

# On the Thermodynamic and Physical properties of Ionic Melts and on Their Role in Ferrous and Nonferrous Metals Production Processes

*Heikki JALKANEN, Sonja NURMI and Seppo LOUHENKILPI,  
Aalto University, School of Chemical Technology, Otaniemi, Finland*

**Abstract:** In this paper the interconnection of acid-base properties and the structure of ionic melts with their thermodynamic and physical properties, thermodynamics of chemical interaction between molten metals and ionic melts especially slag-metal reactions, removal of impurities from metals and alloys are generally discussed on the base of industrial experience, results of equilibrium investigations and thermodynamic calculations. Some comments on the physical and physicochemical properties of slags and their role are included in the presentation. Examples from iron and steelmaking and sulfide smelting processes with contributing results of experimental research are also presented in the context with the treatment of general thermodynamic and physical properties and behavior of slags.

**Key words:** Thermodynamics & physical properties, ionic melt, slag properties, slag phenomena

## 1. Introduction

Ionic melts, slags, fluxes and molten salts have an important role practically in all metals production and processing stages except for solid state processing like roasting and sintering of ores or concentrates. The main role of slag in primary smelting of raw materials is the collection and dissolving the non-reducing minerals like silicates, lime, magnesia, phosphorus oxide etc. present in the ores and concentrates. The secondary task of slag in primary smelting is the removal of other impurities, but as the composition of slag is greatly controlled by non-reducing minerals and iron oxide formed in oxidizing smelting of sulphide concentrates, the choice for optimal composition of slag is usually very limited. In the refining stages of raw metals smelting, like in oxygen converting of hot metal or matte as well as scrap smelting and especially in special treatments of raw metal (like removal of sulphur from hot metal) or final refining stages before casting of the alloys, the slag composition can be more strictly focused to removal of impurities. In casting of metals and alloys the role of fluxes in tundish and mold is to protect the metal melt from oxidation, to act as thermal insulator and lubricant between the solidified alloy and mold, even as inclusion absorption or modifier of inclusions in the solidifying metal. Molten salt electrolysis is an alternative for extraction of metals when reduction by carbon, carbon monoxide and hydrogen or aqueous electrolysis<sup>1</sup> are thermodynamically constrained. Aluminium, alkaline, alkaline earth metals, lanthanides and actinides are extracted through molten salt electrolysis. The role of ionic melt is to dissolve the metal compound in the electrolyte, offer suitable mobility for ions participating in the total electro-reduction process and protect the formed metal or non-oxide compound from oxidation.

---

<sup>1</sup> when oxides of the elements are more stable than water i.e. elements can react and reduce water to hydrogen by absorbing the oxygen from it these elements cannot be principally extracted by aqueous electrolysis (due to kinetic constraints zinc can be reduced by aqueous electrolysis although zinc oxide is more stable than water).

In the pyrometallurgical processes the main roles of slag are the removal of impurities from molten metals and alloys in various stages of the processing and protection the metallic phase from oxidation but also the control of heat radiation from the metal bath surface or electric arc. The role of mold fluxes is to protect the melt from oxidation in tundish and mold, to act as lubricant between the solidifying alloys and mold, in some cases to offer latest agent to modify nonmetallic inclusions in the solidifying alloy. In the molten salt electrolysis the role of ionic solution is to offer optimal conditions for electrochemical reduction of metals including the conduction of the ions, cations to be reduced at the catode and anions to be oxidised at the anode. One factor of increasing importance is the suitability of slags or molten salts from metals processing to recycling that should also be taken into account when the composition of slags, fluxes and electrolytes is planned. Figure 1 is schematically showing the general properties and interaction processes in metallurgical processes where ionic melts play an important role.

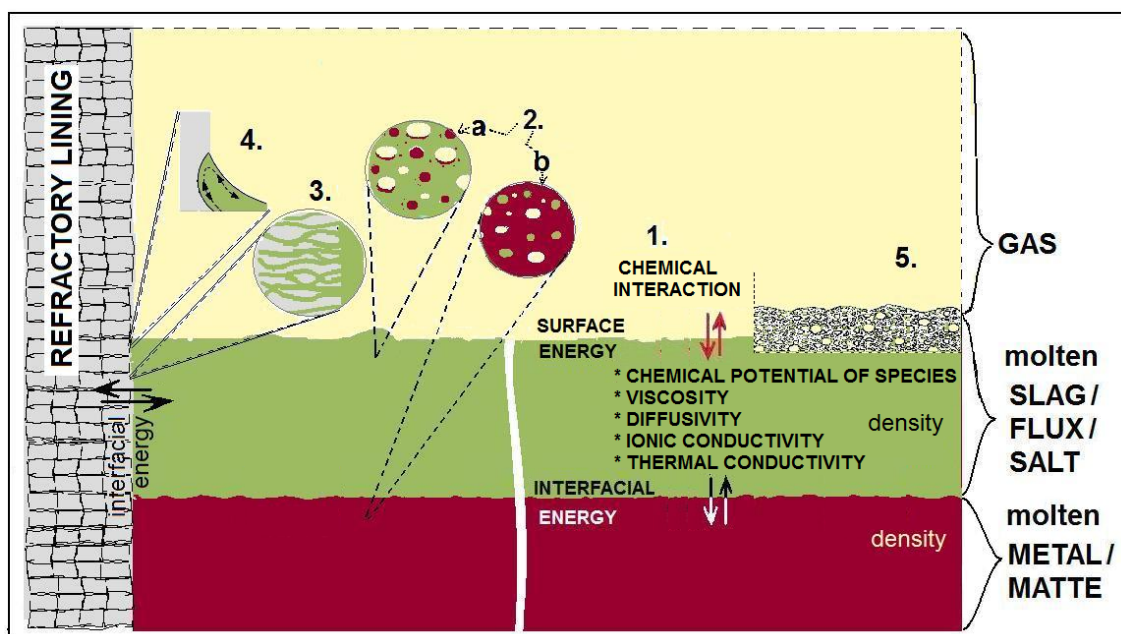


Fig. 1 Schematic description of interaction phenomena of ionic melts in metallurgical processes and properties affecting interaction and physico-mechanical phenomena. 1) Chemical reaction with ionic melt with gas, metal/matte melt, 2a) metal/matte droplets and gas bubbles in ionic melt and 2b) ionic melt droplets and gas in metal/matte melt, 3) infiltration and interaction of ionic melt with the refractory of the reactor, 4) Marangoni phenomenon, 5) foaming of the slag.

## 2. Properties of ionic melts that affect the phenomena in the process environment

The main properties of ionic melt that affect its physicochemical interaction with metallic or sulphide melts are:

1) The chemical potentials of species in ionic melts that affect the chemical interaction with metal, matte melts, gas phase and furnace lining: chemical reactions, dissolution and evaporation of species in phases present in the process environment. Activities of species in molten electrolyte have also influence on the electrochemical reduction processes.

2) Viscosity of melt affects the rate and geometry of fluid flows, movement of metal or matte droplets or gas bubbles inside the melt, formation and stability of foam created by gaseous products of chemical reactions, rate of penetration of melt into the refractory lining (pores) as well as the diffusivity of individual species, electrical conductivity and thermal conductivity in the ionic melt.

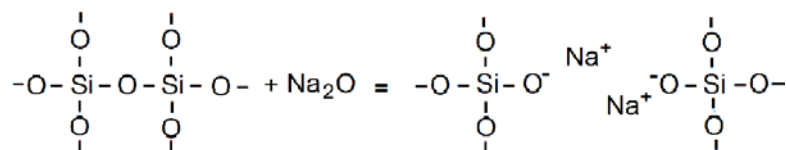
3) Surface properties of the interphases of ionic melt with other phases present in the process environment affect the interaction between the phases; interfacial energy (tension) with metal/matte/gas and furnace lining which affects the formation of metal or sulphide droplets inside the ionic melt and vice versa, foaming in the ionic melt and its penetration into refractory lining of the reactor.

