid slag plus solid oxides, matte consisting of liquid sulphide matte and any sulphur containing solids, metal consisting of liquid and solid metal,  $\text{SiO}_2$  consisting of solid  $\text{SiO}_2$ , and a gas consisting of a number of gaseous components.

The slag phase, being the least dense liquid phase, is flowing upwards, while sulphide, metal and  $\text{SiO}_2(\text{s})$  phases are flowing downwards and are accumulated in the top and bottom segments, respectively.

It is noted that the model does not attempt to predict the actual fluid flow inside the Peirce-Smith converter. The flows are used to create zones with different conditions and thus the flows should be considered more schematically.

In the optimisation work on the model, the number of segments and the distribution coefficients for mass flows were considered as parameters. Available plant data for the slag blow were used, i.e. slag composition and grade of white metal. The optimisation work carried out earlier by Björkman<sup>33</sup> was used in the current model. The optimisation resulted in a model with three segments and distribution coefficients for

the flow according to Figure 7. The figure illustrates the amount of the equilibrium products flowing between segments in the model.

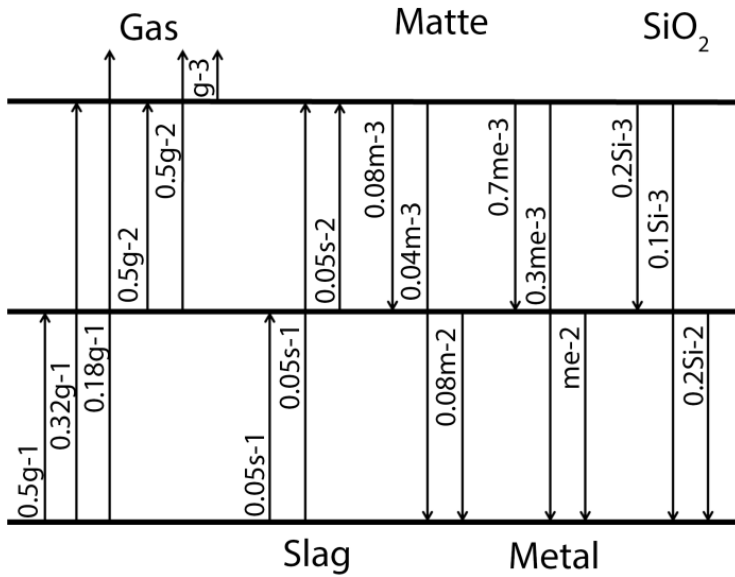


Figure 7 Illustration of the flows between the three segments in the model (segments illustrated with horizontal lines). An arrow reaches the segment where the species react. The equilibrium amounts of gas, matte, slag, metal and SiO<sub>2</sub> streams are denoted by  $g_n$ ,  $m_n$ ,  $s_n$ ,  $me_n$  and  $Si_n$ , respectively

## 4 Model validation

In order to verify the results of the model and the modelling approach a number of charges at the Boliden Rönnskär smelter were followed during 2011 and simulated; the results were then compared with measured plant data. The production samples were analysed on-site by X-ray fluorescence (XRF). It is noted that any entrained material that might be present in a phase was not separated before analysis, a step which could influence the analysis result. A reliable sample of the cold material added to the converter can be difficult to obtain because of the inhomogeneity of the material.

### 4.1 Validation charge

Material input for one of the followed charges is given in Table 4. The chemical analysis of the input material has been normalised to 100%. In addition to matte and silica flux, slag from a previous copper blow and cold material, copper-containing scrap and rejected and spent anodes, was added to the converter. During the simulated charge, an extra slag was skimmed off during the first slag blow. The increment of air for each iteration step was set to 3000 and 6000 Nm<sup>3</sup> during the slag blow and copper blow, respectively, with an oxygen content of 21 vol.-%. Air increments between 1500 and 6000 Nm<sup>3</sup> were tested for the slag blow and it was found that a value of 3000 Nm<sup>3</sup> gave the best agreement with plant data. The influence on the copper blow was small and therefore the higher value was chosen for convenience. The oxygen efficiency during the first and second slag blow was set to 95% and 90%, respectively, and to 85% during the copper blow, based on Boliden Rönnskär's own estimates. The copper content in the matte was used as the end point for the slag blow and sulphur content in the blister was used as the end point for the copper blow. The following

assumptions were made in the simulations: no remaining material from previous charge, the converter has a fresh refractory material and the initial inside temperature of the refractory was assumed to be 1273K. During slag tapping it was assumed that 95%, 20% and 1% of slag, solids and matte, respectively, were skimmed off, based on industry estimates.

**Table 4 Reported inputs for a Peirce-Smith converter charge at the Boliden Rönnskär smelter. Numbers within bracket shows non-normalised wt-% Cu. Input weights are given in tonnes. Cold material refers to copper-containing scrap, rejected anodes, etc.**

Input material [tonne]	Charge 860		
	slag blow 1	slag blow 2	copper blow
Matte:			
Flash furnace	165 (59)	51 (59)	-
Electric furnace	103 (52)	57 (52)	-
Silica flux	23	14	-
Slag from copper blow	14	-	-
Cold material	29	22	115
Blowing air [Nm <sup>3</sup> ]	78800	69700	208200
O <sub>2</sub> enrich. [Nm <sup>3</sup> ]	2358	-	3127
Average blowing rate [Nm <sup>3</sup> min <sup>-1</sup> ]	800		

## 4.2 Validation result and discussion

### 4.2.1 Slag blow

The model approach was first validated for the slag blow and also compared against an equilibrium calculation. The results can be seen in Tables 5 and 6. An equilibrium calculation equals a simulation based purely on thermochemical equilibrium, whereas the model approach includes mass flows as described in chapter 3.

