




TECHNICAL ARTICLE

# Constitutive Topics in Physical Chemistry of High-Temperature Nonferrous Metallurgy—A Review: Part 1. Sulfide Roasting and Smelting

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The prime objective of this review series is to demonstrate the significant role of physicochemical principles in the development and improvement of extraction technologies for different types of metals categorized as common, reactive, rare and refractory. In this part we highlight the roles of phase rule, free energy and activity in roasting and smelting of sulfides. Continuing development of new technologies and reduction in the number of steps in the production of copper, lead, zinc and nickel have been possible because of the thorough understanding and application of the physical chemistry of reactions involved in different extraction steps. The theoretical bases behind the development of several new technologies and the difficulties in realizing certain worthwhile concepts in industrial practices are explained.

## INTRODUCTION

In this Part 1 of the review, we discuss the physical chemistry of high-temperature processing of sulfide minerals in the production of nonferrous metals. To develop new extraction methods or improve existing processes, it is essential to apply physicochemical principles involved in different steps of the process flowsheet. This review will demonstrate how the knowledge of physicochemical principles is critical in the development of different processes for the recovery of metal values and chemicals from concentrates, lean ores and wastes. Based on the discussions, the reader will appreciate the contributions of phase rule, activity and free energy in the selection of particular steps in the production of different metals.

## ROASTING OF SULFIDE MINERALS

A number of metals, namely, antimony, bismuth, cadmium, cobalt, copper, lead, mercury, molybdenum, nickel and zinc, occur as sulfide minerals. These are often roasted with air for a number of purposes, depending on the minerals. Copper and nickel sulfide minerals are sometimes roasted to eliminate the excess sulfur before being smelted or to be converted

into sulfate before being leached. The minerals of lead and zinc, galena and sphalerite are converted into PbO and ZnO, respectively, by dead roasting prior to their reduction with carbon. Mixed oxide and sulfate obtained by partial roasting and sintering are dissolved in dilute sulfuric acid prior to electrowinning in the case of zinc extraction.

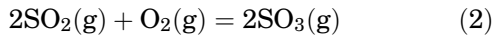
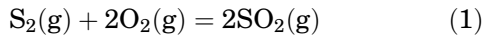
In roasting, sulfide minerals are heated in air/O<sub>2</sub>-enriched air at an appropriate temperature to oxidize sulfur to sulfur dioxide and the metal to form oxides or sulfates without melting the charge. Melting causes agglomeration of fine particles and reduces the surface area and retards the roasting operation, which is essentially a surface reaction. During roasting, a porous oxide layer formed first allows oxygen to pass toward the still unreacted inner sulfide and the SO<sub>2</sub> gas to come out. In general, roasting reactions are exothermic enough to carry out the operation, once it has been initiated by burning a small amount of fuel. Roasting processes may be categorized as oxidizing, sulfation, chloridizing or volatilizing roasts based on the requirement of the product,

## Chemistry and Thermodynamics of Roasting

The chemistry of sulfide roasting is complex because it incorporates numerous reactions,

namely, decomposition of higher sulfides to lower sulfides, oxidation of sulfides to form oxides or sulfates, burning of sulfur, sulfation of metal oxides, decomposition of sulfates to basic (oxy) sulfates, sulfide-sulfate interaction, sulfide-oxide interaction, formation of complex compounds such as ferrites and silicates and formation of sub or higher oxides. The reactions become even more complex in presence of more than one metal sulfide in the concentrate. It is important to note that the chemical and mineralogical composition of the concentrate, temperature of roasting and partial pressures of  $O_2$ ,  $SO_2$  and  $SO_3$  in roasters affect the composition of the product of roasting in addition to other operating variables such as the particle size, method of mixing, time of reaction and roasting technique.

The equilibria for the existing phases in any M-S-O system can be discussed with the aid of the phase rule ( $P = C - F + 2$ ) where  $F$ ,  $C$  and  $P$  represent the degrees of freedom, number of components and phases, respectively. Since there are three components in the M-S-O system, a maximum of five phases (i.e., 4 condensed phases and 1 gaseous phase) can exist. At a fixed temperature there would be four phases (i.e., 3 condensed phases and 1 gaseous phase). Burning of sulfur and further oxidation of  $SO_2$  in excess  $O_2$  give rise to a gaseous phase comprising  $S_2$ ,  $O_2$ ,  $SO_2$  and  $SO_3$  according to the following equilibria:



The partial pressures of any two gaseous components decide the composition of the gas mixture at the chosen temperature. Since the composition of the condensed phase is dictated by the given gas composition, the phase relations in the ternary system at a fixed temperature can be discussed by a two-dimensional diagram in terms of the partial pressures of any two of the above four gases. For convenience,  $p_{SO_2}$  and  $p_{O_2}$  are depicted in the diagram presenting the stability regions of different phases in the system. These diagrams are known as the stability or predominance area diagrams. Many such diagrams are available in the literature<sup>1-12</sup> for M-S-O as well as  $M_1$ - $M_2$ -S-O systems.

In Fig. 1, depicting the stability regions of different phases in the system M-S-O at a constant temperature, lines representing equilibrium between any two condensed phases are expressed by the following chemical reactions: 3.  $M(s) + SO_2(g) = MS(s) + O_2(g)$ ; 4.  $2M(s) + O_2(g) = 2MO(s)$ ; 5.  $2MS(s) + 3O_2(g) = 2MO(s) + 2SO_2(g)$ ; 6.  $2MO(s) + 2SO_2(g) + O_2(g) = 2MSO_4(s)$ ; 7.  $MS(s) + 2O_2(g) = MSO_4(s)$ .

In addition to the above equilibria, other appropriate chemical reactions have to be taken into account on formation of higher oxide ( $M_2O_3$ ), sulfide ( $MS_2$ ), sulfate ( $M_2(SO_4)_3$ ) and basic sulfate ( $MO \cdot MSO_4$ ).

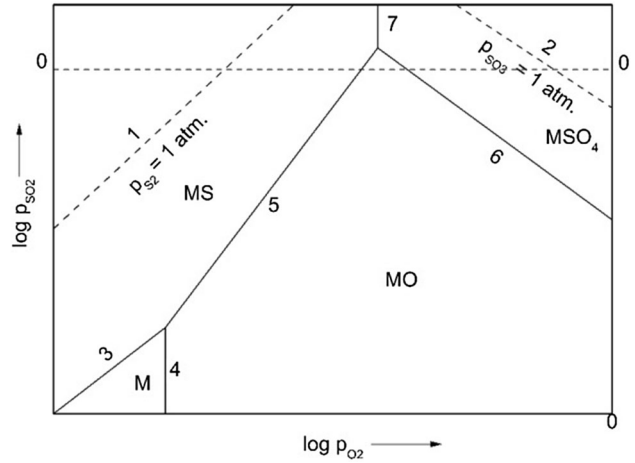


Fig. 1. Stability regions of different phases in the M-S-O system.

Assuming standard states for all the condensed phases, the equilibrium constants for reactions (3-7) can be expressed in terms of  $\log p_{O_2}$  and  $\log p_{SO_2}$ :  
 $\log p_{SO_2} = \log p_{O_2} - \log K_3$ ,  $\log p_{O_2} = -\log K_4$ ,  
 $\log p_{SO_2} = (3/2) \log p_{O_2} + (1/2) \log K_5$ ,  $\log p_{SO_2} =$   
 $-(1/2) \log p_{O_2} - (1/2) \log K_6$  and  $\log p_{O_2} =$   
 $-(1/2) \log K_7$ .

