

THE IMPURITIES BEHAVIOUR ANALYSIS IN THERMODYNAMIC SIMULATION MODELS IN COPPER METALLURGY

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ABSTRACT

Modeling and simulation, including computer simulation/calculation software or program and mathematical representations of physics and chemistry of complex metallurgical systems, have been increasingly used to assist: process development and design, process evaluation and optimization, production scheduling and planning, process control, and business evaluation. Pyrometallurgy provides excellent case studies of thermodynamic principles. Computational modeling is a powerful way to explore the effects of process variables on smelting systems, and in particular on the behavior of minor elements. However, it is necessary to know something about the thermodynamics of the minor metals in the present phases before computational thermodynamics can make reasonable predictions about minor element distributions. The behaviour of minor elements is of great importance during copper smelting operations. These elements can affect adversely the mechanical properties of product copper and also are a major environmental pollutants. Review of thermodynamic simulation models for copper matte production in the conventional copper smelting process were presented in this paper, with special emphasize on thermodynamic analysis of impurities behaviour in copper metallurgy.

Keywords: modeling, copper metallurgy, simulation, thermodynamics, software.

INTRODUCTION

The rapid increase in the standard of living in the developing world means that more and more natural resources are required. Consequently we need new technology and better scientific tools in order to conserve the diversity and beauty of nature, and to simultaneously allow increased consumption by large population groups in all nations.

Simulation models make it possible to optimize process output and minimize waste materials, identify metering errors and improve the understanding of process interdependencies. Model may be used to rapidly

focus expensive experimental research towards ideal process conditions in metallurgy.

Models enables the pre-test simulation of the effect of recycling streams, raw materials and different operating conditions on process efficiency and emissions, all on a desktop computer without needing to disrupt the actual process.

Simulation models are an invaluable tool for any process engineer or scientist because one laboratory experiment may cost much more than a single license of software.

Iron and sulphur are the principal impurities in the copper concentrates comprising on average as much

as 60 % by mass of the concentrate. Another group of impurities present at lower concentrations (often only few ppm in feed) are referred to as “**MINOR ELEMENTS**”. Their detrimental impact on quality of the copper requires a special attention to limit their presence at low levels in the final cathode. Removal of minor elements from copper, even when they are present at low concentration, might be extremely difficult because of their similar thermodynamic and electrochemical properties. In addition, some have been found to be toxic (e.g., arsenic and lead). So their removal might present environmental and health and safety challenges [1].

The behaviour of minor elements is of great importance during copper smelting operations. These elements can affect adversely the mechanical properties of product copper and also are a major concern as environmental pollutants [2]. Basic studies on the behaviour of these elements in the Noranda process [3] and Peirce-Smith converting have been reported in recent years.

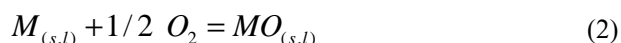
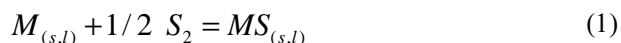
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Chemical reactions are used to describe complex multi-component systems, but they are an oversimplification. In such a system all species interact with each other and the changes in concentrations of individual species affect the concentrations of all other species.

Specifying all phases and species requires some a priori understanding of the system. Specifying the activity coefficients is frequently difficult and requires a thorough search of the literature. Often all activity coefficients can be assumed to be unity if all that is needed is an understanding of the relationships between species concentrations in the system.

Yazawa examined important problems accompanying copper smelting such as the behaviour of magnetite, dissolution of copper in the slag and the behaviour of impurities which are clarified thermodynamically. The harmful elements such as lead, bismuth, arsenic and antimony are easily absorbed into metallic copper. Also, to clarify the behaviour of impurities more quantitatively, their respective activity was calculated by A. Yazawa. He reached the conclusion (agreement) that the stability of an impurity metal in the form of metal, oxide or sulphide can be discussed

by thermodynamic evaluation of the following two reactions [4]:



P. Larouche studied minor element (As, Sb, Bi, Pb, Ni) behaviour, control and removal techniques in the conventional copper smelting/electrorefining process. The effect of various matte smelting furnace operating parameters such as matte grade, oxygen enrichment, concentration in feed, other minor constituents and temperature on minor element partition to gas and distribution coefficient (wt % matte / wt % slag) was analyzed theoretically and validated with industrial data when possible. In the matte smelting furnaces, the volatilization of As, Sb, Bi, Pb, Ni averaged respectively 66 %, 22 %, 46 %, 22 % and 2 % of the total input to the furnace. Volatilization was found to depend mainly on oxygen enrichment and matte grade (% Cu) in addition to feed content for As [1].

The distribution behaviour of Pb, Zn, Bi, Sb, and As between gas, matte and/or copper, and slag phases in copper smelting, converting and combined (smelting + converting) system has been investigated by H. G. Kim and H. Y. Sohn [6]. The minor element behaviour was studied for iron silicate and calcium ferrite slag, and their abilities to eliminate these impurities were compared. For the calcium ferrite slag, the results from computer simulation were compared with the observed data from the Mitsubishi converter, and fairly satisfactory agreement was obtained. The effects on the behaviour of minor elements of the operating parameters such as temperature, the final matte grade in smelting, the initial matte grade in converting, the activity of FeO and the O/Fe ratio in slag are discussed. According to Yazawa et al. [13], the composition of matte produced with calcium ferrite slag is slightly different from that with fayalite slag [3].

The simulation predicted higher elimination by slagging and lower elimination by volatilization due to reduction in gas volume at a higher oxygen content in the injected gas. According to the simulations, the elimination of Bi and As can be greatly affected by the level

Table 1. Chemical reactions and Standard Gibbs Energy of minor elements reaction in Isasmelt and flash furnace [5, 6].

Copper smelters	Isasmelt furnace		Flash furnace	
Element	Reaction, ΔG_i^0 ($cal\ mol^{-1}$) and reference			
Pb	$Pb_{(l)} + 0.5O_{2(g)} = PbO_{(l)}$ $-46930 + 20.20\ T$	[7]	$Pb_{(l)} + 0.5O_{2(g)} = PbO_{(l)}$ $-46930 + 20.20\ T$	[2,10]
	$Pb_{(l)} + 0.5S_{2(g)} = PbS_{(l)}$ $-26730 + 12.20\ T$	[8]	$Pb_{(l)} + 0.5S_{2(g)} = PbS_{(s)}$ $-37580 + 19.12\ T$	[11]
	$PbO_{(l)} + CO_{(g)} = Pb_{(g)} + CO_{2(g)}$ $25750 - 37.31\ T + 4.504\ T\ \log T$	[5]		
Zn	$Zn_{(l)} + 0.5S_{2(g)} = ZnS_{(s)}$ $-63290 + 23.47\ T$	[7]	$Zn_{(l)} + 0.5S_{2(g)} = ZnS_{(s)}$ $-63290 + 23.47\ T$	[10]
	$Zn_{(l)} + 0.5O_{2(g)} = ZnO_{(s)}$ $-82490 + 22.67\ T$	[5]	$Zn_{(l)} + 0.5O_{2(g)} = ZnO_{(s)}$ $-82490 + 22.67\ T$	[10]
	$ZnO_{(s)} + FeS_{(l)} = ZnS_{(s)} + FeO_{(l)}$ $-7900 + 4.10\ T$	[18]		
	$ZnO_{(s)} + CO_{(g)} = Zn_{(g)} + CO_{2(g)}$ $45260 - 45.18\ T + 5.739\ T\ \log T$	[5]		
As	$4As_{(l)} = As_{4(g)}$ $7952 - 14.87\ T$	[9]	$As_{2(g)} = 2As_{(g)}$ $92180 - 27.57\ T$	[9]
	$As_{2(g)} = 0.5As_{4(g)}$ $-26470 + 18.17\ T$	[9]	$As_{2(g)} = 0.5As_{4(g)}$ $-26470 + 18.17\ T$	[9]
	$As_{2(g)} = 2As_{(g)}$ $92180 - 27.57\ T$	[9]	$0.5As_{2(g)} + 0.5O_{2(g)} = AsO_{(g)}$ $-18890 - 3.19\ T$	[2,9]
	$0.5As_{2(g)} + 0.5O_{2(g)} = AsO_{(g)}$ $-9560 - 2.77\ T$	[9]	$0.5As_{2(g)} + 0.5S_{2(g)} = AsS_{(g)}$ $4350 - 2.66\ T$	[2,9]
	$As_{2(g)} + 1.5O_{2(g)} = As_2O_{3(g)}$ $-122700 + 41.8\ T$	[8]	$As_{(l)} + 3/4O_{2(g)} = AsO_{1.5(l)}$ $-79020 + 27.58\ T$	[12]
	$0.5As_{2(g)} + 0.5S_{2(g)} = AsS_{(g)}$ $4350 - 2.66\ T$	[8]	$0.5As_{2(g)} + 0.5S_{2(g)} = AsS_{(g)}$ $4350 - 2.66\ T$	[9]