**Table 5 End composition of liquid slag for the slag blow in charge No. 860. Assays in wt-% and total tonnage of slag including all slag skimming in tonne**

	Liquid slag										Total
	Fe	Cu	Pb	Zn	S	SiO <sub>2</sub>	CaO	MgO	Bi	Sb	Tonnage
Plant data	31.2	6.1	6.5	6.6	-	29.9	0.6	0.3	0.006	0.11	181
Model	33.1	4.7	4.0	10.2	0.01	30.9	0.3	0.1	0.006	0.04	148
Equilibrium	36.4	2.2	3.0	9.0	0.1	32.7	0.3	0.1	0.001	0.05	143

**Table 6 End composition of liquid white metal for the slag blow in charge No. 860. Assays in wt-%**

	White metal						
	Fe	Cu	Pb	Zn	S	Bi	Sb
Plant data	0.4	75.9	0.5	0.1	17.8	0.02	0.1
Model	0.9	75.9	1.7	0.6	20.0	0.03	0.1
Equilibrium	1.1	75.9	1.6	0.6	19.9	0.02	0.1

Comparing plant data with the predicted slag compositions it can be seen that the model which includes mass flows is in better agreement, especially for the copper content in slag, see Table 5. Lead and zinc deviate for both approaches; this could

indicate that the removal of zinc and lead is not solely equilibrium controlled. The reason could also be a result of analytical errors, the presence of entrained matte in slag or potential errors within the thermodynamic data used in the model. For the white metal, Table 6, the difference between the model and the equilibrium calculation is less pronounced. However, the same tendency can be seen for zinc and lead.

The difference in zinc content between that for the plant data and simulated values cannot readily be explained. It could be a result of errors in the thermodynamic data used. As reported by both Jak *et al.*<sup>42</sup> and Björkman<sup>43</sup>, measured and reported activities of ZnO in ZnO-SiO<sub>2</sub> melt are low and inconsistent with the phase diagram. A negative deviation from the ideal activity leads to a stabilisation of ZnO in the melt. This could explain the higher Zn content in the simulated slag versus that indicated by the plant data. In Table 7, observed and calculated distribution coefficients,  $L_{Me}^{i/j}$ , from the present study are compared with literature.  $L_{Me}^{M/S}$  is used, which is the mass fraction ratio between matte and slag. As can be seen, the predicted distribution coefficients for Zn in the present study agree well with the observed in contrast to those for lead.

**Table 7 Calculated and observed distribution coefficients,  $L_{Me}^{M/S}$**

	Charge No. 860		Kyllo <sup>44</sup>	Chen No. 50 <sup>45</sup>		Chen No. 173 <sup>45</sup>		
	Obs.	Calc. Model		Calc. Equilib.	Obs.	Calc.	Obs.	Calc.
Pb	0.07	0.43	0.54	0.07	0.50	0.02	0.45	0.60
Zn	0.01	0.06	0.05	0.03	0.02	0.003	0.77	0.02

This supports the hypothesis that there could be some errors in the data used or that the model approach influences the vaporisation of Zn and Pb negatively. The slightly higher end-point temperatures of the slag blows could also influence the result.

Slag tonnages can be seen in Table 5. The difference in tonnages is most likely due to the use of normalised feed analysis. The normalisation is done because the analyses of the feed do not sum up to 100%. Not all elements are analysed and the inhomogeneity of the material also contributes to the uncertainty. The white metal tonnages were not measured during the plant trials.

#### **4.2.1.1 Antimony and bismuth**

As can be seen in Tables 5 and 6 the model predicts the content of Bi and Sb fairly well, except for Sb in the slag phase. The model approach predicts the content of Bi better than an equilibrium calculation for the liquid slag. Due to low content of minor elements present in the phases and the challenge of proper sampling, distribution coefficients,  $L_{Me}^{M/S}$ , are used. In Table 8 distribution coefficients for Bi and Sb between the phases matte (M) and slag (S) are shown. Bi is in better agreement than Sb using the model.

**Table 8 Distribution coefficient for Bi and Sb  
for validation charge No. 860**

	$L_{Me}^{M/S}$	
	Bi	Sb
Plant data	3.3	0.9
Model	4.2	2.8
Equilibrium	20	2.2

## 4.2.2 Copper blow

During the validation of the copper blow one segment sufficed to describe the process. This indicated that the converting of white metal to blister copper is generally equilibrium governed. The predicted result is shown in Tables 9 and 10. As can be seen, the predicted composition of the blister copper is in better agreement than when predicting the slag composition. This could be a result of the assumption of the amount of remaining slag after skimming, which is always difficult to estimate in the actual converter. Slag formation during copper blowing is quite a complex process: the slag may not be totally liquid which, depending on the samples taken, can give rise to errors in the analysis and therefore result in deviations when comparing against the predicted liquid slag. As can be seen in Tables 9 and 10 the tonnages differ. This is most likely because of the normalised input data, as discussed earlier.