4) Density of the molten phases that affects the separation rate of mixed droplets from molten phases

Acid-base properties of the ionic melt related to its composition and ionic structure affect both the thermodynamic properties, chemical potential of individual species in the melt as well as physical properties, viscosity, surface energies between the molten phases, thermal conductivity, diffusivity of species, electric conductivity. Especially the properties of oxide slags are sensitive to the acidity of the phase due to the radical changes in the atomic/ionic structure of the phase with acid-base relation.

## 2.1 On the structure of ionic melts and its role in physical and thermodynamic properties of the phase

Acid-base relationship/properties of species forming ionic melts control greatly the structure as well as the chemical and physical properties of ionic melts. The compounds forming the ionic melt can be divided in basic, acid and amphoteric species depending to their tendencies to form simple or complex ions and networks. The common slag forming oxides,  $K_2O$ ,  $Na_2O$ ,  $Li_2O$ ,  $BaO$ ,  $SrO$ ,  $CaO$ ,  $MnO$ ,  $FeO$ ,  $ZnO$ ,  $MgO$  and  $BeO$  are usually treated as basic compounds due to high ionic fraction of the bond, basicity decreasing in the showed order.  $Cr_2O_3$ ,  $Fe_2O_3$ ,  $Al_2O_3$  and  $TiO_2$  are treated as amphoteric oxides,  $SiO_2$ ,  $P_2O_5$  and  $V_2O_5$  as acid oxides due to low ionic fraction of their bond [1]. Basic compounds, like sodium oxide tend decompose into simple cations and oxygen anions when they are melting or forming a molten phase with acid compound with network structure. Oxygen anions tend to break the network. This process can be schematically presented by the reaction:



$Na^+$  and  $O^-$  refer to sodium ion and partly bound oxygen by silica network.

Increasing amount of basic oxide, like sodium oxide will break down the network or complex silica anions and when the mixture with strong bases reaches the formal composition  $2CaO \cdot SiO_2$  or  $2Na_2O \cdot SiO_2$ , silicon is mainly present in the form of non-bridging anion  $SiO_2^{4-}$ . When amphoteric oxides are dissolved in a melt of acid compounds, here in molten silica, they react similar way as basic oxides braking the silica network whereas their dissolution in a melt with high basic oxide concentration will lead to formation of complex oxide anions (like  $AlO_4^{5-}$ ) and to some extend they

contribute the network formation by bridging the silica anions in the melt. Molten salt mixtures, like mixtures of chlorides, fluorides, nitrates etc. behave principally the same way, but due to the much weaker acidity of the compounds the networking tendency is generally much weaker. *One has to remember that the effect of the content of the species classified as base or acid to the structure and properties of ionic melt is varying depending on the basicity-acidity relation, charge and the size of the ion in the molten solution.*

The main physicochemical properties of ionic melts that affect its physicochemical interaction with metallic or sulphidic melts, furnace lining and electrolysis are depending on the melt composition, temperature and pressure, and are closely related to the structure and acid-base properties of the phase in molten state. Thermodynamic properties, *entropy, enthalpy and Gibbs energy* of ionic melts are related to the acidity/basicity of the melt, so are also and in more close relation such physical properties as *density, viscosity, surface tension, interfacial tension* between the phases in contact – interfacial properties are naturally depending on the state of both phases as well as the interfacial interaction. Such properties as *density, thermal conductivity, diffusivity and ionic conductivity* of individual species, all having certain role, often of significant importance, in processes in which ionic liquids, slags, fluxes and molten salts are used are also related to the acid – base relation of the melt.

## 2.2 On the thermodynamic properties of molten ionic solutions

The chemical potential of the species  $M_zA_y$  in the solution phase is expressed in the simplest form by

$$\mu_{M_zA_y} = \mu_{M_zA_y}^0 + RT \ln a_{M_zA_y} = \mu_{M_zA_y}^0 + RT \ln x_{M_zA_y} + RT \ln \gamma_{M_zA_y} \quad (1)$$

when the compound in the solution is treated as stoichiometric compound.  $\mu_{M_zA_y}^0$ ,  $a_{M_zA_y}$ ,  $x_{M_zA_y}$  and  $\gamma_{M_zA_y}$  are the standard chemical potential of species  $M_zA_y$  at the reference state, usually as stable stoichiometric compound, activity, mole fraction and activity coefficient of the compound in solution melt, respectively. Standard chemical potential and activity coefficient are functions of temperature and pressure, activity coefficient depending also on solution composition expressing the strength of mutual interaction between the species in the solution phase.

The affinity or driving force of chemical interaction between the species in molten phases is depending on the chemical potentials of species taking part into the interaction process like chemical reaction. When a species  $M$  in a molten metallic phase is moving from the metallic phase to the ionic solution in an oxidized form i.e through an oxidizing reaction



the driving force (at constant temperature and pressure) is related to the chemical potential of species in the reacting phases

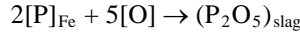
$$\begin{aligned} \Delta_R G_2 &= \mu_{(M_zO_y)} - z * \mu_{[M]} - y * \mu_{[O]} \\ &= \mu_{(M_zO_y)}^0 - z * \mu_{[M]}^0 - y * \mu_{[O]}^0 + RT \ln a_{(M_zO_y)} + RT \ln a_{(M_zO_y)} - z * RT \ln a_{[M]} - y * RT \ln a_{[O]} \\ &= \Delta_R G_2^0 + RT \ln \left( \frac{\gamma_{(M_zO_y)}}{\gamma_{[M]}^z * \gamma_{[O]}^y} \right) + \left( \frac{x_{(M_zO_y)}}{x_{[M]}^z * x_{[O]}^y} \right) \end{aligned} \quad (3)$$

where  $\Delta_R G_2$  and  $\Delta_R G_2^o = \mu_{(M_z O_y)}^o - z * \mu_{[M]}^o - y * \mu_{[O]}^o$  is are the partial Gibbs reaction energy and the standard Gibbs energy of reaction (1). Gibbs energy of mixing, i.e. the change of Gibbs energy when two or more components are mixing and forming a homogeneous phase is related to structure of the phase but especially to the strength of interaction between the individual species in solution.

The equations (1), (2) and (3) are valid but formal. As the compound (here  $M_z O_y$ ) is dissolving in an ionic solution in the ionic form, “decomposing” into cations and anions which can form more or less stable complex ions with the other ionic species present in the solution, the mole fraction is quite formal expression of the concentration. There are several thermodynamic models describing the thermodynamic properties of ionic melts and individual components ranging from the expression of the concentration of dissolved species in the form of stoichiometric compounds to complex expression of concentration based on ionic structure and interaction between the various ions in the solution. The general problem in modeling of thermodynamic properties of ionic melts and its individual constituents is not only the dissipation of compounds into individual ions but also possible change of oxidation state and formation of complex ions that is strongly dependent on the acid-base relation of the solution. Anyway, the activity of a species dissolved in an ionic solution, related to the thermodynamic stability of pure species (here  $M_z O_y$ ) describes its true reactivity in the solution (especially at high temperatures where the rate of chemical reactions is high). The value of activity coefficient of species in the solution is depending on strength of interaction of ionic species in the solution but also on the choice of expression for the concentration of the dissolved species. Anyway the comparison of activity coefficients of individual species is related to the strength of their interaction with the other species in the solution phase and their relative reactivity in the solution. The role of acid-base relation of the ionic solution in determining the activity coefficient in binary oxide solution is demonstrated in Figures 2. and 3.

