

# NON-FERROUS MELT CHEMISTRY

## The Role of Slags and Mattes

Eric J. Grimsey  
Murdoch University  
Perth, W. A.

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### ABSTRACT

This paper reviews the chemical and physical properties of iron silicate slags and mattes, especially those encountered in nickel and copper smelting, as well as the interactions between slag and matte which affect the outcome of smelting and converting processes. The topics covered include phase relationships and activities, viscosity and surface tension, as well as the factors affecting metal loss as a result of chemical dissolution and mechanical entrainment.

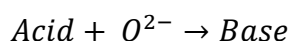
### INTRODUCTION

Most non-ferrous sulphide smelting processes involve the high temperature delivery of oxygen to a concentrate which results in the preferential oxidation of sulfur and iron. Sulfur forms a sulfur dioxide gas; iron oxide is fluxed with silica to form a liquid fayalite slag; the valuable metals are concentrated within a liquid sulphide or matte phase. Metal recovery is affected by chemical and physical factors. Chemical factors determine the equilibrium distribution of metals between matte and slag as well as the mutual solubility of the two phases. Physical factors affect the separation of the phases by pouring, as well as the mechanical entrainment of the matte in slag. This paper considers these factors in a review of the melt chemistry of non-ferrous slags and mattes and their interactions.

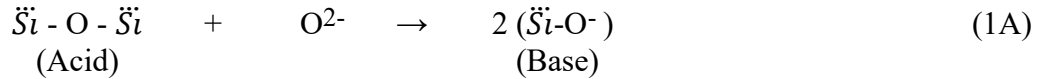
### IRON SILICATE SLAGS

Iron silicate slags are important because they are encountered in numerous smelting (steel, copper, nickel, lead, zinc, tin etc) and converting (nickel and copper) processes. In their pure form, the slags fall within the 'FeO' - Fe<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> system, although in practice other oxides including CaO, MgO and Al<sub>2</sub>O<sub>3</sub> may be present.

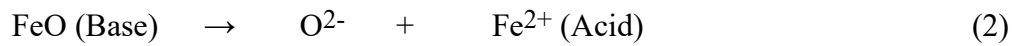
Iron silicate slags are formed through the depolymerisation of SiO<sub>2</sub> which has a three dimensional covalently bonded lattice with a high melting point. The depolymeriser or "network breaker" is FeO which is capable of splitting the Si-O-Si covalent bond in an "acid-base" reaction, in which SiO<sub>2</sub> acts as a Lewis acid and FeO acts as a Lewis base. For metallurgical slags, the acid/base definition is contained in the exchange:



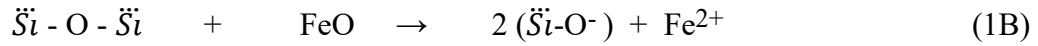
An acid is defined therefore as a species which accepts oxygen ions and a base is a species which supplies them. It is not necessary for free  $O^{2-}$  ions to exist in slag but only that the ion can be assigned an activity. The pH scale, for example, is based on hydrogen ions which do not exist separately in aqueous solutions. For iron silicate slags, the depolymerisation reaction may be expressed as



Where  $\ddot{Si}$  - represents a silicon atom bonded to 4 oxygens in the infinite network structure of  $SiO_2$  (only one O is shown), and  $O^{2-}$  represents an oxygen ion bonded to FeO;  $O^{2-}$  is supplied by a second acid/base reaction:

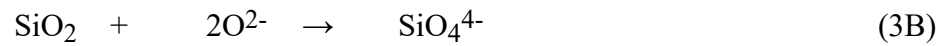


$Fe^{2+}$  resides adjacent or within the lattice of the ionic polymer containing two  $Si-O^-$  bonds in order to maintain electrical neutrality. Reaction 1A may be written therefore as:

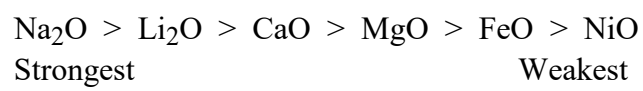


Other oxides such as CaO and MgO act as bases relative to  $SiO_2$ , whereas  $Al_2O_3$  is amphoteric and therefore may be basic according to  $Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-}$  or acidic according to  $Al_2O_3 + 3O^{2-} \rightarrow 2(AlO_3)^{3-}$ .

At the orthosilicate composition, enough  $O^{2-}$  ions are available theoretically to breakdown all of the  $SiO_2$  to  $SiO_4^{4-}$  tetrahedra according to:



The slag is said now to be neutral. Beyond this composition the slag can donate  $O^{2-}$  ions from excess MeO and is designated as basic; for MeO contents below this composition silica is in excess and the slag is acidic. This simple designation applies only for strong bases such as CaO. Weaker bases such as MgO and FeO require higher concentrations to complete the depolymerisation. The strength of a metal oxide base relative to silica depends firstly on the electropositivity of the metal, that is, on its ability to increase the electron density on the oxygen atom which increases its basicity towards the electrophile silicon atom. It depends secondly on the ability of the metal ion to lower the free energy of the solvated complex formed with the polyanion. These factors tend to oppose each other. The following is an indication of the strength of bases relative to silica:



Liquid slags are considered as solutions of depolymerised or partly depolymerised silicate anions whose negative charges are electrically neutralised by cations residing within "holes" or "sites" in the polymer structures. Such cations are unlikely to exist as pairs and neutral slag species are represented most correctly as mono-cationic, namely,

$\text{Fe}^{3+}$  is represented as  $\text{FeO}_{1.5}$ ,  $\text{Al}^{3+}$  as  $\text{AlO}_{1.5}$ ,  $\text{Fe}^{2+}$  as  $\text{FeO}$ ,  $\text{Ca}^{2+}$  as  $\text{CaO}$ ,  $\text{Mg}^{2+}$  as  $\text{MgO}$  as so on. The silica polymers are represented always by  $\text{SiO}_2$  since each  $\text{Si}^{4+}$  must be neutralised by two  $\text{O}^{2-}$  ions.