From the above discussion, it can be concluded that for a particular type of reaction, the expression is similar for all metals whereas the values of the equilibrium constants  $K_3, K_4$ , etc., differ from one metal to another. This difference would alter the position of the equilibrium lines and hence the size and the areas between the lines would be affected. These areas are known as the stability regions or predominance areas of different phases. Three important conclusions are drawn from the figure: (1) in the region of existence of only one condensed phase, at constant temperature the system has two degrees of freedom because  $p_{SO_2}$  and  $p_{O_2}$  can be varied independently; (2) the system has one degree of freedom along the lines between two condensed phases; (3) the system has zero degrees of freedom at point(s) where three condensed phases are in equilibrium. The equilibria for the formation of  $SO_2$  and  $SO_3$  according to reactions (1) and (2) (shown by two lines drawn for  $p_{S_2} = 1$  atm and  $p_{SO_3} = 1$  atm in the figure) are expressed as  $\log p_{SO_2} = \log p_{O_2} + (1/2) \log p_{S_2} + (1/2) \log K_1$  and  $\log p_{SO_2} = -(1/2) \log p_{O_2} + \log p_{SO_3} - (1/2) \log K_2$ . These expressions suggest that the relationship between  $\log p_{SO_2}$  and  $\log p_{O_2}$  depends on the  $p_{S_2}$  and  $p_{SO_3}$ .

In roasting of a mixed sulfide concentrate, simultaneous reaction/conversion of different metals will not take place because the stability regions for different metals have different locations. Hence, during roasting of chalcopyrite (mixed Cu-Fe sulfide), iron sulfide will first oxidize to form  $Fe_3O_4$ , leaving copper as  $Cu_2S$ . Continued operation transforms  $Fe_3O_4$  to  $Fe_2O_3$  and  $Cu_2S$  to  $Cu_2O$  and then to  $CuO$ . However, the presence of iron oxide as a

gangue in the concentrate complicates roasting by forming spinel; for example, in the roasting of sphalerite, zinc ferrite ( $\text{ZnO}\cdot\text{Fe}_2\text{O}_3$ ) is formed. On the other hand, depending on the temperature of roasting, basic sulfates, namely,  $\text{ZnO}\cdot\text{ZnSO}_4$  and  $\text{PbO}\cdot\text{PbSO}_4$ ,  $\text{PbO}\cdot 2\text{PbSO}_4$  and  $\text{PbO}\cdot 4\text{PbSO}_4$ , are formed in the roasting of sphalerite and galena, respectively. The formation of these complex phases alters the shape and size of predominant areas because of lesser activity of the compound in the complex phase compared with the activity of the pure compound. This means a lower partial pressure of oxygen than what is required for zinc oxide formation would form zinc ferrite from sphalerite. Based on a similar argument, higher partial pressures of oxygen and sulfur dioxide are required for  $\text{ZnO}\cdot\text{ZnSO}_4$  equilibrium when ZnO is complexed as a ferrite phase ( $\text{ZnO}\cdot\text{Fe}_2\text{O}_3$ ) instead of its presence as pure ZnO. Thus, depending on the requirement of the process flowsheets, stability diagrams of different M-S-O systems at different temperatures become useful in carrying out selective roasting.<sup>1</sup>

The predominance area diagram of the Zn-S-O system at different temperatures is useful in feed preparation for smelting and leaching by roasting sphalerite concentrates at appropriate temperatures. For the Imperial Smelting furnace, the concentrate, first partially roasted at 800°C for a product with 4% sulfur, is sintered at 1200°C to produce lumpy zinc oxide sinter. Since the stability regions of both  $\text{ZnSO}_4$  and  $\text{PbSO}_4$  in the stability diagrams of Zn-S-O and Pb-S-O (Figs. 2 and 3) systems shrink with an increase in temperature, the product resulting from the roasting/sintering of sphalerite and galena concentrates at 800°C will consist of mixed oxides (larger amount) and little sulfate (respectively,  $\text{ZnO} + \text{ZnSO}_4$  and  $\text{PbO} + \text{PbSO}_4$ ). Shamsuddin et al.<sup>12</sup> have effectively demonstrated the possibility of selective roasting of an off-grade chalcopyrite concentrate containing appreciable amounts of sphalerite and galena making use of the stability diagrams of Cu-S-O, Fe-S-O, Zn-S-O and Pb-S-O.<sup>1,12</sup>

The enthalpy of roasting reactions for one mole of oxygen at constant  $p_{\text{SO}_2}$  can be calculated from the slopes of the  $\log p_{\text{O}_2}$  versus  $1/T$  plots (Fig. 4). The figure marked with two possible roasting paths is useful in discussing effect of temperature on the roasting equilibria. Along path (a), normally, as roasting starts, the sulfide gets roasted to oxide with an increase of temperature, which may partially get converted to sulfate on a decrease of temperature toward the end of the roasting process. On the other hand, along path (b), sulfate first formed at low temperature decomposes to oxide on a rise of temperature because of the additional heat.

### Kinetics of Roasting

Since the roasting of sulfides is exothermic, the mineral particles quickly attain an appropriate

temperature in the roaster for the desired chemical reactions to proceed. During the roasting process, each particle is oxidized from the outside resulting in a layer of solid oxide product leaving a core of unreacted sulfide. The required reaction of the type  $2 \text{MS} (\text{s}) + 3 \text{O}_2 (\text{g}) = 2 \text{MO} (\text{s}) + 2 \text{SO}_2 (\text{g})$  occurs at the MO/MS interface provided the gas ratio  $p_{\text{O}_2}/p_{\text{SO}_2}$  is higher than the equilibrium ratio for the reaction at the temperature under consideration.

The reaction may occur in a number of steps including (1) adsorption of oxygen at the surface of the sulfide mineral particles, (2) capture of oxygen in the lattice of the mineral particle after release of electrons ( $\frac{1}{2}\text{O}_2 = \text{O}^{2-} + 2e$ ) and the neutralization of sulfide ions on the surface by the electrons ( $\text{S}^{2-} + 2e = \text{S}$ ), (3) chemical reaction between the adsorbed atoms of sulfur and oxygen atoms leading to the formation of  $\text{SO}_2$ , (4) desorption of the  $\text{SO}_2$  molecule and finally (5) transportation of  $\text{SO}_2$  creates a vacant site on the mineral surface.

For the roasting reaction to continue further, another sulfide ion moves to occupy the vacant site. However, generally the interface<sup>10</sup> advances into the mineral to interact with more sulfide ions. Although the role of adsorption is not very clear, it may be helpful in decreasing the activation energy and increasing the rate of roasting. The rate is controlled by the number of oxygen molecules adsorbed per unit area of interface, which depends on  $p_{\text{O}_2}$  as governed by the laws of adsorption.

Many investigators have studied the kinetics of roasting of zinc sulfide,<sup>13,14</sup> covellite,<sup>15,16</sup> molybdenite<sup>17</sup> and molybdenite concentrate containing 90%  $\text{MoS}_2$ .<sup>18</sup> Based on his studies on the conversion of PbS to  $\text{PbSO}_4$  [ $\text{PbS} (\text{s}) + 2 \text{O}_2 (\text{g}) = \text{PbSO}_4 (\text{s})$ ] in the temperature range 690–800°C, Khalafallah<sup>19</sup> has proposed the following law:

$$1 + 2(1 - z \cdot f) - 3(1 - z \cdot f)^{2/3} = \frac{k}{4r_0^2} t \quad (3)$$

where  $f$ ,  $z$ ,  $k$ ,  $r_0$  and  $t$  stand, respectively, for the fraction of PbS converted into  $\text{PbSO}_4$ , the volume of  $\text{PbSO}_4$  formed per unit volume of PbS, the rate constant, initial radius of the sulfide particle and reaction time.