**Table 9 Comparison between predicted and observed plant data compositions of slag from copper blow for charge No. 860. Assays in wt-% and tonnages in tonne**

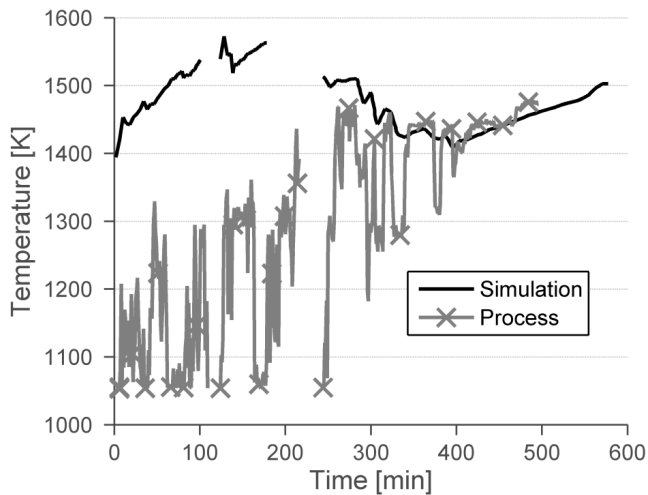
	Liquid slag										Total
	Fe	Cu	Pb	Zn	S	SiO <sub>2</sub>	CaO	MgO	Bi	Sb	Tonnage
Plant data	20.4	28.3	6.3	5.0	0.2	14.1	0.4	0.4	0.02	0.2	7
Model	30.1	23.9	7.4	11.4	0.0	5.8	0.1	0.0	0.02	0.1	13

**Table 10 Comparison between predicted and observed plant data compositions of blister copper for charge No. 860. Assays in wt-% or ppm and tonnages in tonne**

	Blister copper								Total
	Fe [ppm]	Cu	Pb	Zn	S [ppm]	Bi	Sb	Tonnage	
Plant data	30	98.9	0.1	0.0	230	0.01	0.07	322	
Model	6	98.2	0.8	0.03	208	0.02	0.11	358	

### 4.2.3 Heat balance

The predicted and measured temperature profiles for the whole converter cycle are shown in Figure 8. The data are divided into three groups after the three blowing periods. The simulated data are shifted in the x-axis, so that the starting point for each period is the same as for the process data. During operation of the converters (as part of the process control system) an IR pyrometer, located in the converter hood, is pointing to the melt.



**Figure 8 Predicted temperature profile for the whole converter cycle and the temperature measured by an IR pyrometer located in the converter hood**

In general, the predicted temperature profile roughly corresponds to what can be expected from converting copper matte in a Peirce-Smith converter; however, for the slag blow the temperatures are a bit high compared to those measured and values

reported in literature.<sup>10, 27</sup> The predicted temperatures are influenced by the assumed start temperature of the refractory wall, as well as the assumed mass of refractory material. During material additions to a Peirce-Smith converter the converter is normally tilted and the tuyeres will therefore be located over the melt. The converting and heat generation are interrupted because the exothermic reactions are stopped. This is not included in the model and can contribute to the higher predicted temperature. Factors that can also influence the predicted values are the fact that the simulations are run with constant oxygen content in the blast and a constant oxygen yield in each iteration. In the plant operation oxygen enrichment is typically used at the beginning of each blowing step, and then may change. This might also have an influence on the temperature profile and also on the vaporisation of impurities. There is also a possibility that the oxygen efficiency may vary slightly during the blow (mainly because of variations in liquid level). This is not included in the simulation and could lead to a higher predicted temperature because more oxygen is assumed to react than in the process.

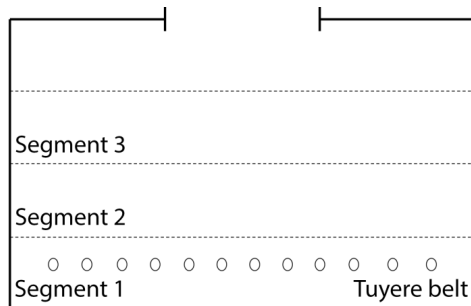
The IR pyrometer is, as mentioned, located in the converter hood and points towards the melt. During the slag blow, dust formation is more prominent than during the copper blow. The dust can interfere with the IR pyrometer and explain part of the deviation. Another reason could be that the predicted temperature is the bath temperature as a weighted average between the segments in the model, whereas the IR pyrometer only measures the top of the bath.

#### **4.2.4 Model parameters**

The influence of the model parameters, i.e. flow distribution parameters, was also tested. The slag composition and, especially, the slag copper content were mostly affected by changed mass flow parameters. By, for instance, altering the blast distribution between the segments, the oxidation conditions in the segments are changed, thereby also affecting the copper content of the slag.

### 4.3 Concluding remarks

By introducing a model with individual but linked segments, non-equilibrium conditions within a Peirce-Smith converter have been simulated. A principle sketch over the model approach is shown in Figure 9. The purpose of employing segments was to consider a number of different reaction zones which yield different conditions within the converter. By allowing a major part of the blast to enter segment one and the rest to the other segments, a variation in oxygen potential can be achieved. The higher oxygen potential results in a higher total copper content of the liquid slag that agrees better with plant data, suggesting that the copper level in slag is governed not only by equilibrium conditions. Another reason can be entrained matte in the slag.