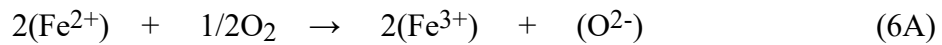
Iron silicate slags always contain an amount  $\text{Fe}^{3+}$  in addition to  $\text{Fe}^{2+}$ . This dual valency provides for an electron transfer medium in smelting systems, namely,  $\text{Fe}^{2+}$  in the melt can exchange electrons with  $\text{Fe}^{3+}$  according to:



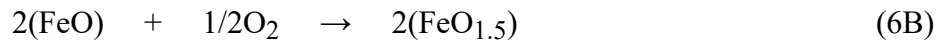
while oxygen in the gas can exchange electrons with the melt according to:



A combination of (4) and (5) yields:



This equation also may be written in the more common form:



Since free oxygen ions do not exist in the melt, equation 6B is a more realistic representation than 6A. The equilibrium constant for 6B may be written as:

$$\begin{aligned} K_{6B} &= \left( \frac{a_{\text{FeO}_{1.5}}}{a_{\text{FeO}}} \right)^2 \frac{1}{p_{\text{O}_2}^{0.5}} \\ &= \left( \frac{\gamma_{\text{FeO}_{1.5}}}{\gamma_{\text{FeO}}} \right)^2 \left( \frac{X_{\text{FeO}_{1.5}}}{X_{\text{FeO}}} \right)^2 \frac{1}{p_{\text{O}_2}^{0.5}} \\ &= \left( \frac{\gamma_{\text{FeO}_{1.5}}}{\gamma_{\text{FeO}}} \right)^2 \left( \frac{(\text{Fe}^{3+\%})}{(\text{Fe}^{2+\%})} \right)^2 \frac{1}{p_{\text{O}_2}^{0.5}} \end{aligned} \quad (7)$$

Here  $(\text{Fe}^{3+\%})$  and  $(\text{Fe}^{2+\%})$  represent the respective mass per cents of ferric ion and ferrous ion in the slag.

Since the activity coefficient ratio of  $\text{FeO}_{1.5}$  to  $\text{FeO}$  can be assumed constant for a slag of given basicity as determined by the  $\text{MeO}/\text{SiO}_2$  ratio, re-arrangement of 7 gives:

$$p_{\text{O}_2} = K' \left( \frac{(\text{Fe}^{3+\%})}{(\text{Fe}^{2+\%})} \right)^4 \quad (8)$$

where  $K' = 1/(K_{6B})^2$ . The  $(\text{Fe}^{3+\%})/(\text{Fe}^{2+\%})$  ratio thus is related to the oxygen pressure in the slag at a given slag basicity. The following equation summarises the relationship for copper smelting slags (Matousek, 1986):

$$\log p_{O_2} = -3.1 + 4.0 \log\left(\frac{Fe^{3+\%}}{Fe^{2+\%}}\right) - 1.0 \left(\frac{Fe\%}{SiO_2\%}\right) \quad (9)$$

The last term accounts for the effect of slag basicity (expressed as Fe/SiO<sub>2</sub> ratio) on the activity coefficient ratio  $\frac{\gamma_{FeO1.5}}{\gamma_{FeO}}$ . The equation can be extended to account for the effects of other oxides such as CaO, and for the effect of temperature through the standard free energy for reaction 6B (Matousek, in press, 1992).

The hypothetical FeO - SiO<sub>2</sub> binary, shown in Figure 1, illustrates most simply the low melting point "fayalite" region utilised in industrial processes. The binary is hypothetical since pure ferrous oxide exists only as "wüstite" in which the O/Fe ratio is greater than 1 since the lattice contains an amount of Fe<sup>3+</sup> as well as Fe<sup>2+</sup>.

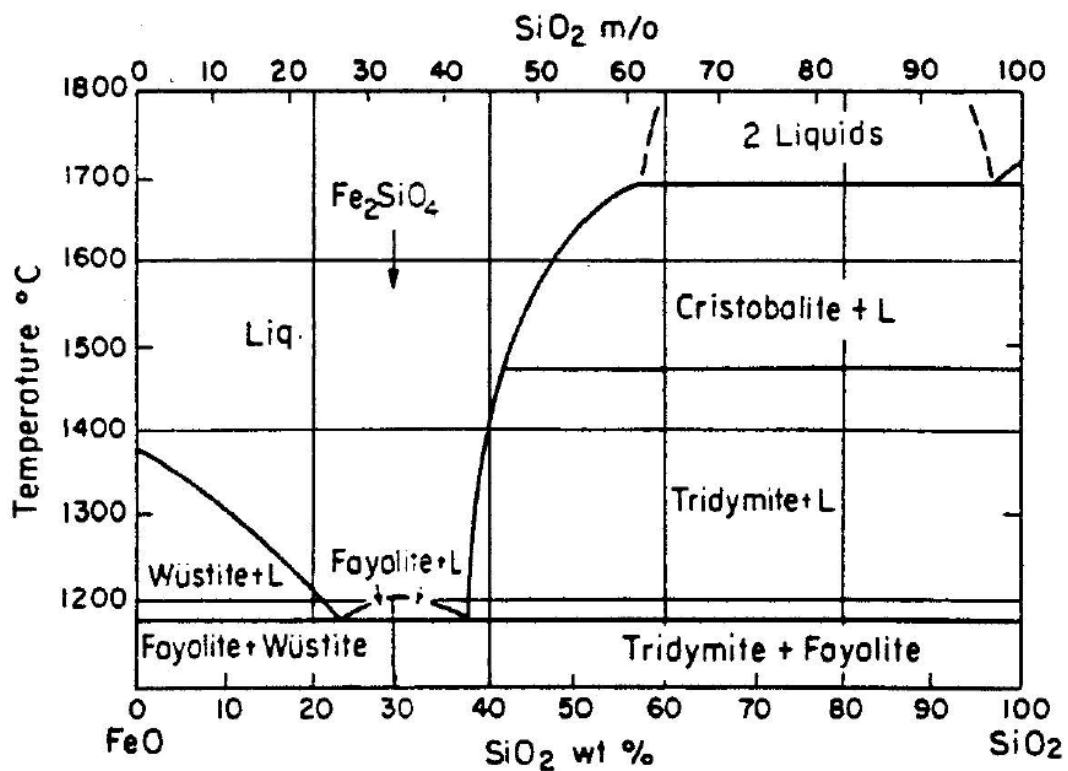


Figure 1: The hypothetical 'FeO' - SiO<sub>2</sub> binary in equilibrium with solid iron (Diaz, 1974)

Pure iron silicate slags can be represented as mixtures of the components FeO - Fe<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub>. The phase diagram at a typical smelting temperature of 1300°C is shown in Figure 2. The isobars on the diagram are given as  $-\log p_{O_2}$ , and thus an isobar marked 8 represents an oxygen pressure of 10<sup>-8</sup> atmospheres and so on. The shaded area represents the liquid fayalite region at 1300°C. The oxygen pressure of such slags can range from as low as < 10<sup>-11</sup> atm to as high as >10<sup>-6</sup> atm, with the pressure increasing as the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio in the slag increases across the liquid region, for example, across the line XY which represents a constant silica content.