Silica is known as one of the most acidic oxides and tends to form the more stable solution with high Gibbs mixing energy the more basic are the other solution components. The more negative is the Gibbs mixing energy in the solution formation the more stable is the solution and the more inactive are the components towards interaction, with other phases dissolution in them or evaporation to gas phase or chemical reactions with species in other phases. Figure 2. shows activity coefficients of several oxides in binary silica solutions. The lower is the activity of component in the solution the less reactive is the component in the solution relative to external phases like metal melts or gas atmosphere. Activity coefficient is the factor expressing strength of the internal interaction between the species in the solution. The activity coefficients of potassium and sodium oxides are extremely low whereas for nickel and iron oxide the values are rather high demonstrating much weaker basicity and weak interaction with silica in the solution. The reactivity of the solution species are naturally not dependent only of the activity of species in the solution phases like silica slags but also by the chemical stability of pure compounds. However, it is a general tendency that the “more noble” are the oxide forming metals the less stable are the solutions with strong acids thermodynamically. This is simply related to the properties of cations of these metals in ionic solutions. As can be seen by comparing the activity coefficients of ferrous and manganese oxides in binary solutions with silica and ternary solutions with silica and lime oxide (Fig.3) an increase in basicity increases the activity coefficients of both oxides already at low concentrations.

An increase in slag basicity enhances the removal of impurities forming acid oxides and vice versa. The slagging of phosphorus from blast furnace or BOS slag is directly related to the basicity of slag. Figure 4. shows the effect of basicity in various iron and steel melting type slags to activity coefficient of phosphorus oxide. Deacreasing acitivity coefficient decreases the activity and chemical potential of phosphorus and enhance the solubility of phosphorus oxides in the slag



the lower is the activity coefficient of phosphorus pentoxide the higher is its equilibrium concentration in slag, the concentration which the solubility tends to reach in the oxidation reaction;  $x_{[\text{P}_2\text{O}_5]} = \frac{a_{\text{P}}^2 \cdot a_{[\text{O}]}^5}{\gamma_{(\text{P}_2\text{O}_5)}}$ .

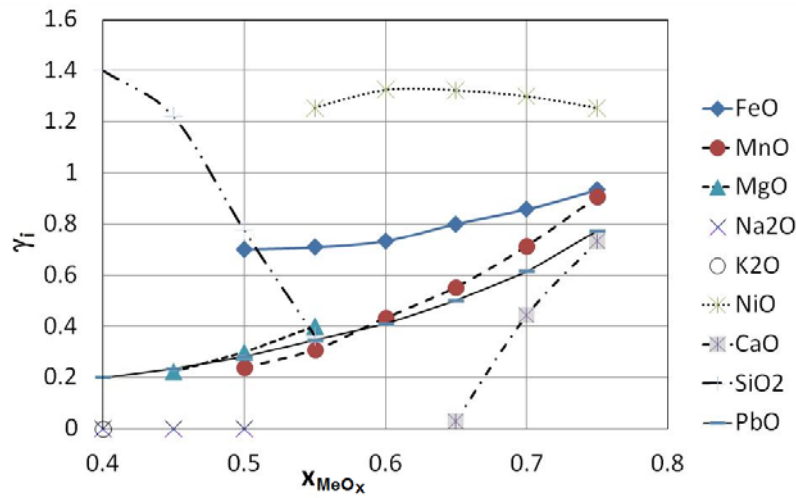


Fig. 2 Qualitative comparison of excess stability of some oxides in binary molten solution with silica ( $\text{Me}_x\text{O}-\text{SiO}_2$ ) through activity coefficient. Temperature for FeO-, MnO- and MgO- binaries [2] is 1873K, for  $\text{K}_2\text{O}$  [2] and  $\text{Na}_2\text{O}$  [3] binaries 1773K. Temperature for NiO- and CaO- $\text{SiO}_2$  -binaries from source [1] was not clearly expressed. Values for  $\text{SiO}_2$ -values are for  $\text{SiO}_2$ -CaO binary at 1873K [4]. PbO- $\text{SiO}_2$ -binary at 1273K [5]

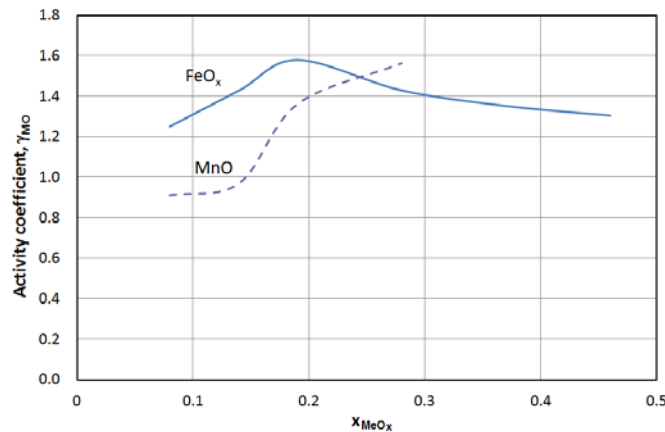
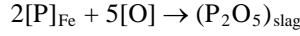


Fig. 3 Activity coefficients of  $\text{FeO}_x$  (1550°C) and MnO (1550°C) in ternary MO-CaO- $\text{SiO}_2$  solutions at  $x_{\text{CaO}}/x_{\text{SiO}_2} = 1$  [2]

An increase in slag basicity enhances the removal of impurities forming acid oxides and vice versa. The slagging of phosphorus from blast furnace or BOS slag is directly related to the basicity of slag. Figure 4. shows the effect of basicity in various iron and steel melting type slags to activity coefficient of phosphorus oxide. Decreasing activity coefficient decreases the activity and chemical potential of phosphorus and enhance the solubility of phosphorus oxides in the slag by reaction



The lower is the activity coefficient of phosphorus pentoxide the higher is its equilibrium concentration in slag, the concentration which the solubility tends to reach in the oxidation reaction -  $x_{[\text{P}_2\text{O}_5]} = \frac{a_{\text{P}}^2 a_{[\text{O}]}^5}{\gamma_{(\text{P}_2\text{O}_5)}}$ .

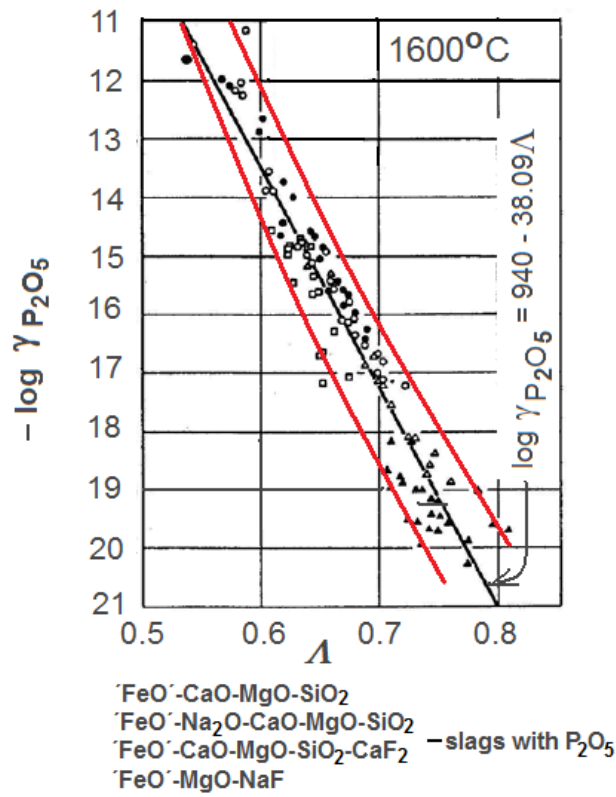


Fig. 4 Activity coefficient of phosphorus pentoxide as a function of (optical) basicity of slags. Redrawn from [6].