**Figure 9 Sketch of the Peirce-Smith converter illustrating the segments and the tuyeres line**

From the validation, it was concluded that the model was preferable to an equilibrium calculation and that the model can be used for predicting the behaviour of Bi and Sb.

## 5 Model application

### 5.1 Case study

A number of simulations were performed to investigate the influence of addition of black copper with or without slag to a Peirce-Smith converter. The calculations have been performed isothermally at 1523K to avoid the influence of temperature, with a maintained Fe/SiO<sub>2</sub> ratio in the slag between 1-1.5. The slag blow is divided into two blows according to normal operating conditions. The first and second blows are charged with 200 and 100 tonnes of matte, respectively. The end points of the blows are the copper content in the matte phase and are set to 75 and 76 wt-% Cu, respectively. 20 tonnes of black copper, with or without slag, is added to the blow either at the start or in the middle of the first or second slag blow, respectively. Air is used as blast. Input materials are listed in Table 11. Two different matte grades are chosen to investigate the influence of blowing time. Compositions of black copper and the mixture between black copper and slag are chosen from a pure theoretical aspect, giving one material with high copper content and the other with a lower copper content but with SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> present. Between the two blows a skimming is performed, which assumes that 95% of the liquid slag, 20% of solids and 1% of matte is removed based on the same assumption as in the validation. Table 12 shows the different simulations made and the respective simulation numbers which will be used for reference within the text. The different addition points are chosen to find guidance for the optimum removal of Bi and Sb from the matte.

**Table 11 Input material. Assay in wt-%**

	Cu	Fe	S	Pb	Zn	Bi	Sb	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
Matte	45	21	26	2	2.5	0.5	0.5	-	-
Matte	65	5	22	2	2.5	0.5	0.5	-	-
Black Copper	64	14	-	8	6	1	1	-	-
Black copper with slag	35	5	-	4	3	1	1	29	19
SiO <sub>2</sub>	-	-	-	-	-	-	-	100	-

**Table 12 Simulation variations**

Sim. No.	Matte grade		Addition		Point of addition			
	45	65	Black copper	Black copper with slag	Start SB1	Mid SB1	Start SB2	Mid SB2
A1	X	-	-	-	-	-	-	-
A2	X	-	X	-	X	-	-	-
A3	X	-	X	-	-	X	-	-
A4	X	-	X	-	-	-	X	-
A5	X	-	X	-	-	-	-	X
A6	X	-	-	X	X	-	-	-
A7	X	-	-	X	-	X	-	-
A8	X	-	-	X	-	-	X	-
A9	X	-	-	X	-	-	-	X
B1	-	X	-	-	-	-	-	-
B2	-	X	X	-	X	-	-	-
B3	-	X	X	-	-	X	-	-
B4	-	X	X	-	-	-	X	-
B5	-	X	X	-	-	-	-	X
B6	-	X	-	X	X	-	-	-
B7	-	X	-	X	-	X	-	-
B8	-	X	-	X	-	-	X	-
B9	-	X	-	X	-	-	-	X

## **5.2 Case study result**

The distribution of Bi and Sb between the off-take gas, matte, metal and slag as predicted by the model is given in Tables 13 and 14, respectively. The values presented are accumulated distribution for the total blowing period. Removal of Bi through vaporisation decreases, while removal through slagging increases with increasing matte grade. According to the simulation, vaporisation of Sb is negligible. Removal of Sb through slagging is decreasing with increasing matte grade.

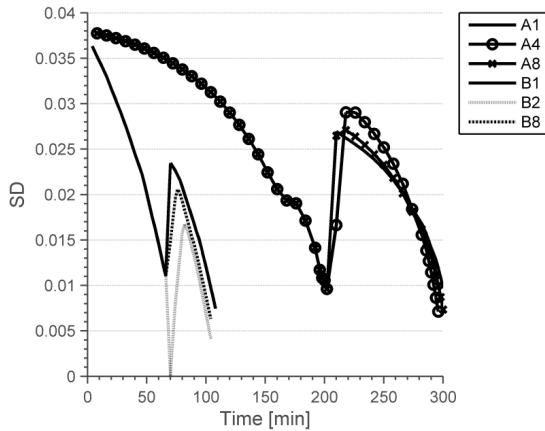
**Table 13 Distribution of bismuth between gas, matte, metal and slag phase**

Simulation	Slag blow 1				Slag blow 2				
	No.	Gas	Matte	Metal	Slag	Gas	Matte	Metal	Slag
A1		99.93	0.04	0.00	0.03	95.72	4.22	0.00	0.13
A2		99.48	0.35	0.01	0.16	95.07	4.67	0.00	0.26
A3		95.32	2.96	0.05	1.68	93.79	4.90	0.00	1.31
A4		99.93	0.04	0.00	0.03	88.66	10.99	0.00	0.36
A5		99.93	0.04	0.00	0.03	86.34	13.06	0.00	0.60
A6		99.42	0.33	0.00	0.25	95.18	4.52	0.00	0.30
A7		97.79	1.22	0.02	0.97	95.00	4.21	0.00	0.78
A8		99.93	0.04	0.00	0.03	90.22	9.46	0.00	0.32
A9		99.93	0.04	0.00	0.03	88.23	11.27	0.00	0.49
B1		69.17	29.62	0.00	1.21	60.39	38.14	0.00	1.47
B2		47.35	50.96	0.00	1.68	48.31	49.30	0.13	2.26
B3		50.98	47.44	0.00	1.57	50.44	47.46	0.00	2.10
B4		69.17	29.62	0.00	1.21	47.68	50.61	0.00	1.71
B5		69.17	29.62	0.00	1.21	50.52	48.04	0.00	1.44
B6		60.61	37.77	0.00	1.62	57.01	41.05	0.00	1.94
B7		57.97	39.81	0.00	2.22	55.90	41.71	0.00	2.39
B8		69.17	29.62	0.00	1.21	51.00	47.35	0.00	1.65
B9		69.17	29.62	0.00	1.21	50.46	47.73	0.00	1.81