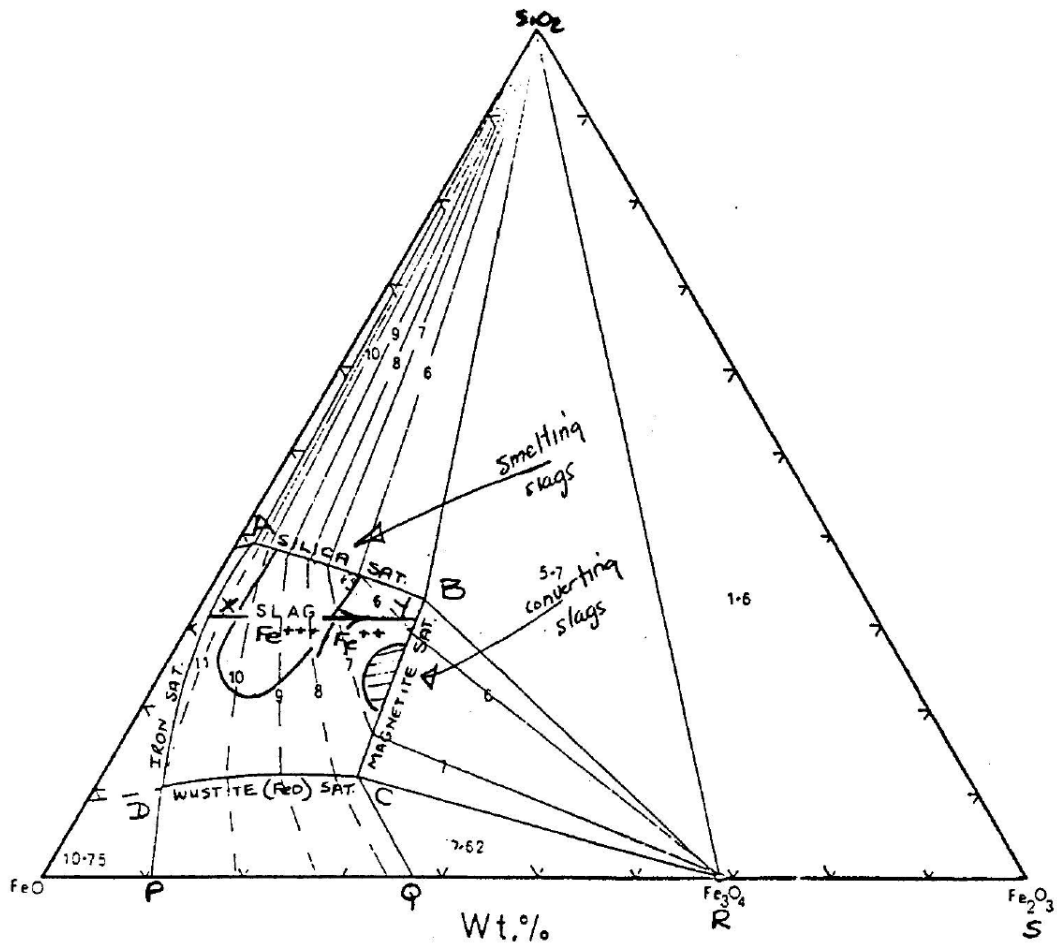


Figure 2: The FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system showing the liquid region at 1300°C

In Figure 2, the lines AB, BC, CD and DA border the liquid regions and represent the boundaries where a second phase will form, namely, AB (solid silica), BC (solid magnetite), CD (solid 'FeO') and DA (solid Fe). No tie lines are shown on the diagram connecting compositions along AD with solid Fe, since Fe is not represented as a component. If it were present as a fourth component (in addition to FeO, Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>), tie lines would extend backward through the page to the far apex of the diagram which would represent pure Fe. In practice, the ferric ion content of slag is expressed usually as "the magnetite content of the slag", since as shown on the diagram ferric iron will never precipitate from slag as hematite, but always as magnetite both at saturation and on cooling.

Figure 3 shows the effect of temperature on the liquidus surfaces for the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. The isobars represent the oxygen pressure of the melt at the liquidus temperature. The figure clearly shows that the solubility of magnetite and wustite increases significantly with temperature, whereas the solubility of silica increases to a much smaller degree.

Diagrams are available also to show the effects of slag additives on the liquidus region (Levin et al., 1969). Alumina in relatively small amounts will lower the melting point of slag but at the same time raise their viscosity which is undesirable; for slags with between 20 and 30 weight per cent silica, 6 to 9 per cent alumina will lower the melting point by

up to 55°C. When CaO is substituted for FeO the melting point decreases, for example, by around 90°C for the addition of 10 per cent CaO. In contrast, the presence of even small amounts of MgO increases the melting point of slag, by around 100°C for the addition of 5 per cent MgO.

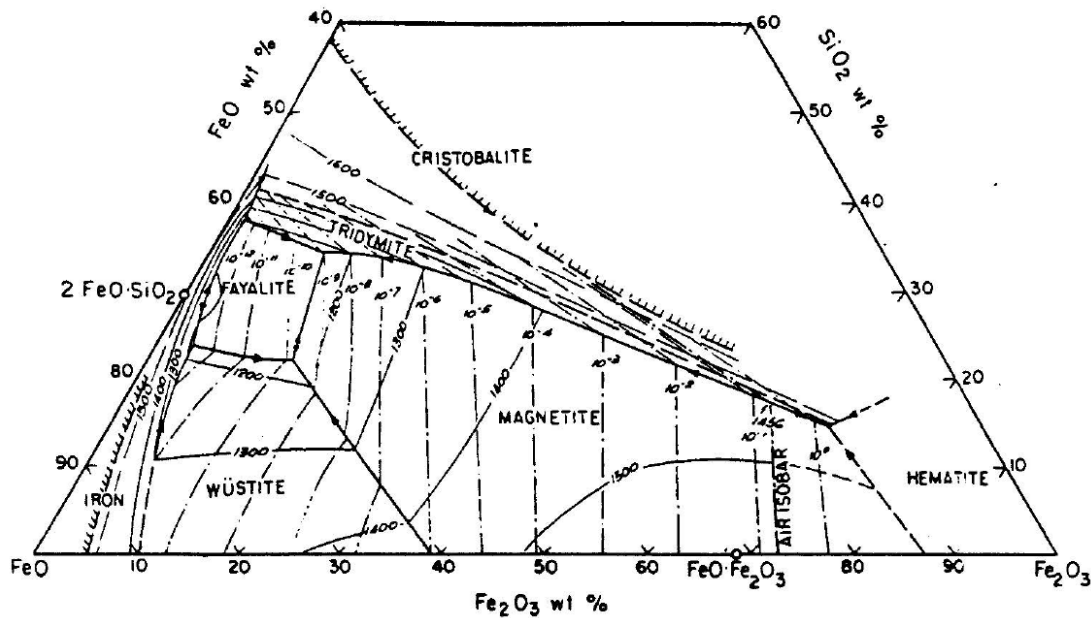


Figure 3: The liquidus lines of the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system (Diaz, 1974)

The activity of iron oxide in iron silicate slag, without oxide additives, is determined mainly by the per cent silica in the slag or the Fe/SiO<sub>2</sub> ratio. The activity of FeO relative to pure liquid FeO is around 0.35 for silica saturated slags ( $\approx 40\%$  SiO<sub>2</sub>, Fe/SiO<sub>2</sub>  $\approx 1/1$ ) at 1300°C and is relatively independent of temperature for smelting and converting operations. The activity increases with decrease in silica content (or increase in Fe/SiO<sub>2</sub>) not only because of an increase in the mole fraction of FeO in the slag, but also because of an increase in the activity coefficient from around 0.7 for silica saturated slags to around 1.0 for slags containing 20 per cent silica. Figure 4 shows the variation in 'FeO' and SiO<sub>2</sub> activities with change in silica content of slag for both 1350°C and 1600°C.