### SMELTING OF SULFIDE MINERALS

Smelting is one of the main steps in extraction of metals from sulfide and oxide minerals via the pyrometallurgical route. It is essentially an operation of melting and separation involving chemical reactions. The term 'smelting' has broad and narrow definitions. In the broadest sense, any metal production process that involves a molten stage is called smelting. The next level of the definition is the overall process of producing primary metals from sulfide minerals by going through a molten stage. The narrowest definition is the first step of

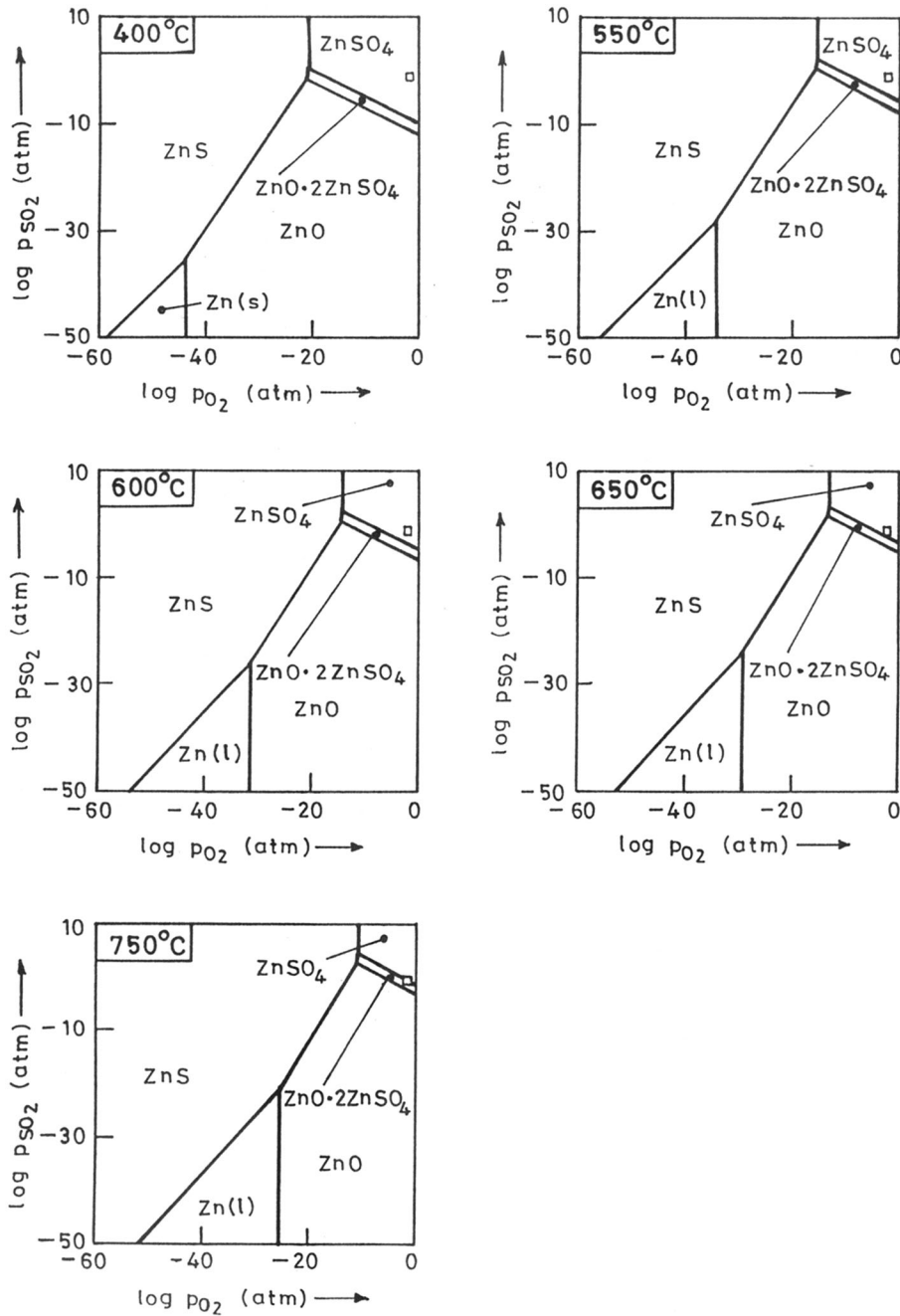


Fig. 2. Stability diagrams of the Zn-S-O system. □ Usual roaster gas composition. Adapted from Shamsuddin et al.<sup>1</sup> with permission.

the two-step oxidation of sulfur and iron from sulfide minerals, mainly Cu and Ni, i.e., matte smelting or matte-making as opposed to 'converting' in which the matte is further oxidized to produce metal.<sup>20</sup> The reason for doing it in two stages is related to oxygen potentials in the two stages as well as heat production. Oxygen potential affects the slag chemistry (magnetite formation, for example) and impurity behavior. If the sulfide mineral is oxidized all the way to metal in one step, many more of the impurities go into the metal, rather than the slag, and too much heat is produced. Thus, in the

first stage—the 'matte smelting step,' much iron, sulfur and harmful impurities are removed into the slag formed in that stage, and the resulting matte is separated and treated in a subsequent step, usually the converting step.

As an example of metal extraction from sulfide minerals by smelting, a general flowsheet of copper production is presented in Fig. 5. The composition of the two immiscible liquids, known as matte and slag, separated into layers, depends on the constituents present in the charge. For example, smelting of mixed sulfide concentrates produces matte (a