of oxygen enrichment, followed by that of Sb and Pb in decreasing order, and the elimination of Zn is little affected by it [6].

A computed model has been constructed to simulate thermodynamically the behaviour of the minor elements Zn, Pb, As, Sb, and Bi as well as the major elements Cu, Fe, Si, O, and S in the Isasmelt process, producing copper matte by M. Nagamori et al. [5]. The model is based on the new concept that there are two independent reaction sites in a slag bath: one for fast oxidation and the other for slow reduction. The process chemistry was analyzed in terms of Fe_3O_4 , FeO, and FeS activities, as well as SO_2 partial pressure. The thermodynamic model explains well the minor element distributions observed in the 15 tons per hour pilot furnace, and it is used to project the optimal smelting conditions for the full-scale 100 tons per hour Isasmelt furnace. The model permits systematic evaluation of an operating condition, and provides a diagnosis of commercial furnace performance, thereby helping to establish the smelting strategies [5].

N. Mitevska and Ž. Živković showed the results of thermodynamic analysis of arsenic, antimony and bismuth distribution between copper matte and discard slag in reverberatory smelting at 1573 K [14]. On the basis of chemical analysis of the melt samples taken during stable operation of the reverb furnace No.2 in the Copper Smelter and Refinery, RTB Bor (Serbia), the distribution coefficients of As, Sb, and Bi between copper matte and slag are calculated.

RESULTS AND DISCUSSION

Computational thermodynamics programs are a very powerful way of looking at the behaviour of chemical systems. They use the Gibbs free energy data of all the individual species in the phases in a system and then change the concentrations of all species until they locate the minimum of the total Gibbs free energy. In order to be able to describe the behaviour of each element it is necessary to determine the activity and the distribution coefficient of the corresponding elements in thermodynamic experiments and calculations. In simulation, a solid feed mixture can contain different types of particles: chalcopyrite, chalcocite or inert. Sulfide particles can also have some amount of iron sulfide

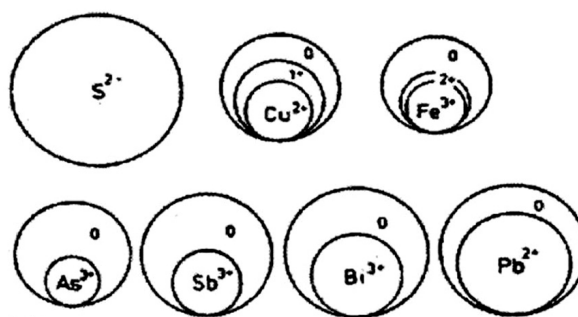


Fig. 1. The effect of valence on ionic sizes [1].

and silica inside the particle. Each type of particle can have a different chemical composition and its own particle size distribution.