The addition of CaO, MgO and Al<sub>2</sub>O<sub>3</sub> to slags of constant silica content all increase the activity coefficient of ferrous oxide. However, the effect on iron oxide activity is discounted since the mole fraction of FeO is decreased by dilution and this off-sets the increase in activity coefficient. An excellent description of activities and activity coefficient relationships in the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO system is available from Kellogg and co-workers. They use interaction parameters coupled with the three suffix Margules equation to provide for a complete description of activities and phase equilibria in the system (Grimsey and Morris, 1992).

Slag viscosity is probably the most important physical property after the liquidus temperature. An increase in viscosity can make slag tapping and skimming difficult as well as increasing the settling time for matte particles entrained in slag (cf. Stoke's law), and also the tendency of slags to foam.

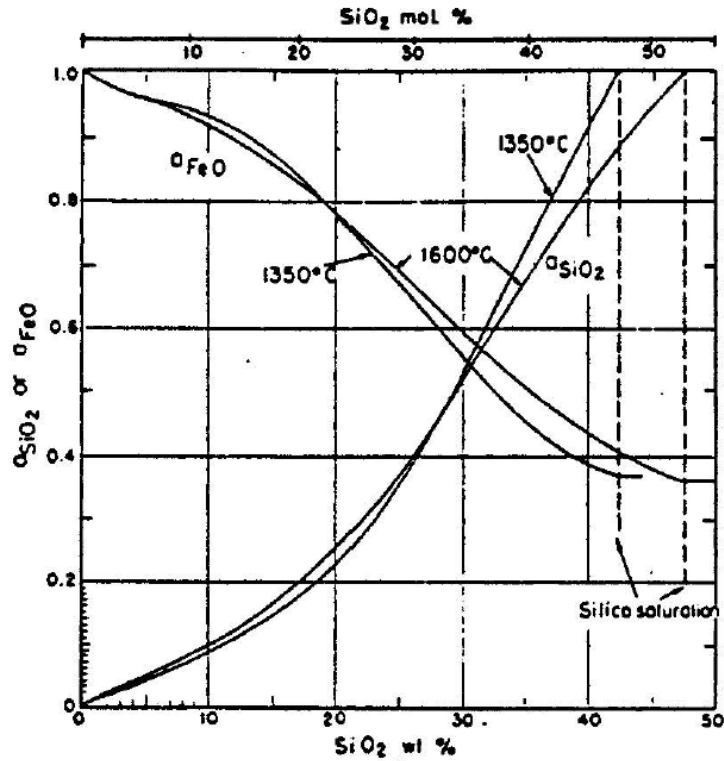


Figure 4: 'FeO' and SiO<sub>2</sub> activities in SiO<sub>2</sub>-FeO melts relative to pure liquid FeO in equilibrium with solid iron and pure solid silica respectively (Elliott et al., Thermochemistry for Steelmaking, 1963)

The viscosity of iron silicate slags is related to the extent of depolymerisation of the melt. Viscosity will increase with an increase in silica content (or decrease in iron oxide content), and with a decrease in temperature. The oxide additives CaO and MgO decrease slag viscosity especially for slags of higher silica content where they are more effective as network breakers. Alumina, in general, increases the viscosity of fayalite slags. An equation partially summarising these effects for industrial slags has been published recently (Kolosov et al., 1987):

$$\ln \mu \text{ (Pa.s)} = - 6.467 + 0.0963 (\text{SiO}_2\%) + 0.0874 (\text{Al}_2\text{O}_3\%) + \frac{11800}{T} - 0.0527 (\text{FeO}\%) - 0.0681 (\text{CaO}\%) - 0.0577 (\text{Fe}_3\text{O}_4\%) \quad (10)$$

where Pa.s = 10 poise.

The surface tension of slags also affects their separation from mattes. The surface tension or surface energy of liquid slags depends on their composition, and especially on the presence of surface active species which lower the surface tension. Silica is surface active for iron silicate slags, and thus the surface tension decreases with an increase in the silica content. For example, the surface tension falls from around 450 to 400 erg/cm<sup>2</sup> as the silica content is increased from 20 to 30 per cent at 1400°C. An increase in the ferric oxide content of the slag decreases the surface tension whereas the replacement of FeO by either CaO or MgO increases it. Alumina appears to have little effect, whereas

sulfur dissolved in slag is surface active and reduces the surface tension (Diaz, 1974; Bodnar et al., 1977)

## MATTES

The important industrial systems for copper and nickel mattes, namely, Cu-Fe-S and Ni-Fe-S, will be considered briefly here. Matte structures seem more complex than those of slags. Copper mattes, for example, can be considered ideally as mixtures along the FeS and Cu<sub>2</sub>S pseudo-binary. However, whereas molten Cu<sub>2</sub>S behaves like a semiconductor, molten FeS is a metallic conductor. Accordingly the structure of a copper matte will depend on the Cu/Fe ratio (Elliott and Mounier, 1982). The situation is complicated further since industrial mattes also contain amounts of dissolved metal as well as oxygen, and their composition can never be truly represented by the Cu<sub>2</sub>S - FeS pseudo-binary. Nickel mattes especially dissolve considerable amounts of metal and their compositions lie far removed from the Ni<sub>3</sub>S<sub>2</sub> - FeS pseudo-binary. Since mattes do not share the same ionic nature as slags, the use of the mono-cationic species representation for mattes, for example CuS<sub>0.5</sub> and NiS<sub>0.66</sub>, has less validity than for slags.

Liquidus temperatures for the Ni-Fe-S system at between 1200°C and 1400°C are shown in Figure 5. The diagram is characterised by a separation of solid iron from an iron rich sulphide melt along the Fe - S binary, and the separation of solid nickel from a nickel rich sulphide melt along the Ni-S binary. The Ni-Fe-S liquid region saturates with a complete range of solid Ni-Fe alloys; melts rich in nickel give high nickel alloys while melts rich in iron give high iron alloys.