An increase of slag basicity promotes also the solubility of sulphur in slags as can be seen from the Figure 5. The explanation for increasing sulphur solubility with increase in **basic** oxide contents in slag is a complex question. The behavior is related obviously to interaction between sulphur or sulphate anions with basic cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ . Although sulphur is not dissolved in slag as formal oxide or sulphate, the stability (Gibbs energy of formation) of pure compounds will tell qualitatively the interaction tendencies with those ions in the solution. The values in Table 1. are informing that sulphides and sulphates (per one mole of sulphur/sulphur trioxide) with basic oxide formers are more

stable than silicon sulphide. Silicon is obviously not able to form stable sulphates. The stability of sulphide and sulphate of amphoteric oxide former aluminium is lower than those with elements forming strong basic oxides.

Table 1. Stability of sulfides and sulphates of some “basic” cations, silica and aluminium (calculated by HSC 7)

	CaO	MgS	Na <sub>2</sub> S	1/2SiS <sub>2</sub>	1/3Al <sub>2</sub> S <sub>3</sub>
T/°C	$\Delta_f G$	$\Delta_f G$	$\Delta_f G$	$\Delta_f G$	$\Delta_f G$
	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol
1400	-455	-292	-284	-93	-177
1600	-433	-282	-278	-89	-173
	CaSO <sub>4</sub>	MgSO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	Si*	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
	$\Delta_f G$	$\Delta_f G$	$\Delta_f G$	$\Delta_f G$	$\Delta_f G$
	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol
1400	-796	-611	-755		-503
1600	-723	-536	-688		-428

\* stability data for Si-sulphates was not found

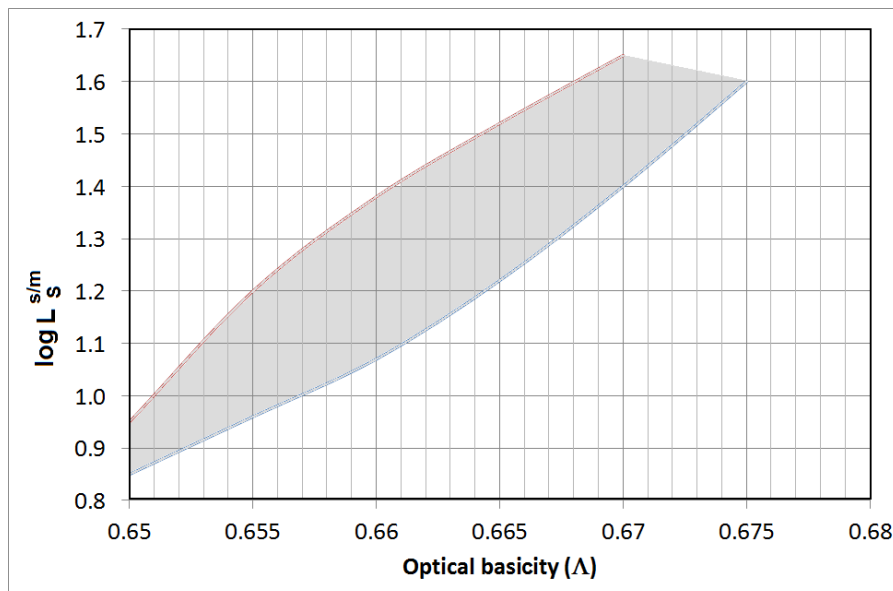


Fig. 5 The effect of slag basicity on the slag - hot metal distribution of sulphur in blast furnace (BF No. 1 at SSAB Luleå, Sweden). During six days period of smelting temperature varied between 1428-1490°C, CaO, MgO, K<sub>2</sub>O and MnO concentrations were taken into account in optical basicity calculations [7]

## 2.2 On the physical properties of molten ionic solutions and their role in interaction in high temperature processes

The chemical as well as electrochemical processes are a combination of driving forces of chemical or electrochemical reactions and rate phenomena, macroscopic flow and chemical/electrochemical diffusion. Physical properties of the reacting phases like viscosity, interfacial tension/energy and density affects such phenomena as mutual mixing of molten phases and formation of suspensions or foams and their stability as well as fluid flow inside the phases. Viscosity and interfacial energies of molten ionic solutions affect the penetration of slag into the refractory lining of the



reactor. Gradient in surface tension of slag and interfacial tension between the slag and metal or matte phase brings about so called Marangoni phenomenon, strong surface flow that can speed up the dissolution of refractory in the slag.

## Viscosity

The properties of slags that play an important role in smelting and refining stages of metals production are as mentioned earlier, viscosity, interfacial energy between the reacting phases as well as with refractory lining. Viscosity of the slag effects the fluid flows in the slag, diffusivity of species in the slag phase, mixing of slag and metallic or matte phase as well as foaming phenomena in slag.

Viscosity of slags and other ionic melts are strongly dependent on the acid-base relation in the ionic melt. Figure 6 shows the change of viscosity of molten ternary mixture of basic ( $\text{Na}_2\text{O}$ ), acid ( $\text{SiO}_2$ ) and amphoteric oxide ( $\text{Al}_2\text{O}_3$ ) with the change of composition and relation of various types of components. Information of the Figure 6 is that viscosity of the binary  $\text{Na}_2\text{O}$ - $\text{SiO}_2$  and in  $\text{Na}_2\text{O}$ - $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  -ternary solutions is strongly increasing with acidity i.e. increasing of silica concentration. Substitution of sodium oxide with alumina increases viscosity until the certain degree of substitution has been reached and behaviour of amphoteric alumina in the solution changes from acid to basic. The presence of solid precipitates in slag increases strongly slag viscosity as presented schematically in Figure 8.

In Figure 8 viscosities of various metallurgical slags are presented as a function of temperature. Viscosity of molten oxide mixtures is strongly dependent on acid base relation of slag and increasing with increasing acidity. Viscosities are greatly dependent on the acidity of the slags especially on silica content with relation to various basic oxides like lime, magnesia and other alkali and earth alkali oxides as well as fluorides (especially in mold fluxes).

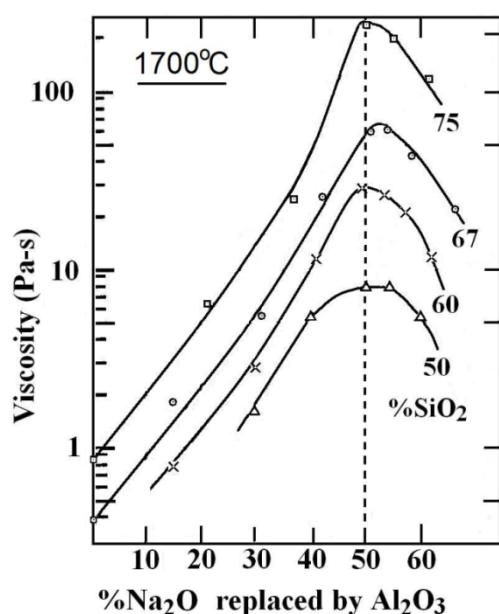


Figure 6 Change of viscosity of  $\text{Na}_2\text{O}$ - $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  ternary when sodium oxide is replaced by alumina at various concentrations of silica; redrawn from [8]

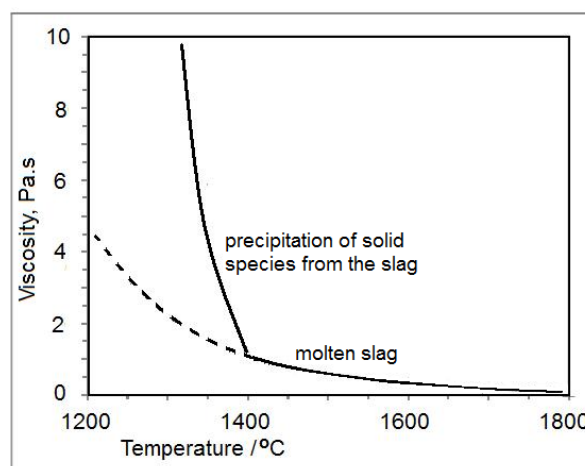


Fig. 7 Schematic presentation of effect of solid precipitates in blast furnace slag to the viscosity; redrawn from [9]

Viscosities in molten salts like mixtures of chlorides and nitrates are in general much lower than those of metallurgical slags being generally under 0.01 Pa.s in homogenous melts (the liquidus temperature for molten salts is usually much lower than that of slags). This is due to the properties of molten salt mixtures used in molten salt electrolysis like chlorides or nitrates in which the tendency to formation of network i.e. acidity of components is much lower than in slags containing strong acids. Also in oxide slags without high concentration of acidic constituents like calcium ferrite slags the viscosities are lower. The viscosity of calcium ferrite slags within temperature range 1250 – 1600°C vary on a level of 0.07 to 0.01 Pa.s [10,11].