**Table 14 Distribution of antimony between gas, matte, metal and slag phase**

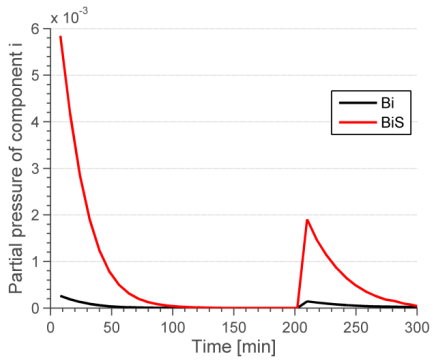
Simulation	Slag blow 1				Slag blow 2			
	No.	Gas	Matte	Metal	Slag	Gas	Matte	Metal
A1	0.10	80.02	0.00	19.88	0.11	71.05	0.00	28.85
A2	0.09	80.51	0.37	19.02	0.10	70.02	0.00	29.87
A3	0.07	84.18	0.40	15.35	0.10	72.26	0.00	27.65
A4	0.10	80.02	0.00	19.88	0.09	69.48	0.00	30.42
A5	0.10	80.02	0.00	19.88	0.09	69.04	0.00	30.87
A6	0.09	83.97	0.00	15.94	0.10	70.96	0.00	28.94
A7	0.09	77.82	0.29	21.81	0.10	69.24	0.00	30.65
A8	0.10	80.02	0.00	19.88	0.10	71.84	0.00	28.06
A9	0.10	80.02	0.00	19.88	0.09	69.10	0.00	30.80
B1	0.04	88.19	0.00	11.78	0.04	85.14	0.00	14.82
B2	0.03	86.70	0.00	13.27	0.04	82.12	1.15	16.59
B3	0.02	90.86	0.00	9.11	0.03	85.29	0.00	14.68
B4	0.04	88.19	0.00	11.78	0.03	83.33	0.00	16.63
B5	0.04	88.19	0.00	11.78	0.03	87.82	0.00	12.15
B6	0.04	86.99	0.00	12.98	0.04	83.53	0.00	16.43
B7	0.03	83.95	0.00	16.02	0.04	81.90	0.00	18.06
B8	0.04	88.19	0.00	11.78	0.04	84.18	0.00	15.78
B9	0.04	88.19	0.00	11.78	0.03	83.31	0.00	16.65

Figure 10 shows calculated sulphur deficiency, SD, for the matte phase plotted vs. blowing time. SD drops to its minimum faster with a higher starting grade of matte.

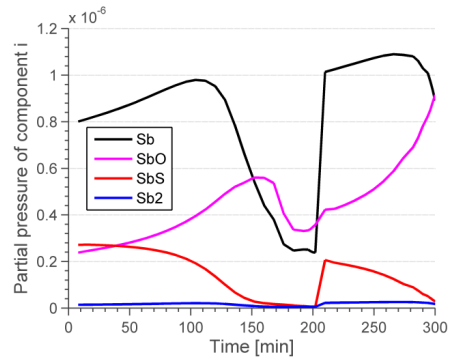


**Figure 10 Sulphur deficiency versus blowing time**

Figures 11 and 12 show the partial pressures for the dominant gaseous components for bismuth and antimony during a simulation with a starting matte grade of 45 wt-% Cu. According to the simulation, Bi is vaporising in the form of bismuth sulphide in the beginning of the blow. Antimony is, however, vaporising during the whole blow but at a much lower level. As the blow proceeds, antimony oxide becomes the dominant component together with monoatomic antimony.