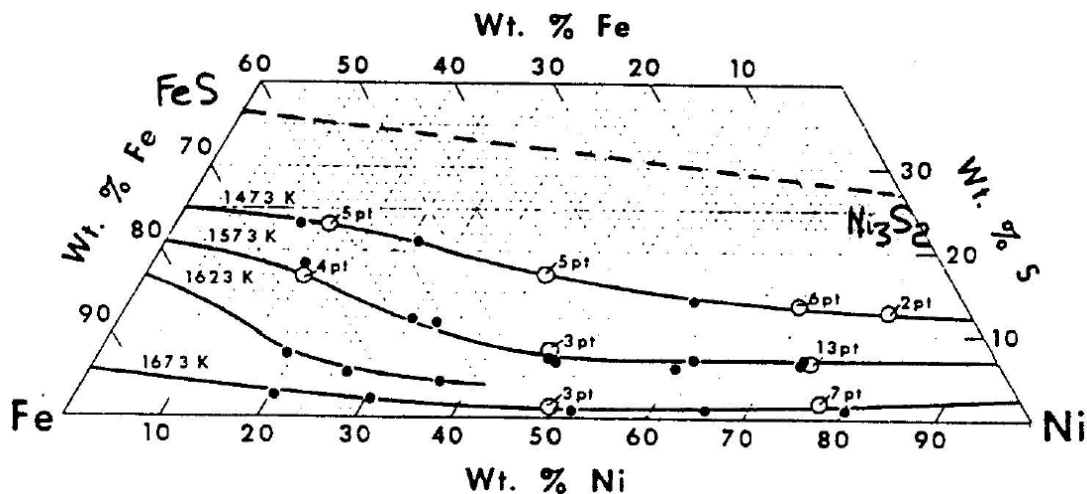


Figure 5: Liquidus temperatures for the Ni-Fe-S system between 1200 and 1400°C (Lenz et al., Met. Trans B, 9B: 459, 1978)

The position of the liquidus is well below the FeS - Ni<sub>3</sub>S<sub>2</sub> pseudo-binary which shows that nickel mattes dissolve considerable amounts of metal. The movement of the liquidus towards the base of the diagram with an increase in temperature shows that the metal solubility increases significantly with an increase in temperature. Industrial smelting and converting mattes contain between 20 and 30 per cent sulfur, whereas mattes formed from slag cleaning are virtually saturated with alloy and contain sulfur at levels less than 20 per cent.



The Cu-Fe-S ternary system at 1200°C is shown in Figure 6. The Cu-S binary is fundamentally different from Ni-S since it exhibits a liquid-liquid miscibility gap, in which almost pure liquid  $\text{Cu}_2\text{S}$  is separated from a liquid copper containing a small amount of sulfur. Within the ternary, the Cu-Fe-S liquid saturates on the copper rich side with a liquid copper containing small amounts of sulfur and up to 18 per cent iron, and on the iron rich side with a solid iron containing very little sulfur and up to 8 per cent copper.

The compositions for a number of industrial mattes, ranging from a 40 per cent copper matte from a reverberatory furnace (A), to a 75 per cent matte from a Noranda furnace (D), are shown on the diagram. The extent of metal solubility is much less than for nickel mattes and so the compositions are restricted by the position of the miscibility gap to a region just below the  $\text{Cu}_2\text{S}$  - FeS pseudo-binary. In contrast to nickel mattes also, the metal solubility increases very little with increase in temperature because the liquidus at the miscibility gap is quite steep, especially for high copper melts.

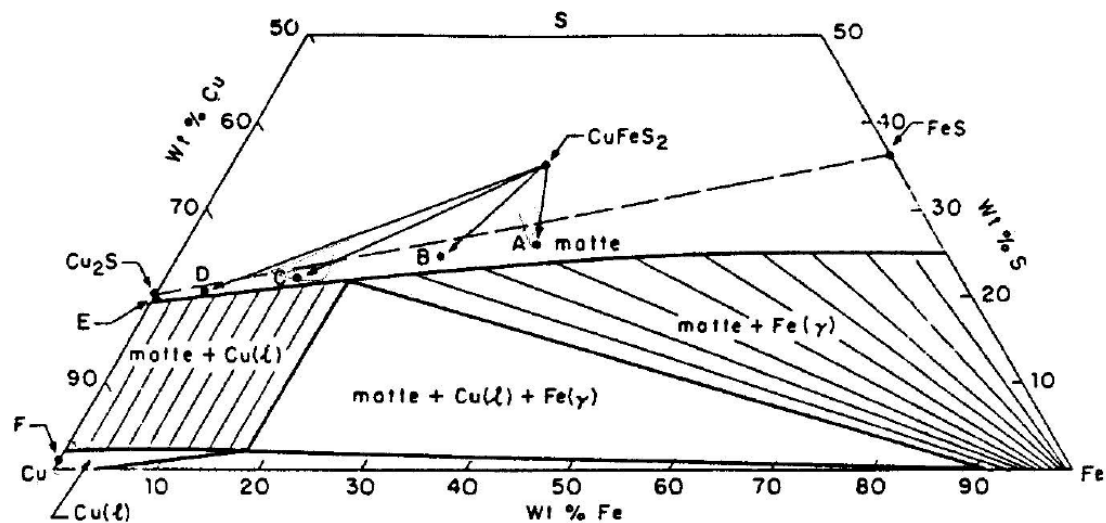


Figure 6: The Cu-Fe-S system at 1200°C (Themelis et al., *Advances in Sulfide Smelting*, Vol. 1: 1, 1983)

An excellent activity model for Ni-Fe-S mattes is available from Chang and co-workers using the three suffix Margules equation (Grimsey and Morris, 1991). While no such detailed model currently exists for Cu-Fe-S, the work of Krivsky and Schuhmann (1957) shows that industrial mattes, especially in the high copper region, can be described reasonably as ideal mixtures of  $\text{Cu}_2\text{S}$  and FeS, despite the fact the  $\text{Cu}_2\text{S}$  and FeS have quite different structures as noted earlier.

Activities in liquid matte systems are characterised firstly by a rapid decrease in metal activity with an increase in sulfur content away from the miscibility gap, and secondly by a rapid increase in the activity of sulfur which accompanies the fall in metal activity. The relative change in these two activities is especially pronounced for compositions around the pseudo-binaries. This behaviour is significant for the oxidation of iron and sulfur from mattes during converting. Since the depletion of either iron or sulfur is

accompanied by a significant increase in the reactivity of the other species, iron and sulfur are removed from the melt by oxidation in an almost 1:1 molar ratio. The matte composition moves therefore along a path directly away from FeS, and the composition approaches either Cu<sub>2</sub>S (white metal) in the case of copper converting or high grade matte (Ni<sub>3</sub>S<sub>2</sub> + Ni) in the case of nickel converting.