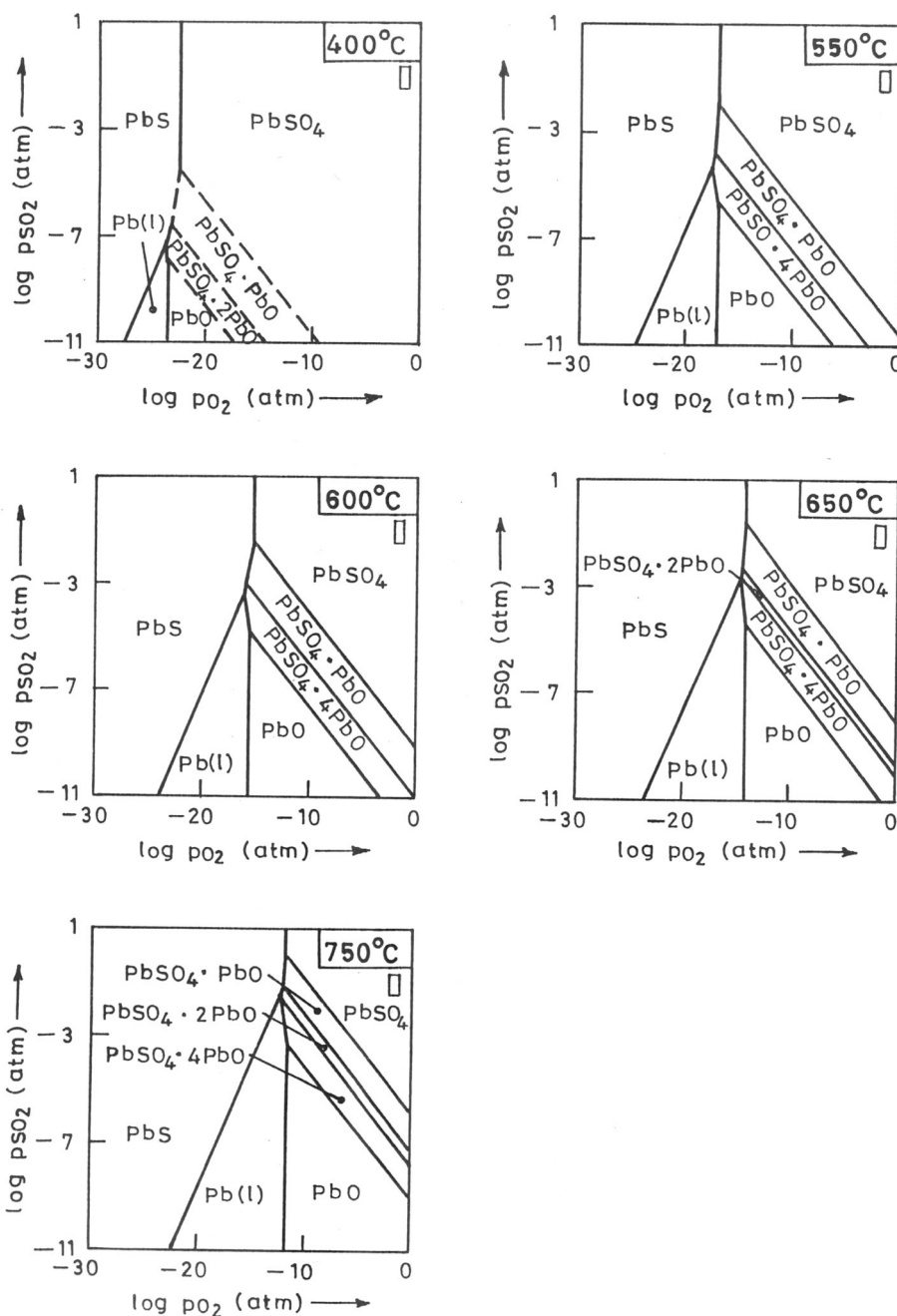


Fig. 3. Stability diagrams of Pb-S-O system. □ Usual roaster gas composition. Adapted from Shamsuddin et al.<sup>1</sup> with permission.

solution of molten sulfides), slag and flue gases consisting of some components of the charge. Flux addition not only facilitates slag formation, but also helps control the fluidity of the slag. A third immiscible liquid layer (speiss) containing a mixture of arsenides and antimonides of iron, cobalt and nickel is formed if the concentrate is associated with arsenic and antimony. During sulfide smelting impurities may be collected into speiss or flue gases by adjusting the operating variables. For example, copper is collected into matte in lead smelting, cobalt into speiss in copper smelting and sulfur into slag in iron smelting. In this way, smelting produces

two immiscible liquid phases, slag and a matte or metal and slag for further processing. The former, being lighter, gets collected over the latter and acts as an absorber of impurities.

### Matte Smelting of Chalcopyrite

Chalcopyrite concentrate containing mainly sulfides of copper and iron as the major components and some gangue consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{SiO}_2$  is first smelted with the prime objective of obtaining a liquid matte (solution of  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ ) containing almost all the copper present in the

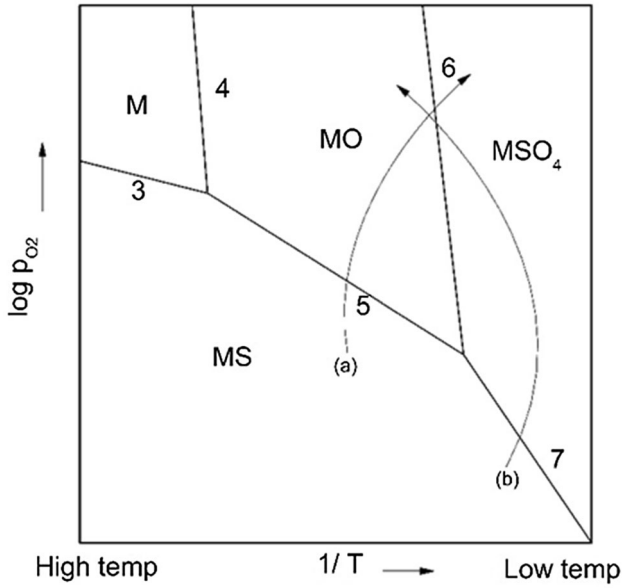
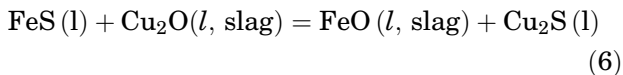
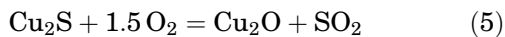
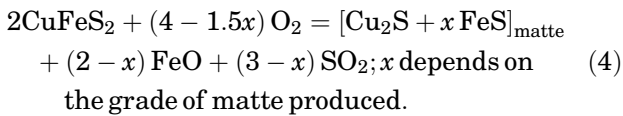
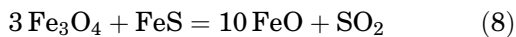
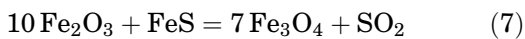


Fig. 4. Effect of temperature on the equilibrium constant.

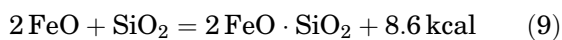
charge and a slag with little copper.<sup>21</sup> Additional silica is added as a flux to produce a low melting ( $\sim 1150^\circ\text{C}$ ) and fluid slag, with smelting generally carried out at  $1250^\circ\text{C}$ . In recent years, high-grade mattes containing approximately 70% Cu and slag with most of the gangue minerals are produced by modern matte smelting processes. The matte and slag having respective densities of  $5.2 \text{ g cm}^{-3}$  and  $3.3 \text{ g cm}^{-3}$  separate into two layers of different phases. The oxidation of copper sulfides is suppressed in the presence of an appropriate amount of FeS in the matte. A slag with a relatively low viscosity is desirable for the separation and collection of droplets of matte from it. The following reactions occur in the matte smelting of chalcopyrite concentrate:



As iron has a higher affinity for oxygen than copper, FeS gets oxidized to FeO.  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ , if formed, are reduced to FeO by FeS:



A low-melting fayalite slag is formed according to the reaction:



The high value of equilibrium constant<sup>9</sup> ( $K = \frac{a_{\text{Cu}_2\text{S}} a_{\text{FeO}}}{a_{\text{Cu}_2\text{O}} a_{\text{FeS}}} \sim 10^4$  at  $1200^\circ\text{C}$ ) for reaction (6) favors the sulfidization of  $\text{Cu}_2\text{O}$  to bring the copper back into the matte as  $\text{Cu}_2\text{S}$ . The partial pressure of oxygen in the furnace atmosphere affects the quality of the matte. Even 1% oxygen in the furnace gas will oxidize iron in the slag to  $\text{Fe}_3\text{O}_4$ . Since magnetite does not easily dissolve in the slag because of its high melting point of  $1597^\circ\text{C}$ , the slag becomes highly viscous, which retards the process of separation of matte and slag, and hence continuous operation becomes difficult. This suggests that sulfide smelting should be carried out with minimum excess oxygen in the furnace to avoid magnetite formation.

In recent years, flash smelting furnaces developed by the International Nickel Company of Canada (INCO)<sup>22</sup> and Outotec (formerly Outokumpu)<sup>23</sup> of Finland have replaced the reverberatory and electric furnaces. In these furnaces, dried concentrate is charged through the burner. Both INCO and Outotec processes are based on industrial oxygen (95%  $\text{O}_2$ ), which makes the operation autogenous. The reaction of chalcopyrite concentrate with oxygen produces molten matte ( $\sim 70\%$  Cu) and molten slag (1–2% Cu) at  $1250^\circ\text{C}$  and flue gas containing approximately 80%  $\text{SO}_2$  that is converted into sulfuric acid. The matte is subjected to a converting operation for the production of blister copper, and the slag is treated for copper recovery. The input ratio of oxygen and dried concentrate<sup>24</sup> is adjusted to control the matte grade, whereas the input ratio of flux and dried charge regulates the slag composition.