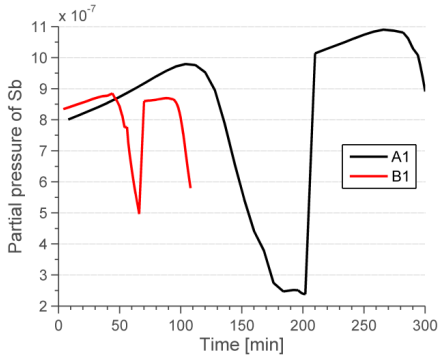


**Figure 11 Partial pressures of dominant Bi containing gas species for simulation A1**

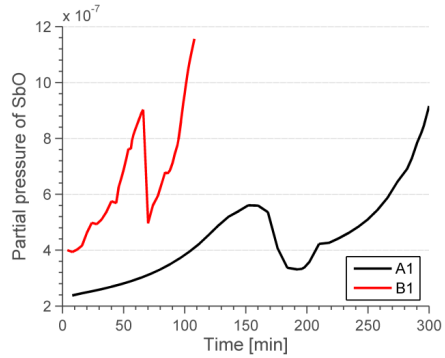


**Figure 12 Partial pressures of dominant Sb containing gas species for simulation A1**

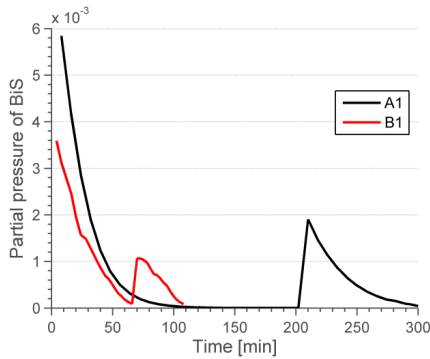
Figure 13 to 15 show the partial pressure of the gaseous components BiS, Sb and SbO for simulations A1 and B1. The simulations show that when starting with a matte grade of 45 wt-% Cu a higher partial pressure of BiS(g) is obtained compared to when starting with higher matte grade. A similar tendency can be seen for Sb(g) in Figure 13, whereas for SbO(g), see Figure 14, the opposite is valid. However, the partial pressures for Sb(g) and SbO(g) are low compared to BiS(g).



**Figure 13 Partial pressure of Sb(g) versus time for simulations A1 and B1**



**Figure 14 Partial pressure of SbO(g) versus time for simulations A1 and B1**



**Figure 15 Partial pressure of BiS (g) versus time for simulations A1 and B1**

Figures 16 and 17 show the total distribution vs. time for Bi and Sb. As can be seen, the vaporisation rate for Bi is higher at the beginning of the blow than near the end of the blow. During an addition of black copper with or without slag the vaporisation rate decreases. Antimony does not show the same tendency. Antimony is eliminated mainly through slagging, which seems to be dependent on the starting matte grade. A lower matte grade gives a higher slagging rate than a higher matte grade. Addition of black copper with or without slag does not seem to influence the distribution.

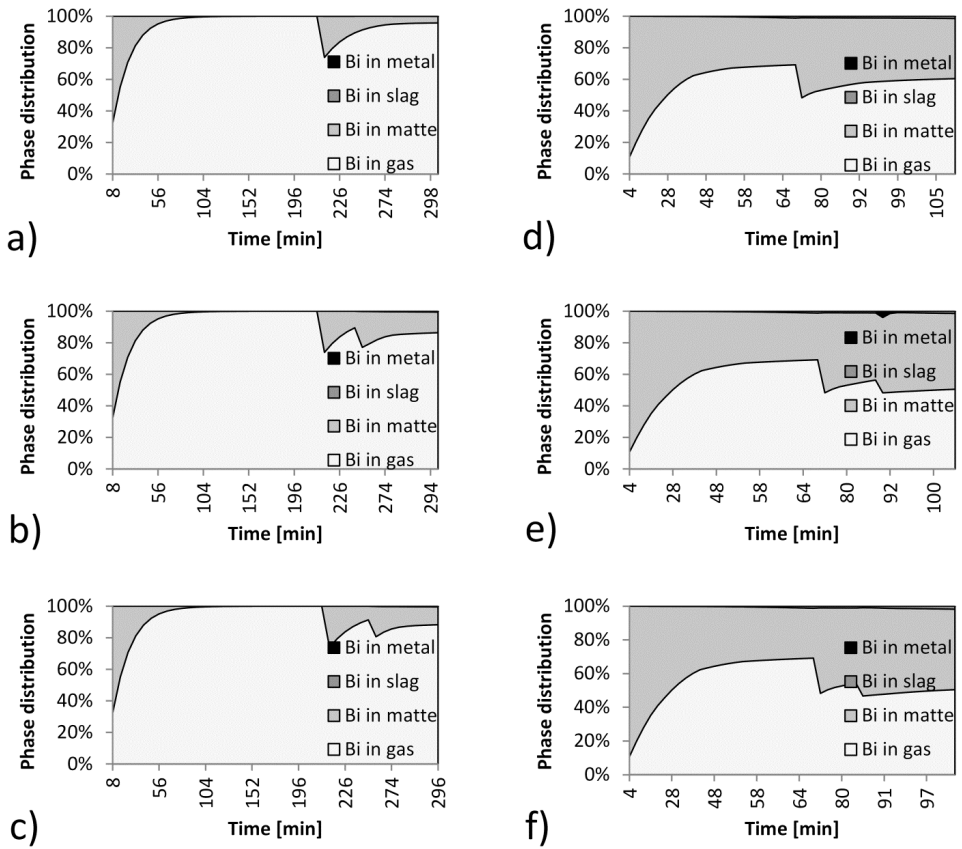


Figure 16 Distribution of Bi vs. time between the phases. a-c show simulations A1, A5 and A9 and d-f show simulations B1, B5 and B9