Commercial mattes must contain amounts of oxygen since they are in contact with iron silicate slags with finite FeO and FeO<sub>1.5</sub> activities. Very little data exists, however, on the activity coefficients of oxide species in mattes, and the oxygen content is therefore usually neglected in practice. The solubility of oxygen in copper and nickel mattes has been measured by a number of workers and may be as high as 5 per cent for very low grade mattes (Figure 7). The oxygen solubility increases as iron replaces nickel or copper in the matte presumably due to the greater stability of FeO compared to NiO or Cu<sub>2</sub>O

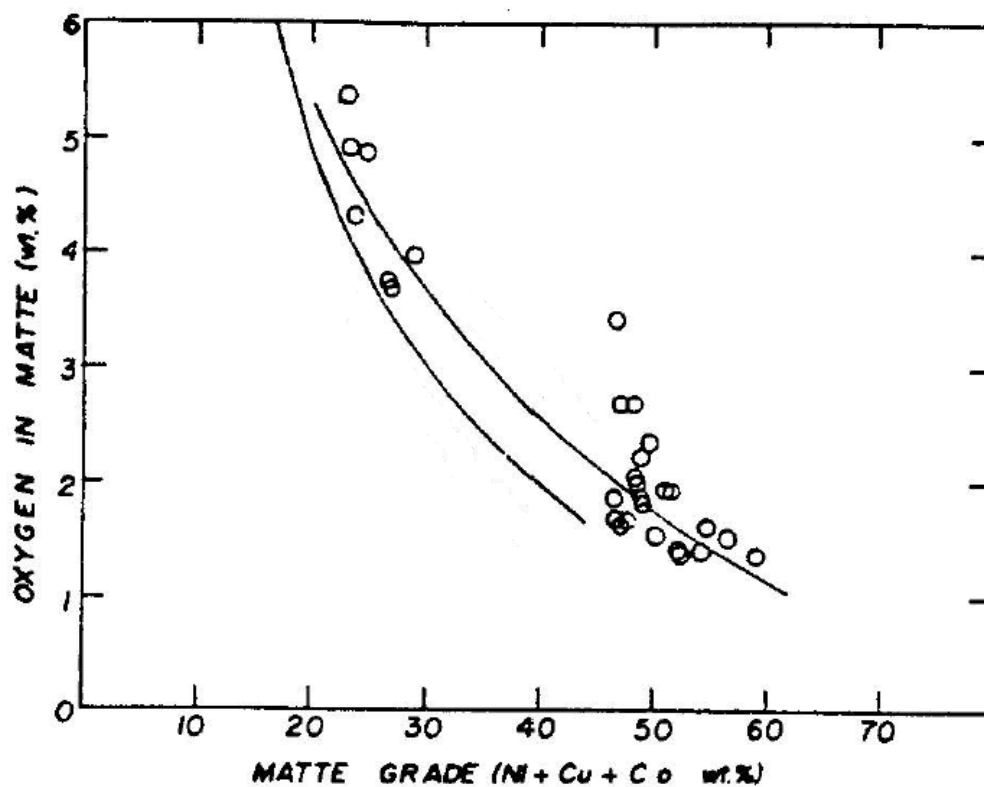


Figure 7: The solubility of oxygen in nickel (upper line with data points, Grimsey, 1980) and copper mattes (lower line, Spira and Themelis, 1969) as a function of matte grade expressed as Ni + Cu + Co per cent.

The surface tension of mattes decreases with an increase in FeS content since this species is surface active. For example, the surface tension of copper mattes at 1200° C decreases from 0.36 to 0.33 J/m<sup>2</sup> as the matte grade is decreased from 60 to 0 per cent copper (Elliott and Mounier, 1982). The values for nickel mattes show greater variation but are of similar magnitude (Vaisburd et al., 1987).

## MATTE AND SLAG INTERACTIONS

Smelting and converting are operations which employ oxygen for the progressive removal of both iron and sulfur from sulphide concentrates. Oxygen is delivered to the condensed phase at high temperatures so that iron as oxide may combine with silica flux to form an iron silicate slag, and sulfur may report to the gas as SO<sub>2</sub>. Once the oxygen has been delivered, the condensed phases separate into matte and slag and an equilibrium between matte, slag and gas is approached.

If an equilibrium is finally achieved (or closely approached), the two fundamental thermodynamic parameters affecting the chemical distribution of elements between the matte and slag are the oxygen and sulfur pressures. The greater the oxygen pressure at equilibrium then the greater the proportion of metals reporting to the slag phase; the greater the sulfur pressure at equilibrium then the greater the proportion of metals reporting to the matte phase.

In practice, the final oxygen and sulfur pressures are greatly influenced by the exchange equilibrium of iron between slag and matte, mainly because iron constitutes a major part of the slag, and the slag mass is usually significantly greater than matte. The matte/slag/gas exchange equilibrium for iron can be written as:



where [ ] represents the matte phase and ( ) the slag phase respectively.

The oxygen and sulfur pressures for this equilibrium are linked further to the pressure of sulfur dioxide generated in the smelting system according to the equilibrium:



A combination of (1) and (2) yields:



$$K_{13A} = \frac{a_{\text{FeO}} p_{\text{SO}_2}}{a_{\text{FeS}} p_{\text{O}_2}^{3/2}} \quad (13B)$$

Here the equilibrium activity is represented by a and the equilibrium partial pressure by p. Equation 13 focuses upon the major factors which determine the oxygen pressure of a matte/slag/gas system after the oxygen has been delivered in the smelting reactions and the system adjusts to provide the final equilibrium position. These factors are the activity of FeO in the slag, the pressure of sulfur dioxide and the activity of FeS in the matte.

The activity of iron oxide is buffered substantially by the basicity of the slag which is dominantly determined by the Fe/SiO<sub>2</sub> ratio when other oxides are in minor or constant amounts. The SO<sub>2</sub> pressure of the matte/slag system will not necessarily be the same as that of the furnace gases, but will depend on the manner in which the slag and matte approach equilibrium. Flash smelting, for example, is characterised by an over-oxidation of the condensed phases in the shaft, followed by a back-reduction as the phases settle and separate under the shaft. The back-reduction substantially occurs through the reaction of FeS with Fe<sub>3</sub>O<sub>4</sub> according to:



This reaction will proceed vigorously only when the generated  $\text{SO}_2$  pressure equals or exceeds one atmosphere, and the equilibrium  $\text{SO}_2$  at the matte/slag interface should settle near one atmosphere regardless of the sulfur dioxide pressure in the furnace gas. Both smelting reactions are characterised by a more controlled oxidation process in which the oxygen is delivered to the bath in the presence of flux such that the activity of  $\text{FeO}$  is controlled and the tendency for over-oxidation to form magnetite is reduced. Under these conditions, the final  $\text{SO}_2$  pressure of the matte/slag system is more characteristic of the furnace gas, with a value of around 0.1 atmospheres.