Further advancements in sulfide smelting technology include the submerged tuyere (bath) processes developed by Noranda<sup>25</sup> and Teniente.<sup>25,26</sup> In these processes, the concentrate is charged with oxygen into a mixture of molten matte and slag contained in horizontal-cylindrical furnaces, lined with magnesia chrome bricks and fitted with a horizontal row of submerged tuyeres. To achieve better distribution of heat and concentrate, high thermal efficiency and low dust evolution, moist or dry concentrate and oxygen-enriched air are blown through the tuyeres into the molten matte layer, maintained in the furnace. Faster melting and oxidation of the charge and also reduction in the accumulation of solid magnetite in the furnace are achieved by violent stirring of the matte/slag bath because of the submerged blowing. In both processes the copper content in the matte varying from 72% to 75% is controlled by adjusting the input ratio of oxygen and concentrate and the slag composition by regulating the input ratio of flux and solid charge (aimed at  $\text{SiO}_2/\text{Fe} = 0.65$ ).

The top submerged lancing process, currently available in the name of Ausmelt/Isasmelt and TSL Technology,<sup>27</sup> is a new addition to the field of pyrometallurgical extraction of metals from sulfide,

## COPPER SMELTING FLOWSHEET

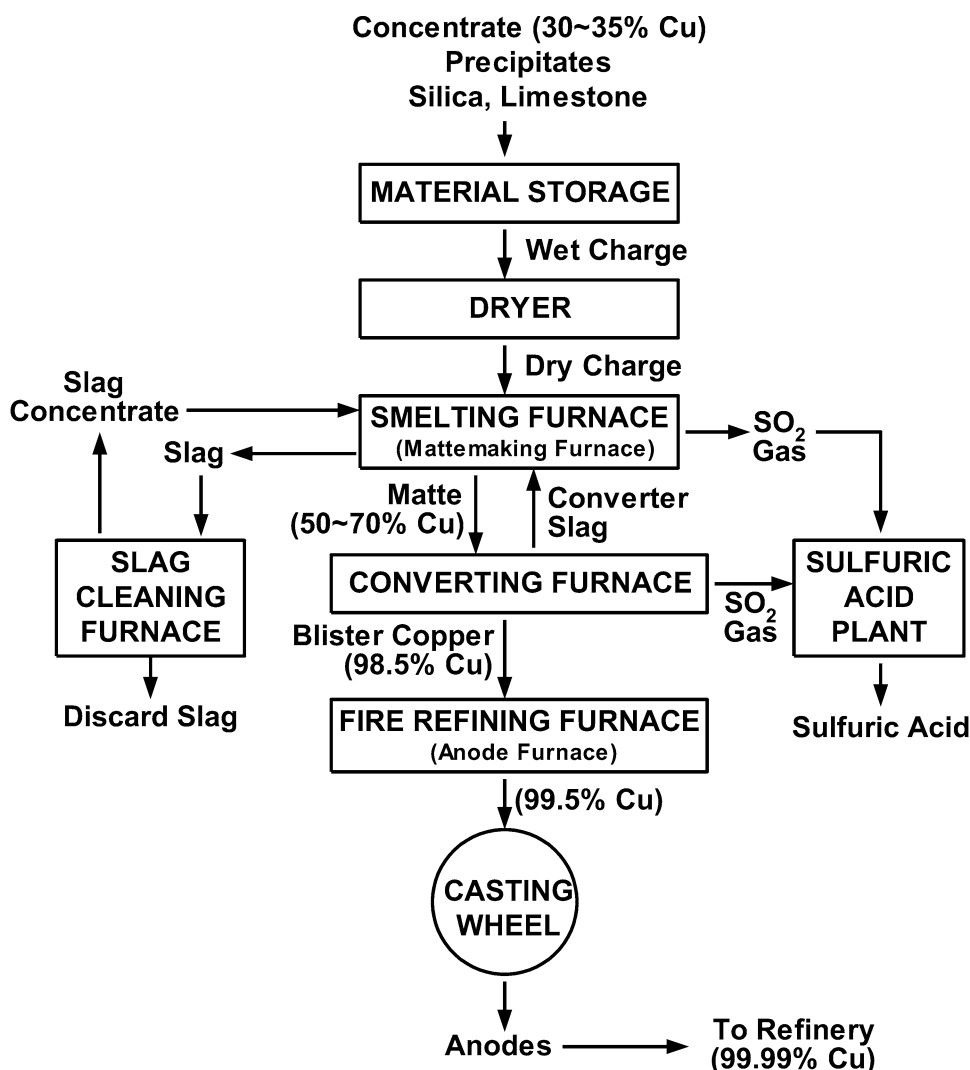
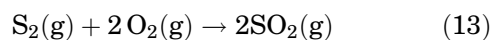
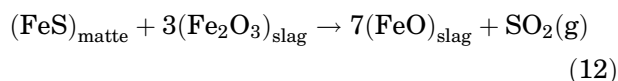
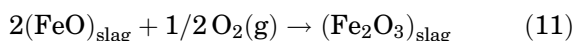
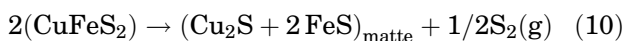


Fig. 5. A Typical copper production flowsheet. Adapted from Ref. 21.

oxide and complex minerals and the recovery of metals from a variety of metallurgical wastes including slags and residues. The furnace is charged with a mixture of moist concentrate, flux and recycled materials, and oxygen-enriched air is injected through a lance into a molten slag/matte bath contained in a vertical cylindrical furnace (3.5 m diameter and 12 m height). In this process, smelting reactions take place mainly in the bath, whereas in flash smelting they occur above the bath. The sequence of reactions<sup>24</sup> is summarized below:



It has been reported that the above reactions are catalyzed by magnetite dissolved in the slag<sup>24</sup> to the extent of approximately 5%. The resulting high-grade matte and slag contain nearly 60% and 0.7% Cu, respectively, and the off-gas is loaded with about 20% SO<sub>2</sub>.

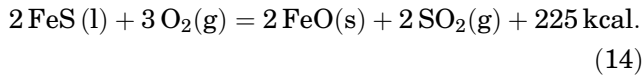
Mounsey and Robilliard<sup>28</sup> reported on the possibilities of recovery of copper, lead, nickel, tin, silver and antimony from sulfidic ores by the Ausmelt process. In recent years, this technology has gained prominence in the lead–zinc industries because of the development of efficient and flexible pyrometallurgical reactors with better environmental performance.<sup>29</sup> Ausmelt furnaces are currently in operation in various parts of the world, including one at Hindustan Zinc Limited.<sup>30</sup>

## Converting of Copper Matte

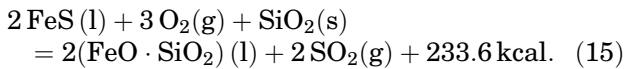
### Peirce–Smith Converting

In this process, the matte produced from the flash/bath smelting processes is converted in a cylindrical-horizontal vessel to further remove the remaining iron and sulfur<sup>21</sup> by blowing air through the tuyeres located on the side wall of the vessel. The process is autogenous because of the exothermic oxidation of iron and sulfur. The products of converting, namely, slag and blister copper, are tapped at two different stages of the process.