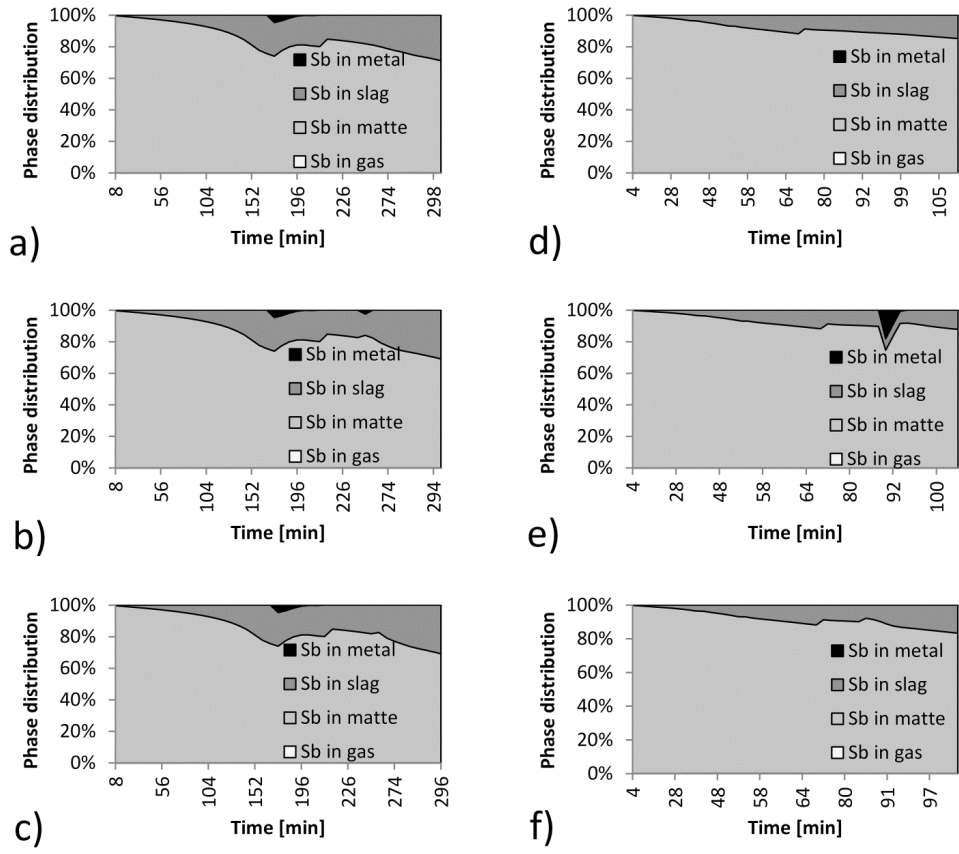


Figure 17 Distribution of Sb vs. time between the phases. a-c show simulations A1, A5 and A9 and d-f show simulations B1, B5 and B9

## 5.3 Case study discussion

The removal of minor elements during converting of copper matte is an important factor that must be considered when operating parameters and or feed materials are to be changed. With an increasing interest from smelters to treat secondary material such as WEEE and e-scrap it is necessary to understand the behaviour of minor elements, because the content of these can be high.

The developed model for the Peirce-Smith converter was used to investigate the distribution of Bi and Sb during addition of black copper. Bismuth distributes mainly between the gas phase and the matte, as can be seen in Figure 16. The distribution to the gas phase reaches its maximum at the end of the first slag blow. This suggests that materials containing higher amounts of bismuth should be added in the beginning of the blow. The distribution of bismuth to the slag phase is negligible. Johnson *et al.*<sup>46</sup> have in their experiments also seen a low solubility of Bi in slag. Larouche<sup>47</sup> has in his Master's thesis work collected distribution data from laboratory work and industry. The findings also show a low distribution of Bi to the slag phase. For Sb, the distribution to the slag increases as the blow proceeds, see Figure 17. This has also been seen by Yazawa<sup>48</sup> and Johnson *et al.*<sup>46</sup>. The explanation is that as the blow proceeds, the partial pressure of oxygen increases and Sb forms  $\text{SbO}_{1.5}$ .

### 5.3.1 Effect of matte grade

The case study shows that a higher matte grade lowers the distribution of Bi and Sb to the gas phase, see simulations A1 and B1 in Tables 13 and 14 and in Figures 16 a and d and Figures 17 a and d. The distribution to the slag phase increases with an increasing matte grade for Bi and decreases for Sb. The total removal of both Bi and Sb from the produced white metal decreases with increasing matte grade. It is difficult

to compare distribution of minor elements between matte with different copper content and slag from laboratory experiments with the simulation. Lower matte grade yields longer blowing period and more time for vaporisation.

To explain the influence of matte grade the concept of sulphur deficiency can be used. The melts can be viewed as consisting of the molecules  $\text{Cu}_2\text{S}$  and  $\text{FeS}$  and whose bonds are not purely covalent, making sulphur electronegative. The sulphur deficiency is zero for compositions on the  $\text{Cu}_2\text{S}$ - $\text{FeS}$  pseudo binary line. A composition with a positive value is located on the sulphur-rich side and can be interpreted as the melt that has an excess of available sulphur sites, whereas a composition with a negative value is located on the metal-rich side and the melt has a lack of sulphur sites. This means that, in sulphur-deficient melts, minor elements dissolve as metals and as sulphides in sulphur-rich melts. This concept is explained in more detail and elaborated by Lynch *et al.*<sup>17</sup>. As the blow proceeds, the sulphur deficiency drops, as can be seen in Figure 10. It can also be seen that for a blow that starts with a higher matte grade the sulphur deficiency drops faster and to a lower value compared to when starting with a lower matte grade (compare simulations A1 and B1 in Figure 10).