The composition of industrial copper matte is very close to the Cu_2S -FeS line across the ternary Cu-S-Fe system often leading to the misconception that copper matte is covalently bounded. Thermodynamic behavior of high grade (% Cu) molten copper matte is better explained by ionic melt theory. The ionic theory was used with success to explain laboratory and industrial observations in modern copper smelting systems [15]. In practice, it seems like copper matte has a mixed behavior (covalent and ionic) but phenomena related to minor element distributions are better explained with the ionic theory. In the ionic theory, a structural representation of molten copper matte as a complex ionic network consisting of large S^{2-} ions and small Cu^+ and Fe^{2+} ions has been adopted. Fig. 1 is a comparative representation of the ionic sizes of major constituents in copper matte at different valences.

For high grade matte similar to the operation of most modern industrial smelting furnaces, **arsenic** and **antimony** are believed to exist mainly in the molecular state in copper matte [1]. Due to the relatively large size (Fig. 1) of these molecules compared with Cu^+ and Fe^{2+} ions, they should substitute for S^{2-} ions in the melt.

The state of **bismuth** in copper matte has not been clearly identified in the literature and is believed to depend on the nature of the smelting system as follows. Under oxidizing conditions (low sulphur partial pressure) as observed in modern copper smelting systems, Bi is most likely present in the molecular state. This phenomena can be explained from the interpretation by the hypothesis that the fewer sulfur ions (higher P_{O_2}) would preferentially bound with Cu^+ and Fe^{2+} ions leav-

ing less to stabilize Bi^{3+} . Comparable sizes of molecular bismuth permit the substitutional for sulphur in the ionic melt. In fact, a mixed behaviour is more realistic (Bi and Bi^{3+} ions) from which the predominance of Bi and Bi^{3+} ions would be determined by the sulfur and oxygen partial pressures. Under oxidizing conditions (flash furnaces), the molecular state is dominant and the Bi^{3+} ions prevalence is believed to increase in vessels with a high sulphur partial pressure (e.g. reverberatory furnace).

For **lead**, it was found that Pb^{2+} ions are more stable than molecular Pb in the matte smelting system. Because of their positive charges, Pb^{2+} ions substitute for Cu^+ and Fe^{2+} ions in the melt even if significantly larger in size. Similarly, but a lower extent than Bi, Pb is believed to exist in the molecular state in the molten copper matte under highly oxidizing conditions (low sulphur partial pressure).

Nickel has a similar behaviour to copper and Ni^+ ion is the major state of Ni in molten copper matte. Ni^+ ion should substitute for copper and iron ions in the ionic melt.

General trends can be estimated, e.g. the sulphides of iron and zinc tend to change into oxide during the smelting process, but the metallic form might be stable for some elements such as lead.

CONCLUSIONS

Computer simulation which are used for thermodynamic evaluation of the distribution behaviour of minor elements in the smelting stage of the copper smelting process is based on thermodynamic data and operating data of the process. One of the main difficulties with predicting the distribution behaviour of an element is in knowing in which form the element is present in each phase. Elements may be present as neutral metal species, as an oxide or as a sulfide in the metal, slag and matte, and in the gas. The actual oxide or sulfide species present depends on the oxidation state of the element, which is a function of the process conditions and the element in question. The speciation of the oxides in the slag may further be influenced by slag basicity. In principle, computational thermodynamics could predict overall distribution behavior by considering all possible species to be present in all phases, but it is necessary to

be able to assign a value to the activity coefficient of each species in each phase. Rarely is this possible because activity coefficient values are obtained by experiment, and this it self requires assumptions regarding the speciation of the element in the phases present.

During smelting minor elements will be distributed between all phases in a way which depends on the thermodynamic properties of the elements concerned and the operating conditions.

Thermodynamics can be used to predict and/or explain minor element behaviour in copper smelting. The use of these equilibrium sciences requires that numerous assumptions be taken. The most significant is to assume that chemical equilibrium conditions are prevailing. In modern copper smelting process, this assumption can be taken with reasonable confidence due to the high operating temperature and large turbulence that promotes fast process kinetics. It is believed that the future of copper smelting and refining developments will go hand-to-hand with improved control over minor elements.

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