In the first stage the molten matte is vigorously stirred with air to oxidize FeS to FeO according to the reaction:



The first stage of blowing is known as the slag-forming stage because FeO is slagged off ( $2\text{FeO} + \text{SiO}_2 = 2 \text{FeO} \cdot \text{SiO}_2$ ) by adding silica when the blast is turned on. The slag-forming reaction is described by



The above reaction is the principal source of heat in the converter. Any  $\text{Cu}_2\text{O}$  formed by oxidation of  $\text{Cu}_2\text{S}$  is re-sulfidized in the bulk by reacting with FeS ( $\text{Cu}_2\text{O} + \text{FeS} = \text{Cu}_2\text{S} + \text{FeO}$ ) since  $\text{Cu}_2\text{O}$  is less stable compared with FeO. The activity of FeO in slag decreases in the presence of acid silica, which helps in the pushing reaction (15) in the forward direction to facilitate the removal of iron from the melt. This can be explained by the van't Hoff isotherm for reaction (14) under non-standard conditions, caused by the presence of silica:

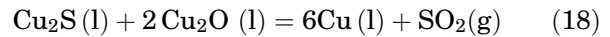
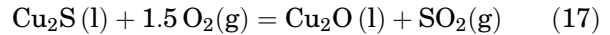
$$\Delta G = \Delta G^\circ + RT \ln \left[ \frac{(a_{\text{FeO}}^2) \cdot p_{\text{SO}_2}^2}{a_{\text{FeS}}^2 \{p_{\text{O}_2}^3\}} \right] \quad (16)$$

The second term in the above equation becomes negative because the quotient is less than unity as  $a_{\text{FeO}}$  is much less than unity in the presence of  $\text{SiO}_2$ . Thus, the resulting more negative value of  $\Delta G$  increases the overall driving force for the transfer of iron from molten matte to the slag. After the slag-forming stage the principal product is molten  $\text{Cu}_2\text{S}$  (white metal;  $\sim 1200^\circ\text{C}$ ) containing  $< 1\%$  Fe.

During the slag-forming stage, the converter is charged with the matte several times. The slag is tapped after every oxidation step and thus the amount of  $\text{Cu}_2\text{S}$  gradually increases.

In the second stage, called the copper-making stage, the white metal ( $\text{Cu}_2\text{S}$ ) is oxidized to  $\text{Cu}_2\text{O}$ . In this stage there is no need for a slag because the white metal contains little iron to form iron oxide.

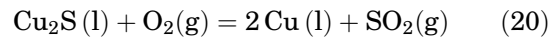
The interaction between  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{O}$  leads to the production of metallic copper and  $\text{SO}_2$ :



At the beginning of the second stage of blowing the copper produced dissolves in  $\text{Cu}_2\text{S}$  at the converting temperature of  $1200^\circ\text{C}$ . Thus, for a while, the converter retains a single-phase melt, which separates into two phases: a Cu solution in  $\text{Cu}_2\text{S}$  and a  $\text{Cu}_2\text{S}$  solution in Cu with the progress of oxidation. The melt again becomes a single phase of copper with some sulfur dissolved in it as the amount of  $\text{Cu}_2\text{S}$  in the melt decreases to its limit of solubility in copper. The equilibrium constant for reaction (18) is given by

$$K = \frac{a_{\text{Cu}}^6 p_{\text{SO}_2}}{a_{\text{Cu}_2\text{O}}^2 a_{\text{Cu}_2\text{S}}} \quad (19)$$

On neglecting the mutual solubility of the Cu,  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{O}$ ,  $K$  may be expressed in terms of the equilibrium partial pressure of  $\text{SO}_2$  (ie.,  $K = p_{\text{SO}_2}$ ). The respective values of the equilibrium constant, 1.14, 11.0 and 55.1 for reaction (18) at  $900^\circ\text{C}$ ,  $1100^\circ\text{C}$  and  $1300^\circ\text{C}$ , indicate that the reaction producing metallic copper may begin at as low as  $900^\circ\text{C}$ . However, it is definitely faster at the converting temperature of  $1250^\circ\text{C}$ . With continued blowing, the amount of blister copper goes on increasing according to the overall reaction:



With the continued decrease of sulfur from the melt, the sulfide phase disappears and hence the converter contains only molten copper with  $\sim 1\%$  S. For the final removal of sulfur by further blowing, the operator has to be extremely careful in preventing over-oxidation of copper to  $\text{Cu}_2\text{O}$  because there is no sulfur to re-sulfidize  $\text{Cu}_2\text{O}$  back to  $\text{Cu}_2\text{S}$ . The entire converting cycle from start-to-finish takes 6–12 h<sup>24</sup> and the metal obtained contains 98–99% Cu.

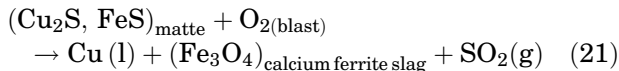
During charging and tapping, the Peirce–Smith converter has to be rotated to keep the tuyeres above the melt. Hence, it is a batch process, which has to be discontinued intermittently and causes difficulties in the collection of  $\text{SO}_2$ . These limitations led to the development of continuous converting processes by Noranda, Kennecott/Outotec and Mitsubishi.

### Kennecott-Outotec Matte Converting

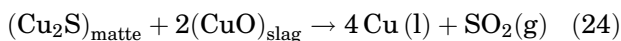
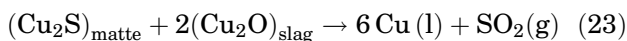
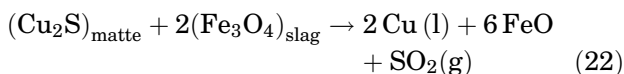
The combination of the Outotec Flash Smelting with Kennecott's Solid Matte Oxygen Converting (SMOC) concept emerged as the Kennecott-Outotec Flash Converting process.<sup>31</sup> In this process the flash smelting furnace matte containing about 70% Cu is first subjected to granulation and then crushed to 50



microns and dried. The dried matte powder mixed with limestone is blown with industrial oxygen continuously into a flash furnace, which is similar in design to the Outotec flash smelting furnace. Copper is obtained according to the following overall reaction by appropriate adjustment of the oxygen supply:



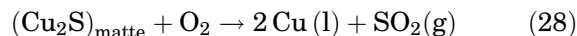
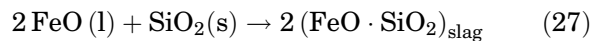
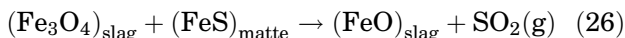
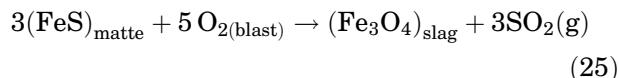
The molten copper containing 0.2% S and 0.3% O and the molten calcium ferrite slag containing ~20% Cu and ~16% CaO are intermittently tapped and sent, respectively, to the refinery to produce cathode copper and a water-granulation plant to produce slag granules to be recycled to the matte smelting furnace. The off-gas loaded with 35–40% SO<sub>2</sub> is subjected to de-dusting before being sent to the sulfuric acid plant. The calcium ferrite slag, having a lesser tendency to foam and being capable of absorbing magnetite/hematite while maintaining better fluidity than the fayalite slag, is necessary because the oxygen potential required to produce the Cu phase in the presence of a slag in a continuous converting process oxidizes iron to higher oxides. Copper metal and SO<sub>2</sub> gas are formed below the slag layer according to the following reactions:



The productivity of the Kennecott-Outotec flash converter is typically two to three times larger than the Peirce–Smith converter.

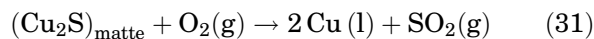
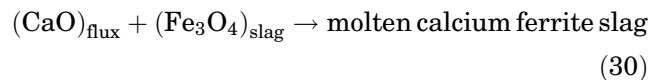
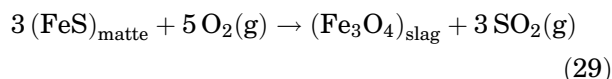
#### *Other Continuous Converting Processes of Copper Matte*

Further advancement in the Noranda submerged tuyere smelting led to the Noranda continuous converting<sup>32</sup> process in which the molten matte and scrap are charged through a large mouth, flux and coke through a hole and the off-gas is directed to an acid plant through another opening. For continuous operation, layers of molten copper, matte (65–70% Cu, 5–10% Fe and 20–24% S) and slag are maintained in the converter and O<sub>2</sub>-enriched air is blown through tuyeres. The slag and metal formation reactions may be represented by



Blister copper containing 1.3% S and slag with a high percentage of Cu (about 10%) are tapped intermittently. The high oxygen potential required for production of copper is responsible for high residual copper in the slag.