Table 2. Composition ranges of some common metallurgical slags

SLAGS	BF	BOS	EAF (C-steel)	EAF (alloy/SS)	ladle	Cu-smelting
CaO	30 – 49	30 - 55	35-60	39-45	30-60	1-12
SiO <sub>2</sub>	27 - 47	8 - 20	9-20	24-32	2-35	25-40
MgO	3 – 18	5-15	5-15	8-15	1-10	1-11
Al <sub>2</sub> O <sub>3</sub>	5 – 17	1-6	2-9	3-7.5	3-35	2-10
FeO	0.1 – 1.6	10-35	15-30	1-6	0.1-15	
Fe <sub>2</sub> O <sub>3</sub>						34-43
MnO	0.1 – 6	2-8	3-8	0.4-2	0-5	7-10
K <sub>2</sub> O	0.2 – 1.9					
Na <sub>2</sub> O	0.1 – 0.6					
TiO <sub>2</sub>	0.4 – 2.5	0.4-2				
P <sub>2</sub> O <sub>5</sub>		0.17				
S	0.2-2.5	0.05-0.15	0.08-0.2	0.1-0.3	0.1-1	0.4-2.7
P		0.2-0.25	0.01-0.25	0.01-0.07	0.1-0.4	
Cr		0.1-0.5	0.1-1	0.1-20	0-0.5	
Cu						0.3-5
*"Basicity"	0.5-2.1	1.3-6.7	1.4-6.8	1.2-2.2	0.4-14	0.04-0.9

\*formal basicity -  $(\text{CaO}+\text{MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3)$ ; the true basicity is depending also on the concentration of "non-acid" metal oxides like FeO and MnO and is expressed much more reliably by optical basicity

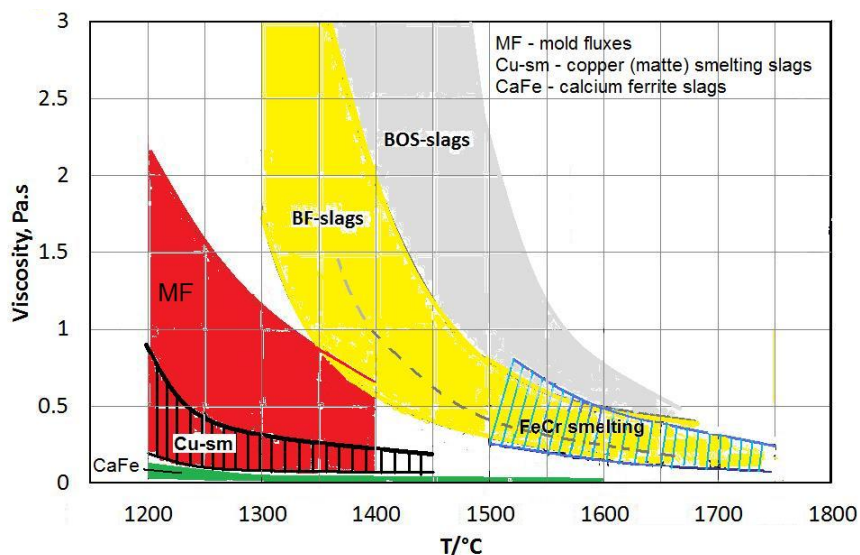


Fig. 7 Qualitative comparison of viscosities of various types of silica containing industrial slags and silica free calcium ferrite slags: blast furnace, BOS, mold fluxes for continuous casting of steel and copper matte smelting slags; calcium ferrite slags could be applied in copper or nickel matte converting and direct blister smelting from low silica concentrates. Viscosity data from sources [9,12,13,14,15,16,17,18]

## Interfacial energy

The interfacial properties of slag, surface tension and interfacial energy between slag and molten metallic or matte phase as well as with furnace refractory lining affect the intensity of interaction between the phases, as well as mutual mixing of molten phases in the form of small droplets or formation of foam. Interfacial energies are depending on the presence of surface active species in the molten phases in contact and on the chemical interaction between the phases. In Figure 9 surface tension of some binary silicates are presented as a function of silica content (**acidity**) and in Figure 10 surface tension of iron silicate slag and its interfacial tension with copper matte are presented as a function of Fe/SiO<sub>2</sub> ratio. The surface tensions of molten salt mixtures, like chlorides and nitrates at temperatures close to the liquidus temperatures are generally on a level of 50 to 200 mN/m.

Strong chemical interaction between the molten phases decreases the interfacial energy as can be seen from the Figure 11. As the chemical interaction between molten metal/matte and slag as well as with gas atmosphere is obviously very strong in oxidizing or reducing pyrometallurgical processes the interfacial energies of phase boundaries including the droplets suspended in the contacting melts or gas bubbles inside the molten phases are obviously far from the values measured at equilibrium conditions. Marangoni phenomena, intensive fluid flow at interfaces caused by gradient of interface energy is known to intensify the dissolution of refractor materials in slag and the same phenomena would also affect the formation of metal suspensions in slag and vice versa and intensify the chemical interaction between the droplets and their sudden “mother” phase.

### 3. Two examples on the role of slag and its properties in metallurgical processes

#### 3.1 Alternative for traditional silicate slag in sulphide smelting – calcium ferrite

The composition of slag, especially a radical change in slag acidity, affects the interaction of dissolving species with slag constituents and their activity coefficient. The removal of sulphur from hot metal or molten steel increases with increasing basicity of slag by lime addition. Iron silicate slag has been the traditional and self-evident choice in sulphide smelting processes. In primary smelting of sulphide concentrates, like copper or nickel matte smelting there is practically no alternatives for iron silicate slags due to silica content of concentrates. Also in matte converting stage silica has been the traditional choice for slag former due to its ability to form relatively low melting iron silicate slag even at highly oxidizing conditions. Iron silicate slag has however some disadvantages like its low “affinity” to some harmful impurities like arsenic and antimony. The choice of silica free slags for removal of impurities from copper and nickel mattes in matte converting stage or copper refining can improve radically the removal of certain impurities like arsenic or antimony. Calcium ferrite slags are very efficient in this respect. In Figure 12 the stability range of molten slag and oxygen potential lines are compared for calcium ferrite and iron silicate slags. The liquid range of calcium ferrite slag is extending to very high oxygen potentials.