### **5.3.2 Distribution to gas phase**

The difference between Bi and Sb regarding distribution to the gas phase can be understood by comparing Figures 11 to 15.  $\text{BiS(g)}$  is the gas component among the Bi-containing components with the highest partial pressure. For Sb,  $\text{Sb(g)}$  and  $\text{SbO(g)}$  have the highest partial pressures. However,  $\text{BiS(g)}$  has a partial pressure that is 1000 times higher compared to Sb-containing components. The partial pressure of  $\text{BiS(g)}$  drops very rapidly with increasing matte grade. A low matte grade is favourable for

good removal of Bi through vaporisation. This was also pointed out by Chaubal and Nagamori <sup>49</sup>. Vaporisation of Sb behaves differently compared to Bi. At the start of a blow, Sb(g) is the main component together with SbO(g) and SbS(g), which have slightly less partial pressure. As the blow proceeds, the partial pressure of SbS(g) decreases, whereas SbO(g) and Sb(g) increase. Sb(g) reaches its maximum before SbO(g), see Figure 12.

### **5.3.3 Addition of black copper**

Addition of black copper as a secondary material to the converting process leads to lower removal of Bi through vaporisation, see simulations A1-A5 and B1-B5 in Table 13. To maintain a good removal the addition should be made at the beginning of a blow. The effect is not as evident for high-grade matte as for low-grade matte. Figures 16 b and c show the progress during simulations A5 and B5, addition of black copper in the middle of slag blow 2. The addition corresponds to the peak seen in the diagrams. Directly after the addition the distribution to the gas phase drops. The explanation may be that the metal phase is dissolved into the matte phase. It should be noted that the model assumes that added material is directly mixed with the material already in the converter, which means that the dissolution is equilibrium-controlled in the simulation. Starting the blow with a higher matte grade as in simulation B5, the total addition of black copper cannot directly be sulphidised by the matte phase and a metal phase is formed. Antimony behaves differently; see simulations A1-A5 and B1-B5 in Table 14. As mentioned earlier, removal of Sb through vaporisation is negligible; on the other hand, slagging is more prominent. Black copper should be added early during a blow to maintain a good removal through slagging. Because of the discrepancy for Sb from the validation the actual values should not be seen as absolute, but the trends can be used.

### 5.3.4 Addition of black copper with slag

Addition of black copper with slag slightly improves the removal of Sb to the slag phase; compare Figures 17 a and c or d and f. This can be explained by the extra addition of fluxing agents by the black copper slag. Johnson *et al.*<sup>46, 50</sup> investigated the addition of Al<sub>2</sub>O<sub>3</sub>, MgO and CaO to fayalite slag and the effect it had on the distribution of minor elements. The result showed that small amounts of the slag additives slightly increased the solubility of Sb in slag. The distribution of Bi to the slag increased at low matte grades with the slag additives. Addition of Al<sub>2</sub>O<sub>3</sub>, MgO and CaO will, however, influence the properties of the slag. The slag viscosity and melting point are, for instance, dependent on the Al<sub>2</sub>O<sub>3</sub> content, as seen by Mostaghel *et al.*<sup>51</sup>, and a high viscosity and melting point can cause problems with slag tapping and solidification of slag in the process vessel. If slag additives are used to improve the removal of unwanted elements, caution must be taken with respect to the slag properties.

## **5.4 Concluding remarks**

The dynamic non-equilibrium model developed and validated as described in chapters three and four was used to investigate the influence on the distribution of Bi and Sb during addition of black copper with or without slag. Addition of either lowers the removal of Bi and Sb compared to a blow without addition. To maintain a good total removal of Bi and Sb, black copper should be added as early as possible during converting of copper mattes. The same is true for addition of black copper together with slag. It should be noted that the simulations were run isothermally. The influence addition of black copper has on the converter temperature was not studied within this work. The added black copper is also assumed to directly mix with the other material present in a segment. The effect of mixing times is therefore not studied.

The model can be used to simulate the impact of different feed materials on, for instance, the removal of impurities and parameters that affect the overall heat balance.



## 6 Conclusions

Building on previous work reported in the literature, a dynamic, non-equilibrium model based on thermodynamic calculations and a new segmented concept of the vessel has been developed to predict the chemistry and heat balance in a Peirce-Smith converter. From this study the following conclusions have been stated:

- 1) Calculated data were compared with actual plant data. The model was found to predict the composition of the condensed phases quite well.
- 2) Antimony and bismuth were included as dilute solutes into the slag, matte and liquid copper phases. The model describes the distribution of Bi well, whereas the distribution of Sb is not as good and should only be used for trends.

The model has been demonstrated to work as a simulation tool for process changes. In the current case, the influence of black copper (originating from recycling of e-scrap) addition on the distribution of Bi and Sb was investigated.

- 3) Black copper with or without slag, originating from melting e-scrap, lowers the removal of Bi and Sb when added to the converting process.



## 7 Future Work

From this work it can be concluded that to be able to properly predict minor-element distribution during copper converting and addition of secondary material it is important to have valid thermodynamic data describing the system. To further develop the model, the following work is suggested for the future:

- Evaluate and optimise thermodynamic data for minor elements relevant for copper smelting systems
- Expand the model to include process events
- Full-scale trials to validate the behaviour during addition of melted e-scrap
- Use a combination of simulations, laboratory experiments and full-scale trials to improve the recycle rates of minor elements
- Use the model to simulate the impact of different feed materials on, for instance, the removal of impurities and parameters that affect the overall heat balance and in the long term improve the total recycling rate of a metal entering a copper smelter.



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# Paper I

Development of a model for copper converting

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# Paper II

Thermodynamic process modelling of black copper addition to a Peirce-Smith converter: Effect on the distribution of antimony and bismuth

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Submitted