For a specific process type and slag composition (which buffer the  $\text{SO}_2$  pressure and the ferrous oxide activity respectively), equation 13 shows that the oxygen pressure at equilibrium will depend essentially on the amount of  $\text{FeS}$  remaining in the matte after the stoichiometric oxidation process, and the smaller this amount then the higher the equilibrium oxygen pressure in the matte/slag system. The sulfur pressure at equilibrium is fixed through reaction 12 for given oxygen and sulfur dioxide pressure, and decreases as the oxygen pressure increases when the sulfur dioxide pressure is buffered.

Valuable metals are lost in the slag as a result of chemical dissolution and mechanical entrapment. For a given  $p_{\text{O}_2}$  and  $p_{\text{S}_2}$  in the system, the chemical dissolution in the slag of a divalent metal oxide is considered best through the exchange equilibrium:



$$K_{15A} = \frac{a_{\text{MeO}} a_{\text{FeS}}}{a_{\text{FeO}} a_{\text{MeS}}} = \left( \frac{X_{\text{MeO}} X_{\text{FeS}}}{X_{\text{FeO}} X_{\text{MeS}}} \right) \left( \frac{\gamma_{\text{MeO}} \gamma_{\text{FeS}}}{\gamma_{\text{FeO}} \gamma_{\text{MeS}}} \right) \quad (15B)$$

A rearrangement of this equation yields an expression for the distribution of metal  $\text{Me}$  between matte and slag ( $L_{\text{Me}}$ ) namely:

$$L_{\text{Me}} = \frac{[\text{Me}\%]}{(\text{Me}\%)} = \frac{1}{K_{15A}} \frac{[\text{Fe}\%]}{(\text{Fe}\%)} \left( \frac{\gamma_{\text{MeO}} \gamma_{\text{FeS}}}{\gamma_{\text{FeO}} \gamma_{\text{MeS}}} \right) \quad (15C)$$

Here  $X$  is mole fraction,  $\gamma$  is activity coefficient,  $[\%]$  represents mass per cent in the matte and  $(\%)$  represents mass per cent in the slag.

Equation 15C shows that the distribution of metal to matte is increased (i) by a decrease in the equilibrium constant  $K_{15A}$ , (ii) by an increase in the per cent iron in the matte, (iii) by a decrease in the per cent iron in the slag, (iv) by an increase in the  $\text{FeS}$  to  $\text{MeS}$  activity coefficient ratio in the matte, and (v) by an increase in the activity coefficient ratio of  $\text{MeO}$  to  $\text{FeO}$  in the slag.

Thus, the activity coefficient ratios rather than individual activity coefficients are seen to be important in determining the distribution of metal between matte and slag. When the metal has similar chemical properties to  $\text{Fe}$  (e.g.  $\text{Co}$  and  $\text{Fe}$ ), the ratios and thus the metal distribution will be less sensitive to changes in either the matte or slag compositions.

An improved metal distribution, however, does not necessarily result in an improved metal recovery since other factors must be considered. Grimsey (1992) has introduced a simple yet powerful equation which directly expresses the recovery of metal to matte ( $R_{Me}$ ) in terms of a mass balance and a thermodynamic parameter, namely:

$$R_{Me} = \left( \frac{1 - y}{1 - y + \frac{y K_{15A}}{K_\gamma}} \right) \times 100\% \quad (16)$$

Here  $y$  is the mass fraction of the total iron which reports to the slag and  $K_\gamma$  is a pseudo-constant which represents the activity coefficient ratio, namely:

$$K_\gamma = \left( \frac{\gamma_{MeO} \gamma_{FeS}}{\gamma_{FeO} \gamma_{MeS}} \right)$$

Equation (16) shows that the direct recovery of a valuable metal  $Me$  decreases (i) as the mass of iron transferred to the slag increases, (ii) as the value of  $K_{15A}$  increases and (iii) as the value of  $K_\gamma$  decreases.

The presence of sulfur dissolved in slag can enhance the dissolution of valuable metals. The ionic radius of sulfur (1.84 Å) is much larger than that of oxygen (1.40 Å) and sulfur cannot readily substitute for oxygen in silicate bonds. Sulfur therefore enters the slag as a substitute for oxygen covalently bonded to ferrous ion. The FeO-FeS-SiO<sub>2</sub> diagram (MacLean, 1969), for example, shows a marked increase in the solubility of sulfur within the silicate melt when the ferrous oxide content increases. The level of sulfur solubility depends therefore on the activities of both iron oxide and iron sulphide in the matte/slag system; the dissolved sulfur will increase with a decrease in matte grade (which results in an increase in iron sulphide activity), or an increase in the Fe/SiO<sub>2</sub> ratio in slag (which results in an increase in iron oxide activity).

The tendency for slag to dissolve sulfur can be expressed in terms of a "sulphide capacity",  $C_s$ , as defined by Fincham and Richardson (1954):

$$C_s = \frac{(S\%) pO_2^{0.5}}{pS_2^{0.5}} \quad (17)$$

The  $\frac{pO_2^{0.5}}{pS_2^{0.5}}$  ratio for a matte/slag system is obtained from a rearrangement of the equilibrium constant for the FeS/FeO exchange reaction (equation 11), namely:

$$\frac{pO_2^{0.5}}{pS_2^{0.5}} = \frac{a_{FeO}}{a_{FeS} K_{11}} \quad (18)$$

where a combination of (17) and (18) gives:

$$C_s = \frac{(S\%) a_{FeO}}{a_{FeS} K_{11}} \quad (19)$$

The sulphide capacity will therefore vary as changes in slag composition affect the FeO activity. For a given slag composition (i.e. fixed  $a_{FeO}$ ), the sulphide capacity quantifies the effect of matte grade on sulfur solubility in slag since the  $a_{FeS}$  in matte decreases as the matte grade increases.

An increase in sulfur solubility in slag also enhances the solubility of copper which is well established experimentally. The enhancement can be quantified either as a summation of separate  $CuS_{0.5}$  and  $CuO_{0.5}$  solubilities as proposed by Nagamori (1974), or as an enhancement by sulfur of the activity coefficient of  $CuO_{0.5}$  as proposed by Davey and Willis (1984). The approaches are equivalent in terms of chemical thermodynamics which neither provides nor requires any information regarding the internal structure of a system. The approach which provides the simplest analytical expression for the variation of activity coefficients is the most convenient in practice.

In addition to loss of metal through solubility in slag, valuable metal can also be lost by mechanical entrainment of matte within the slag as a result of incomplete settling of the heavier liquid sulphide matte through the liquid slag. Entrainment is exacerbated by the generation of gas bubbles at the matte/slag interface through reaction 14, since matte can be transported into slag by rising bubbles either as a coating on the surface of a bubble or as a globule of matte attached to the bubble surface and lifted into slag by flotation.