In the Mitsubishi Continuous Converter,<sup>33</sup> which is a part of the three furnace-system described below and fed with matte produced in the smelting furnace, five to ten vertical lances (each consisting of two concentric pipes) are introduced from the roof of the vessel. Air along with CaCO<sub>3</sub> flux and recycled materials are blown through the central pipe and O<sub>2</sub>-enriched air through the annulus between the two pipes. The jet impinges on the surface of the molten bath to form an emulsion of molten copper, matte, slag and gas. The emulsion facilitates solid–liquid–gas reactions leading to the formation of copper and slag in accordance with the following reactions:



Copper flows through the siphon and calcium ferrite slag containing Cu<sub>2</sub>O through the slag notch. The flue gas loaded with 25–30% SO<sub>2</sub> is finally treated in a sulfuric acid plant after passing through a waste heat boiler and a series of gas cleaning units.

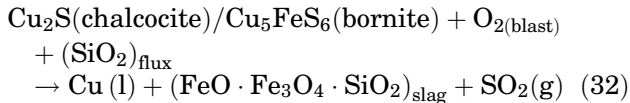
In the above continuous converting processes, a great deal of attention has to be paid for maintenance of the refractory lining because of the constant presence of calcium ferrite slag and molten copper in the converter.

#### **Direct Copper Extraction from Concentrate**

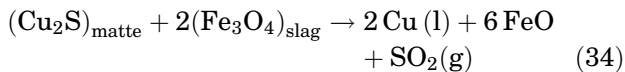
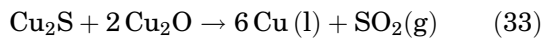
The two main steps, namely, smelting and converting in the extraction of copper from sulfide concentrates, are similar in generating sufficient heat from the oxidation of sulfur and iron and slagging of iron by fluxing FeO with silica. Hence, extractive metallurgists have long desired to perform these steps in one furnace. However, the processes to treat the chalcopyrite mineral pursued by WORCRA<sup>34</sup> and Noranda<sup>35</sup> on pilot plant levels failed on commercial scales because of the high loss of copper into the large amount of slag and high levels of impurities in the copper. Only with high-grade chalcocite (Cu<sub>2</sub>S) and bornite (Cu<sub>5</sub>FeS<sub>6</sub>)

concentrates having less iron than chalcopyrite did Outotec and Mitsubishi succeed in producing copper by direct smelting of the mineral.

In the Outotec blister flash smelting process,<sup>36</sup> O<sub>2</sub>-enriched air is blown with a mixture of chalcocite/bornite concentrate, flux and recycled materials. The products of smelting comprise molten copper (99% Cu), slag (14–24% Cu) and off-gas (15–25% SO<sub>2</sub>). The percent oxygen of the enriched blast controls the furnace temperature. The chemical reaction leading to the production of copper directly from chalcocite/bornite concentrate may be represented as



Depending on the supply of oxygen, Cu<sub>2</sub>S or Cu<sub>2</sub>O may be formed. The interaction between the over-oxidized Cu<sub>2</sub>O and Cu<sub>2</sub>S results in the formation of molten copper, molten slag and gas according to the reactions:



The copper content of the slag and sulfur in molten copper and the ratio of oxygen input to the concentrate feed rate control reaction (33). The copper content of the slag can be reduced by decreasing the O<sub>2</sub>/concentrate ratio, whereas the ratio of flux to concentrate input rate controls the overall composition of the slag. The furnace operation with a high O<sub>2</sub>/concentrate ratio not only eliminates the building up of a Cu<sub>2</sub>S layer but also avoids the possibility of slag foaming.

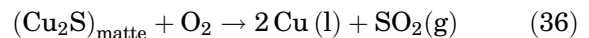
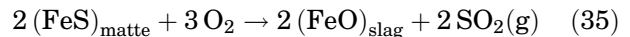
During the settling period of nearly 10 h, the copper oxide present in the slag is reduced to metallic copper in an electric slag cleaning furnace under a thick layer of coke. The furnace conditions also favor the reduction of magnetite, first to FeO and then to Fe.

In the recently developed Outotec<sup>36</sup> blister flash smelting unit, a chalcopyrite concentrate blend with copper matte is processed. However, the Outotec process will probably be restricted to the treatment of chalcocite and bornite for direct conversion to metallic copper because of the higher cost involved in the reduction and recovery of copper from the slag.

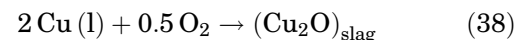
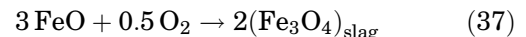
Despite problems of handling a large amount of slag in the treatment of chalcopyrite concentrate, Mitsubishi Materials Corporation<sup>37</sup> succeeded in developing a continuous process for the treatment of more widely occurring chalcopyrite (CuFeS<sub>2</sub>) compared with chalcocite (Cu<sub>2</sub>S) and bornite (Cu<sub>5</sub>FeS<sub>6</sub>) to produce metallic copper. Rather than in one furnace, however, smelting, slag cleaning and

converting are carried out in this process in three furnaces, connected in series. The system transfers molten matte and slag from one to another by gravity. A mixture of the dried concentrate, silica flux and recycled materials is charged through the central pipe of a double-piped lance, and O<sub>2</sub>-enriched air (55% O<sub>2</sub>) is blown through the annulus between the two pipes. On impinging on the surface of the molten bath, the solid–gas mixture gives rise to the formation of a matte-slag-gas emulsion. A tremendous increase in the availability of surface area to the reacting species markedly increases the rate of reaction between the liquids, solids and gas. The resulting products, matte (65–70% Cu) and iron silicate slag, flow continuously through the tap hole to the electric slag cleaning furnace. Separation between the matte and slag is achieved by holding the melt in the cleaning furnace for about 1–2 h. The off-gas loaded with 20–25% SO<sub>2</sub> is directed to the sulfuric acid plant after passing through a waste heat boiler and gas cleaning units.

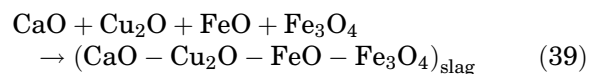
The converting furnace, described previously in “Other Continuous Converting Processes of Copper Matte” section, produces molten copper (~ 0.7% S), molten slag (14% Cu) and off-gas (25–30% SO<sub>2</sub>) by blowing O<sub>2</sub>-enriched air (30–35% O<sub>2</sub>) together with limestone flux and granules of converter slag into the matte received from the slag cleaning furnace along with additional charge of copper and anode scrap. Iron oxides and molten copper are formed in the converter by reactions between continuously flowing matte over the molten copper layer present and oxygen injected through lances:



The FeO and Cu formed may undergo further oxidation:



A low-melting slag is formed by CaO generated by the decomposition of limestone:

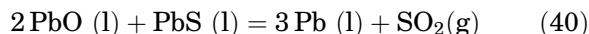


The converting operation in the Mitsubishi process requires the use of CaO-based slag<sup>38</sup> because SiO<sub>2</sub> cannot absorb the magnetite and hematite formed under the high oxygen potential needed to form copper metal. In the absence of CaO, the solid magnetite crust stops further converting. In the Mitsubishi process, 15–20% CaO in the slag has been found optimum for the converting operation. Although the process based on the three-furnace system, connected in series, is capable of treating different types of concentrates including low iron

chalcocite and bornite as well as high iron chalcocopyrite with less material handling, it suffers from refractory issues and the fact that three furnaces are connected.