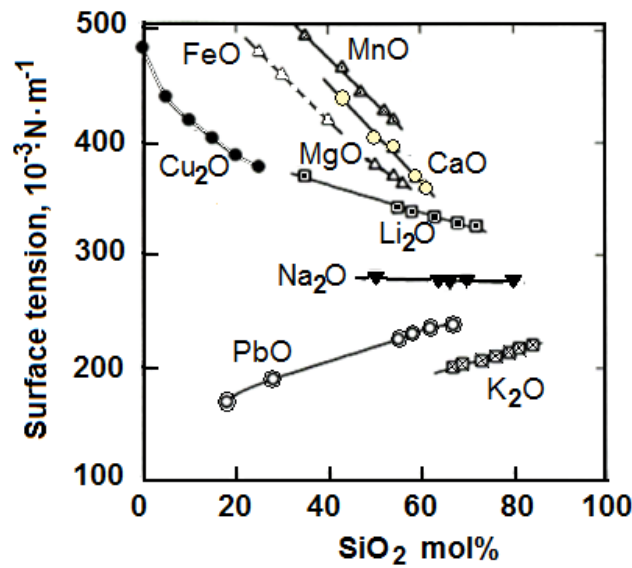


Fig. 9 Surface tension of  $\text{Me}_x\text{O} - \text{SiO}_2$  binaries at 1573K. Redrawn from [16]

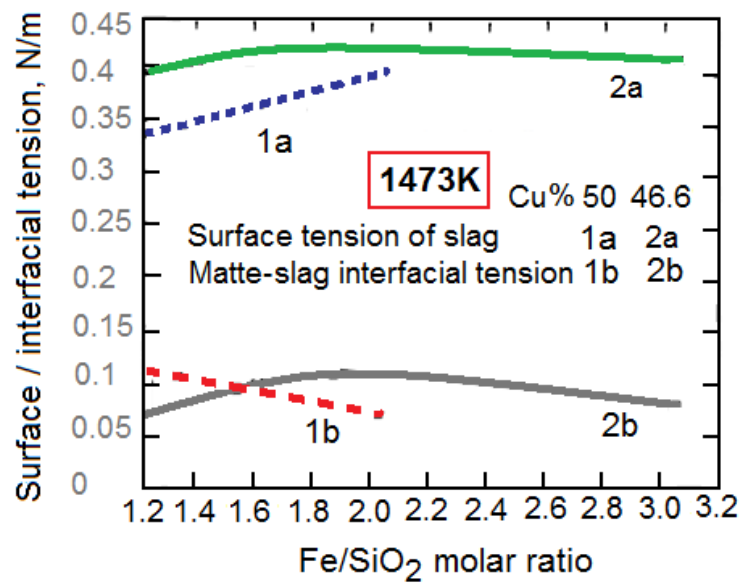


Fig. 10 Surface tension of fayalite slag and slag-copper matte interfacial tension at two different matte grades; Redrawn from [16]

As can be seen from Figure 13, the sulphur (sulphide/sulphate) solubility in the calcium ferrite melt is much higher than in the iron silicate melt. Solubility is decreasing with increasing matte grade / increasing oxygen potential. Solubility of certain impurities, especially As and Sb, are also much higher in calcium ferrite slags than in iron silicate slags as can be seen from the results of laboratory scale experiments and industrial scale tests presented in the Figure 14. Table 3 is showing distribution of As, Sb, Pb and Bi between matte and slag. Similar distribution behavior between copper matte - slag [19, 20], copper - slag [21] as well as between nickel matte - slag [15,22] has also been reported in

literature. The much more efficient slagging of As and Sb in calcium ferrite slags is caused by stronger interaction of cations of these elements with anions in calcium ferrite slag (including sulphur species?).

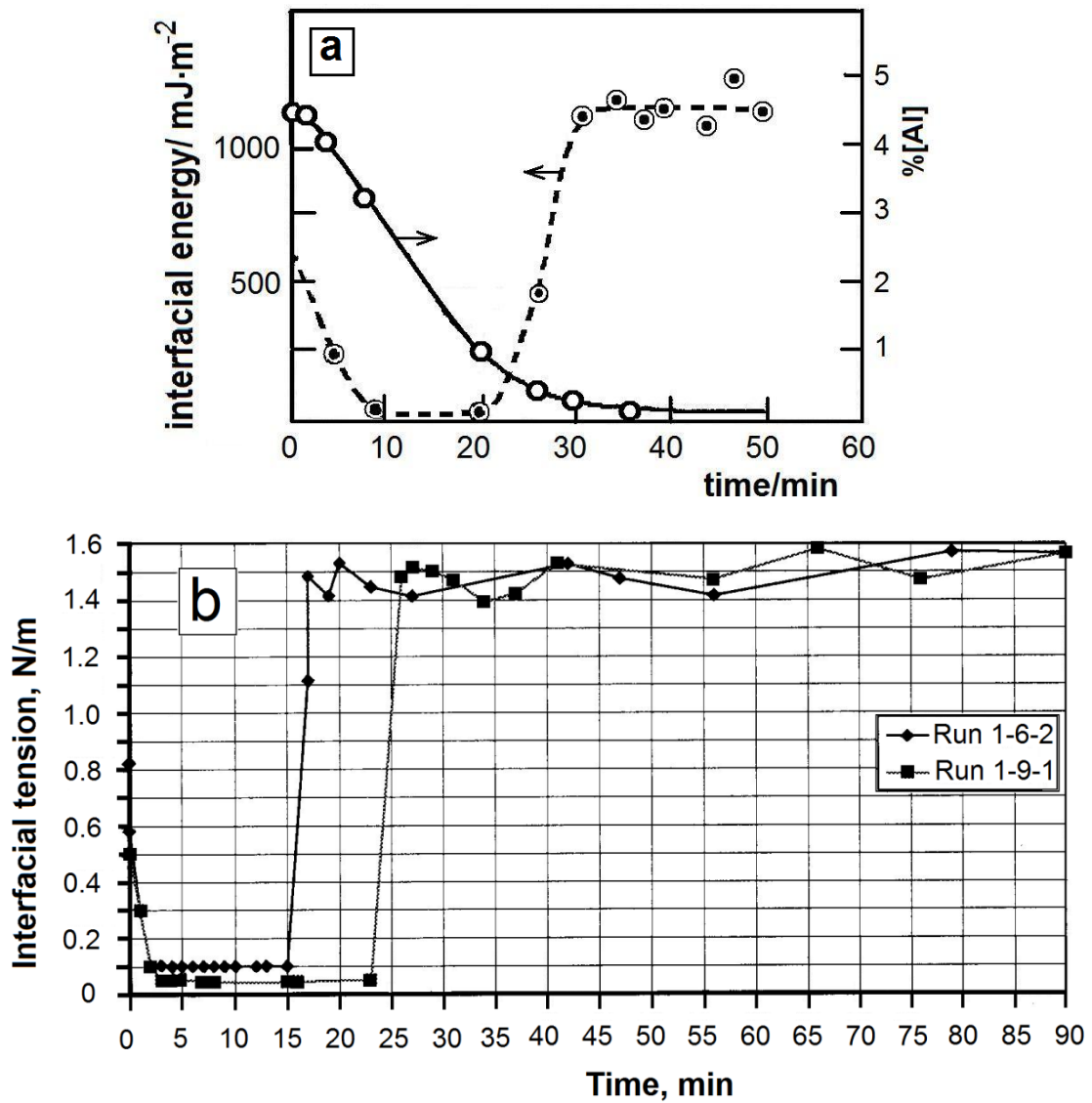


Fig. 11 The effect of oxidation of aluminium and its dissolution as alumina in molten slag to the slag – iron melt interfacial energy. 11a redrawn from [23], 11b from [24] (The unit  $\text{J}/\text{m}^2$  of interfacial energy corresponds to the interfacial tension unit  $\text{N}/\text{m}$ )

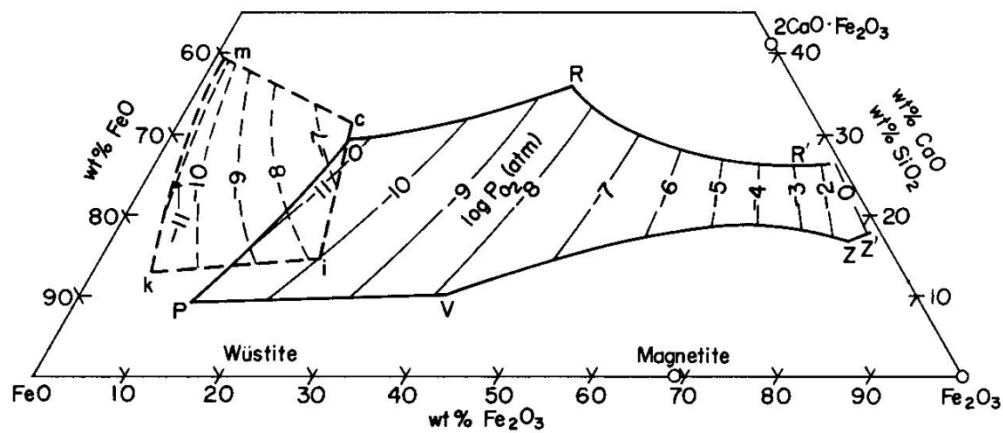


Fig. 12 Comparison of liquidus isotherms in ternary FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (dashed lines) and FeO-Fe<sub>2</sub>O<sub>3</sub>-CaO (solid lines) systems at 1300°C.[25] The melt range of calcium ferrite system extends to much higher oxygen potentials than in the iron silicate system.