The tendency of a matte to wet slag and form a stable film around a bubble can be quantified (Elliott and Mounier, 1982) by the so-called "spreading coefficient"  $\emptyset$  ( $J/m^2$ ). If  $\gamma_{s/g}$  is the surface tension of the slag,  $\gamma_{m/g}$  the surface tension of the matte and  $\gamma_{m/s}$  the interfacial tension of the matte/slag interface then:

$$\emptyset = \gamma_{s/g} - \gamma_{m/g} - \gamma_{m/s} \quad (20)$$

If the spreading coefficient  $\emptyset$  is positive, then then the matte can wet the slag and form a stable film around a bubble as it emerges from the matte. If  $\emptyset$  is negative, the matte film is unstable and sheds the bubble at the surface to form a stable matte globule. The susceptibility of this globule to flotation can be quantified (Elliott and Mounier, 1982) by the so-called the "flotation coefficient"  $\Delta$ . This is a measure of energy of cohesion ( $J/m^2$ ) of the matte droplet to the gas bubble as given by:

$$\Delta = \gamma_{s/g} - \gamma_{m/g} + \gamma_{m/s} \quad (21)$$

For copper mattes (and also likely nickel mattes) an increase in matte grade and/or Fe/SiO<sub>2</sub> ratio in slag will increase the interfacial tension between the matte and slag ( $\gamma_{m/s}$ ). This decreases the spreading coefficient  $\emptyset$  (equation 20) and increases the flotation coefficient  $\Delta$  (equation 21). Both favour the flotation over film formation; thus lower grade mattes form stable films around gas bubbles whereas higher grade mattes form stable globules which are readily floated into slag. The effects of increasing matte grade on the spreading and flotation coefficients for copper matte in contact with iron silicate slag are illustrated in Figure 8.

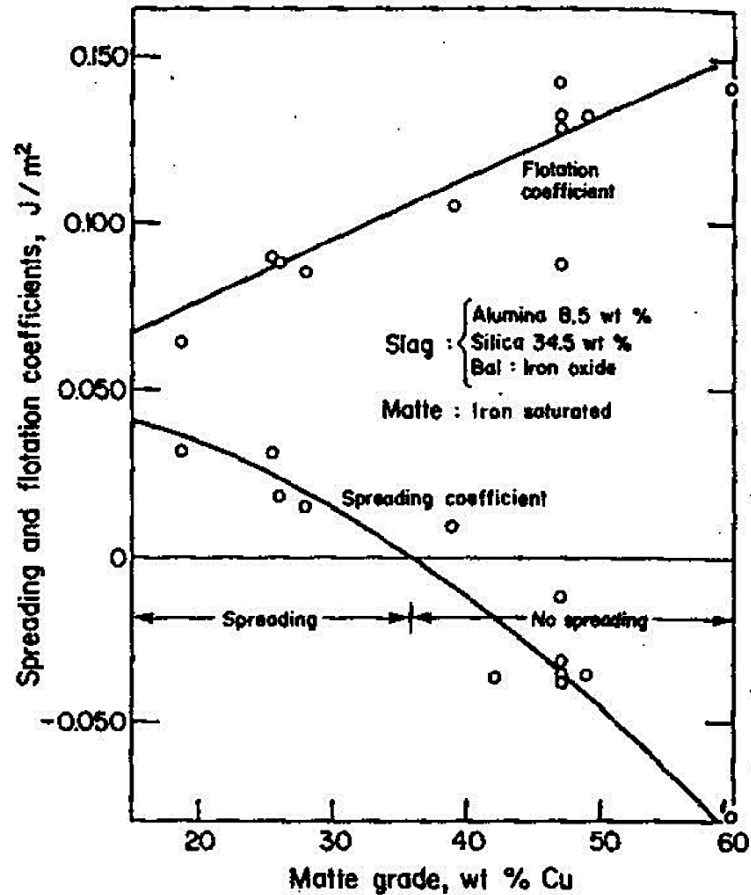


Figure 8 – Effect of Cu matte grade on spreading and flotation coefficients in matte-slag-gas system at 1200°C (Elliott and Mounier, 1982).

Since industrial nickel and copper sulphide smelting operations target high matte grades, the flotation of matte particles by SO<sub>2</sub> bubbles rising through slag is a significant source of matte entrainment. Ultimately, the amount of entrained matte present in slag after a given settling time will depend on (i) the extent of matte flotation, (ii) the rate of coalescence of matte globules and the rate at which they settle back through slag under gravity, and (iii) the amount and direction of movement in the slag bath.

After a bubble carrying matte rises to the slag surface, the bubble will rupture if foam is not stable and the matte globule will be released. Small matte droplets floating on the surface will coalesce; if they grow to sufficient size they will sink at a terminal velocity ( $V_t$ ) ideally described by Stokes Law:

$$V_t = \frac{D_m^2(\rho_m - \rho_s)g}{18\mu} \quad (22)$$

Here  $D_m$  is the diameter of the matte globule,  $\rho_m$  and  $\rho_s$  are the respective densities of matte and slag,  $\mu$  is slag viscosity and  $g$  the acceleration due to gravity.

Equation 22 shows that settling of matte into slag is favoured by an increase in the density of matte relative to slag ( $\rho_m - \rho_s$ ) and a decrease in the slag viscosity ( $\mu$ ). Matte densities increase with an increase in matte grade, while slag densities decrease with an

increase in silica content (Li et al. 1989). However, variations in the slag viscosity have the greatest effect on settling rate, and the settling rate can be increased by a decrease in silica content of slag or an increase in temperature.

A rising bubble can rupture as it exits the slag as a result of liquid draining from the interface mainly as the result of gravity. The rate of draining is reduced for slags of higher viscosity and lower surface tension, especially in the presence of surface active agents. This can reduce the rate of draining sufficiently to stabilise the film and cause slag to foam. The presence of fine suspended solids in slag will also enhance the stability of foam by providing a stabilising surface along the bubble interfaces.

Iron silicate slags high in silica and close to or saturated with magnetite have the greatest tendency to foam, especially at lower temperatures. Such slags combine a high viscosity with a relatively low surface tension since both silica and ferric oxide are surface active. If a fine precipitated magnetite is present the potential for foaming is also greatly increased (Li et al., 1989).

Slag foaming is undesirable in conventional smelting furnaces since it increases metal entrainment in slag and can even fill the uptake shaft and block the waste heat boiler with slag if the foaming reaction is intensive enough. However slag foaming also greatly increases the interfacial area between matte, slag and gas and is essential for the operation of high intensity bath smelting processes such as that developed by Vanyukov in the former Soviet Union

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