### Smelting of Galena

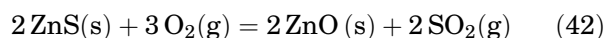
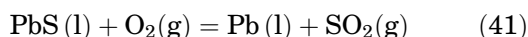
In the hearth process,<sup>39</sup> lead is obtained by the roast reduction of sintered galena concentrate at 800–900°C. Air blown into the furnace hearth through the tuyeres oxidizes lead sulfide to oxide, which interacts with the remaining lead sulfide according to:



The metallic lead trickles through the charge to the bottom.

In a blast furnace, a charge consisting of sinter, coke, limestone and quartz is smelted in excess air at a higher temperature (1100–1200°C). The resultant products separate in four distinct layers depending on specific gravity. These are collected in the furnace hearth, from top to bottom, slag (sp. gr. 3.6), matte containing copper and other elements (sp. gr. 5), speiss (FeAs<sub>4</sub> + impurities: sp. gr. 6) and lead bullion (sp. gr. 11).

The TSL process produces lead bullion in two stages from high (50–75% lead) or low (< 50% lead) galena concentrates.<sup>28</sup> The first smelting stage of the high-grade concentrate at a relatively low temperature (950–1000°C) produces lead bullion in contact with molten slag containing 60–75% lead. The fume containing about 11% lead is recycled to the furnace. Sphalerite (ZnS), generally associated with galena (PbS), also gets oxidized to ZnO. The overall chemical reactions are



To recover lead from the slag containing a significant amount of zinc and lead, the slag is subjected to further reduction and fuming in another furnace during the second stage of the operation. When the lead content of slag approaches 2–5%, zinc vapor is generated by the reduction of ZnO. The slag from the second-stage operation is discarded because it contains little lead or zinc.

Lead bullion is not produced directly by smelting low-grade concentrate. In this case the first stage involves fuming of lead based on the high vapor pressure of PbS. A high sulfur potential in the bath is ensured by smelting the concentrate under reducing conditions. In the second step, the fumed lead obtained as a fine oxide/sulfate dust containing 70% lead is pelletized and reduced with coal to produce lead bullion and a discard slag.

The efficiency of the TSL process has been improved by making use of the appropriate

knowledge<sup>29</sup> of the slag phase equilibria, the activities of Pb, Zn, PbO and ZnO in the multi-component slag system SiO<sub>2</sub>-CaO-FeO-PbO-ZnO, and the transfer kinetics of species from the slag to the metal and vice versa.

The technology invented by Queneau and Schuhmann<sup>40,41</sup> and developed by Lurgi and Korea Zinc has gained prominence as the QSL process. It is a continuous and direct lead-making process that allows carrying out roast-reduction smelting of galena concentrate and carbon reduction of lead oxide slag<sup>42</sup> in a single reactor (a long horizontal, cylindrical vessel). A bath of molten lead bullion is maintained below the slag layer contained in the converter. Green pellets prepared from a mixture of concentrate, recycle flue dust and fluxes are charged into the oxidation zone of the reactor. There is rapid oxidation of sulfide in the molten bath at 950–1000°C by bottom injection of oxygen through the Savard–Lee injectors to form lead bullion, lead oxide slag and sulfur dioxide gas. The lead oxide slag continuously flows to the reduction zone of the vessel and is reduced by bottom injection of pulverized coal. In this zone the temperature gradually increases from 1000°C to 1250°C. The lead bullion is tapped continuously, and the slag from the reduction zone passes through a settling zone and is continuously tapped to be water granulated.

### Smelting of Pantlandite (Nickel-Copper-Iron Sulfide)

#### Matte Smelting of Pantlandite

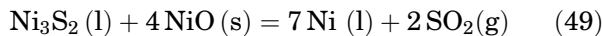
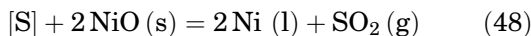
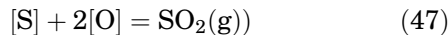
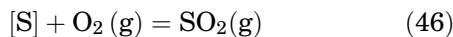
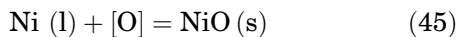
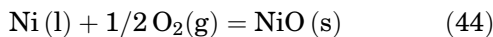
A nickel sulfide concentrate containing sulfides of copper, iron and cobalt together with silver, platinum and some arsenide and siliceous gangue is obtained by mineral processing of pentlandite [(NiFe)<sub>9</sub>S<sub>8</sub>]. Smelting of this concentrate produces nickel matte containing Ni<sub>3</sub>S<sub>2</sub>, Cu<sub>2</sub>S and FeS. Most of FeS is oxidized to FeO and SO<sub>2</sub>, and FeO is slagged off with silica whereas SO<sub>2</sub> joins the flue gases. Several steps follow for separation of sulfides of copper and nickel due to their similar chemical characteristics.

#### Converting of Nickel Matte

The sulfide-oxide interaction leading to the formation of metal that takes place in the production of blister copper (Cu<sub>2</sub>S + 2 Cu<sub>2</sub>O = 6 Cu + SO<sub>2</sub>) and lead bullion (PbS + 2 PbO = 3 Pb + SO<sub>2</sub>) does not produce nickel by the Ni<sub>3</sub>S<sub>2</sub>-NiO interaction because the free energy of the reaction (4 NiO + Ni<sub>3</sub>S<sub>2</sub> = 7 Ni + 2 SO<sub>2</sub>) is positive (ΔG° = +21 kJ at 1200°C). Instead, a Ni<sub>3</sub>S<sub>2</sub>-Cu<sub>2</sub>S matte and a Cu-Ni alloy are produced by the converting operation.<sup>43,44</sup> Per the normal practice of the converting operation, heat is derived by the oxidation of FeS present in the matte to FeO. The product has to undergo a series of operations to separate Ni<sub>3</sub>S<sub>2</sub>, Cu<sub>2</sub>S and Cu-Ni alloy.

These operations include extremely slow controlled cooling (from 1100°C to 400°C in 3 days), grinding, magnetic separation and froth flotation. Ni<sub>3</sub>S<sub>2</sub> may either be cast into anodes and directly electrolyzed or roasted to NiO and reduced with carbon or hydrogen [NiO + C (or H<sub>2</sub>) = Ni + CO (or H<sub>2</sub>O)] to produce nickel.

Metallurgists had long wanted to produce nickel by blowing nickel matte the way copper matte is blown to blister copper in a conventional side-blown converter. After many trials, it was realized that the formation of a large amount of solid nickel oxide (a refractory material with a melting point > 1900°C) during the blowing of nickel sulfide brings the process to a halt. Since NiO forms a number of high melting compounds, namely, silicates, aluminates, spinels and solid solutions such as NiO-MgO, nickel production by this method is not feasible. The following simultaneous reactions<sup>44</sup> must be taken into consideration in the production of nickel from nickel sulfide:



Since reaction (44) is favorable even at a high temperature of 1650°C when  $\alpha_{\text{Ni}} = 0.6$  and  $p_{\text{O}_2} > 5 \times 10^{-4}$  atm, it is difficult to stop the formation of NiO. Queneau et al.<sup>44</sup> presented a detailed discussion of the various conditions required and difficulties encountered for converting a nickel matte, leading to the development of a rotary top-blown converter for this purpose.

### CONCLUDING REMARKS

This Part 1 highlights the importance of physical chemistry in the development and improvement of processes for the extraction of non-ferrous metals from sulfide minerals. It is illustrated how the continuing development of new technologies and reduction in the number of steps in the production of various nonferrous metals have been possible by the thorough understanding and application of the physical chemistry of reactions. The theoretical bases behind the development of several new technologies and the difficulties in realizing certain worthwhile concepts in industrial practices are explained.

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