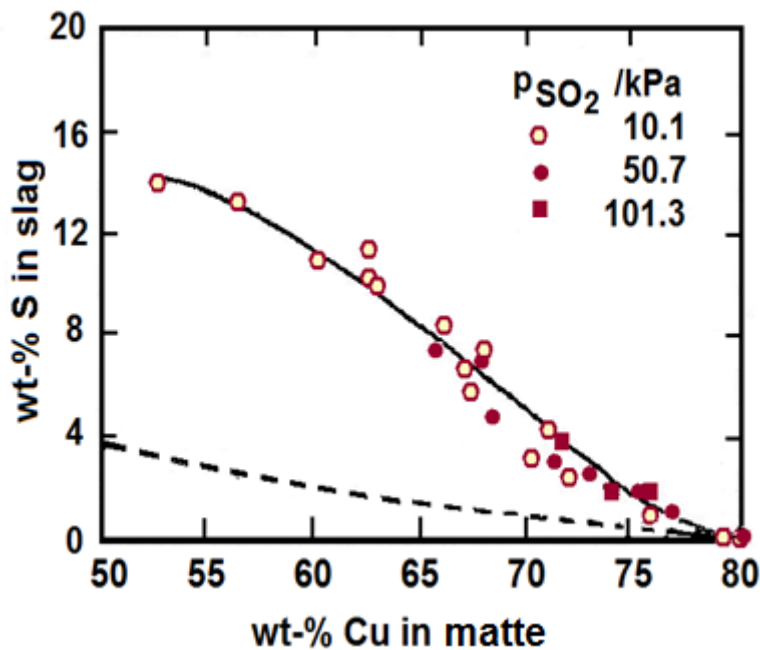


Fig. 13 Equilibrium solubility of sulphur from copper matte to calcium ferrite (at 1523K) and calcium silicate slag (at 1573K) as a function of matte grade under various sulphur dioxide pressures in laboratory experiments. Solid line – calcium ferrite slag, dashed line iron silicate slag at silica saturation (under equal sulphur dioxide pressure as in calcium ferrite experiments) [26].

Thermodynamically the higher distribution coefficient means that the formal activity coefficients of oxides of these elements are much lower in calcium ferrite slag compared with iron silicate slag. The decrease of As and Sb distribution coefficient when copper saturation is approached (at about 79-80% of copper in matte) can be explained by lower activity coefficient of these elements in molten copper precipitating within matte and/or by effect of decreasing sulphur

content of slag. In industrial tests the precipitation of copper starts at lower copper concentration corresponding to non-equilibrium conditions caused by continuous oxidation reactions.

The substitution of iron silicate slags with calcium ferrite slags in sulphide smelting and converting is problematic if the feed contains silica or silicates. The solubility of silica in calcium ferrite slag is very limited in matte smelting or converting temperatures and silica tends to precipitate as calcium silicates with high melting temperatures ( $3\text{CaO}\cdot\text{SiO}_2$  and  $2\text{CaO}\cdot\text{SiO}_2$ ). One problem related to the substitution of traditional iron silicate slag with calcium ferrite slag is its lower viscosity that increases its aggressiveness toward the furnace refractories. One factor that can also boost the penetration of slag into the refractory pores is the (equilibrium) surface tension of slag that is reported to be higher in calcium ferrite slags. This problem could be resolved by choosing refractory materials that are less sensitive to calcium ferrite slag attack. The substitution of silicate slag with other low silica ionic melts, like Na-Ca carbonate fluxes has been studied and realized in the matte converting and copper refining stages.

Table 3. Weight-% distribution coefficients of As, Sb, Pb and Bi between copper matte and iron silicate / calcium ferrite slags [27]

Matte grade	$L^{s/m}_{\text{As}}$		$L^{s/m}_{\text{Sb}}$		$L^{s/m}_{\text{Pb}}$		$L^{s/m}_{\text{Bi}}$	
wt-% Cu	FeSi	CaFe	FeSi	CaFe	FeSi	CaFe	FeSi	CaFe
60	0.8	8	1	5	0.2	0.05	0.2	0.2
75	0.5	17	0.8	11	2.8	0.2	0-3	0-3

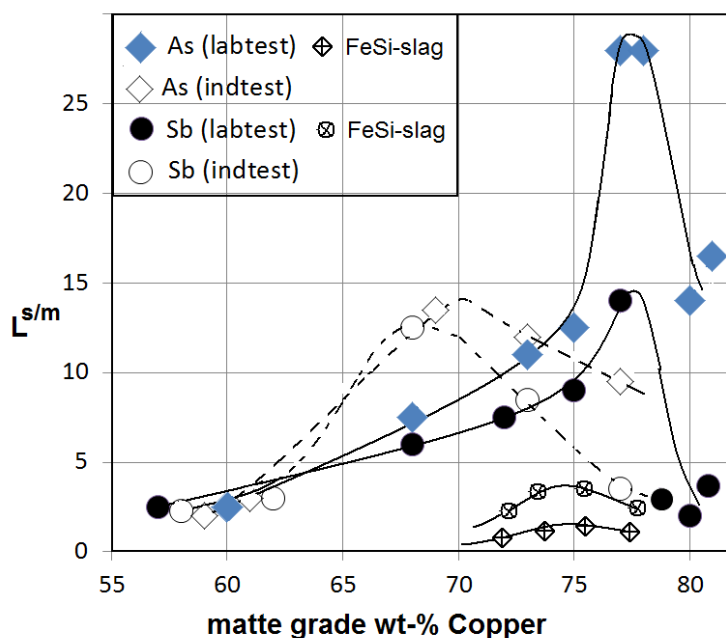


Figure 14. Slag-matte distribution ratio of As and Sb for calcium ferrite slag in laboratory and industrial tests compared with laboratory tests for iron silicate slag [28]

### 3.2 Comments on the role and behavior of slag in BOS

The role of slag in oxygen converting of hot metal is to offer molten environment for “impurities” oxidizing during the decarburizing of iron melt - Si, Mn, P, S, (Al, Ti, V). The composition of BOS slags during the blow depends on the fluxing and blowing practice. If the blow is started with “high lance”, iron will preferably oxidize, when thermodynamically preferable impurity components are oxidized and due to weak mixing and slow fluid flow mass transfer in the iron bath their concentrations and activities in the surface layers of iron bath are low. Oxidation of iron results in low melting calcium-iron oxide slag with relatively low liquidus temperature. The same result is obtained by adding iron oxide concentrate or BOF dust before the blow which was the blowing practice at Koverhar steelworks until the late 90<sup>ies</sup>. Figure 15 shows the forming of slag in blows of top-blowing converter at Koverhar steel works in 70<sup>ies</sup>. Foam height as a function of blowing time is presented as an average for a set of test runs at Koverhar steel works in Figure 19 and for one specified blow in Figure 15b. Slag foaming was assumed and observed to have a positive effect to the blow at Koverhar plant. The portion of iron droplets in slag from the total mass of iron was estimated by the droplet density in slag from taken samples and total amount of iron in the blow at the same blowing time, Figure 17. Also higher portions of recirculating iron in slag during BOF blow have been reported in literature [29,30].

Figure 16 is showing qualitative change of amount of iron oxide in the slag - the reducing behavior of iron oxide content in slag was clear in the several blows analyzed, but quantitative amount of iron oxide(s) in slag is difficult to determine exactly. Iron oxide in slag acts obviously oxidizer for the various impurities in iron droplets circulating in the slag. In Figure 17 the carbon content in iron droplets circulating in the slag is compared with the carbon content in iron bath (analyzed from samples taken from the bath). It is very probable that on the “hot spot” at iron bath surface everything, including iron, is oxidized. The formed oxide layer is adhering the droplets thrown by the impinging oxygen jet acting as oxidizer of minor components in droplets. The rest of formed oxide is dissolved in the slag acting further as oxidizer for minor constituents in iron droplets, (silicon, carbon, manganese and other species thermodynamically “willing” to be oxidized) circulating in the slag. It also obvious that some oxygen is dissolved in the iron melt at the surface and when this high oxygen iron from the surface of the bath is circulating inside the bath and mixing with iron with higher impurity levels, some oxidation proceeds also inside the iron bath.

Controlled foaming, controlled in the respect of optimal height, has obviously a positive effect for the role of slag as oxidizer and as collector of the oxidized products. Slag foam is also evening the temperature gradient in the converter and decreasing heat losses. There seems, however, not to be a clear, common acceptance in the literature what is the optimal blowing practice, optimal composition of slag and its optimal physical properties like viscosity or surface properties<sup>2</sup> of slag formed in converting of carbon steels with various carbon contents or low and high alloyed steels.

Converter processes are a combination of complex phenomena, chemical reactions, dissolution/precipitation of solids, mass transfer by fluid flow and diffusion as well as change of properties in reaction environment(s) like temperature, slag composition, formation and depression of the emulsion and foam within the progress of the process.

---

<sup>2</sup> As mentioned earlier, the surface properties like surface energy or interfacial energy between the slag and circulating iron droplets might be something else than the under equilibrium conditions measured values



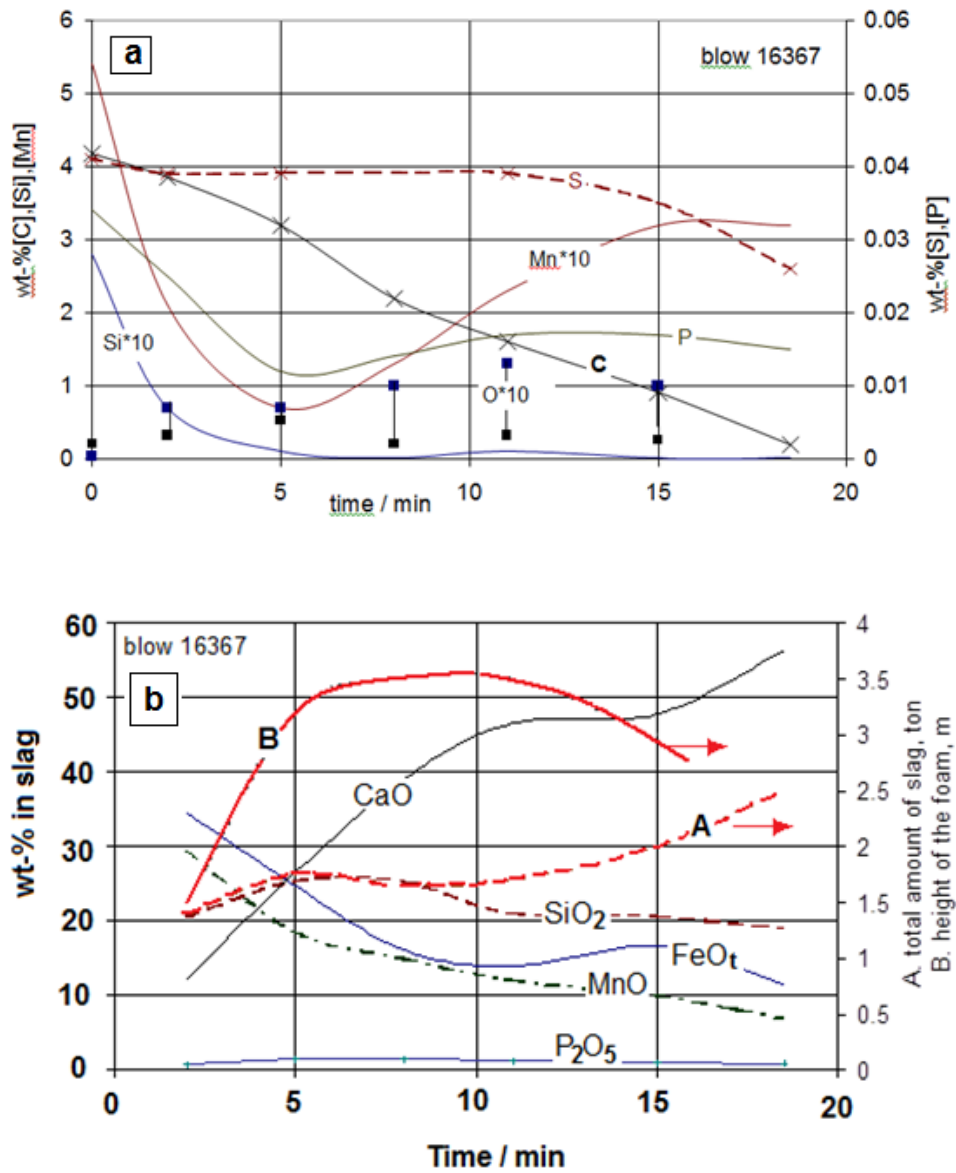


Fig. 15a and 15b Evolution of iron bath a and slag b composition in a blow in 55 ton LD- converter at Koverhar steelworks[31,32]. The temperature of the steel with 0.22% C in the end of the blow was reported to be close to 1700°C. Charge: 48 ton of hot metal, 5 ton scrap and 1 ton converter dust with high iron oxide content.

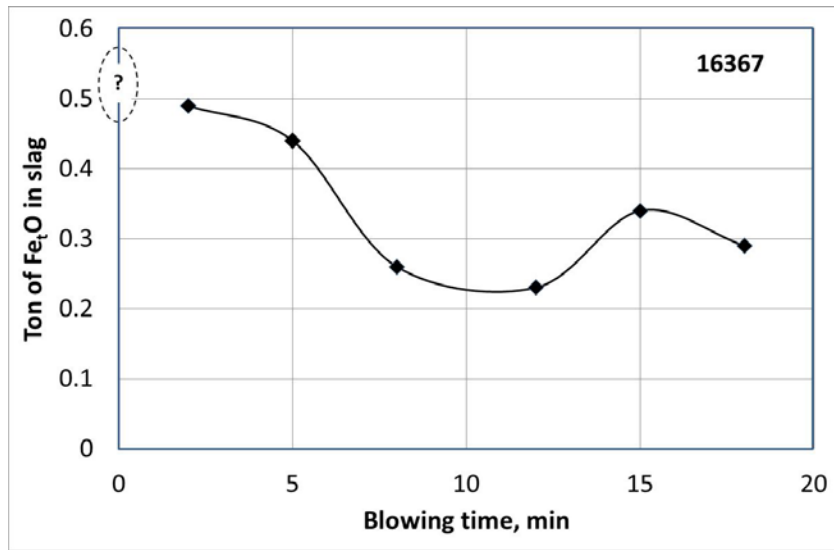


Fig. 16 Change of iron oxide (fayalite) content in slag as function of blow time. The initial amount of iron oxides in the dust added to the converter (1 ton) was not clear as dust contains 2- and 3- valent iron oxides as well metallic iron. At 12 min the lance height was raised that could have been causing the increase in iron oxide content in slag [32].

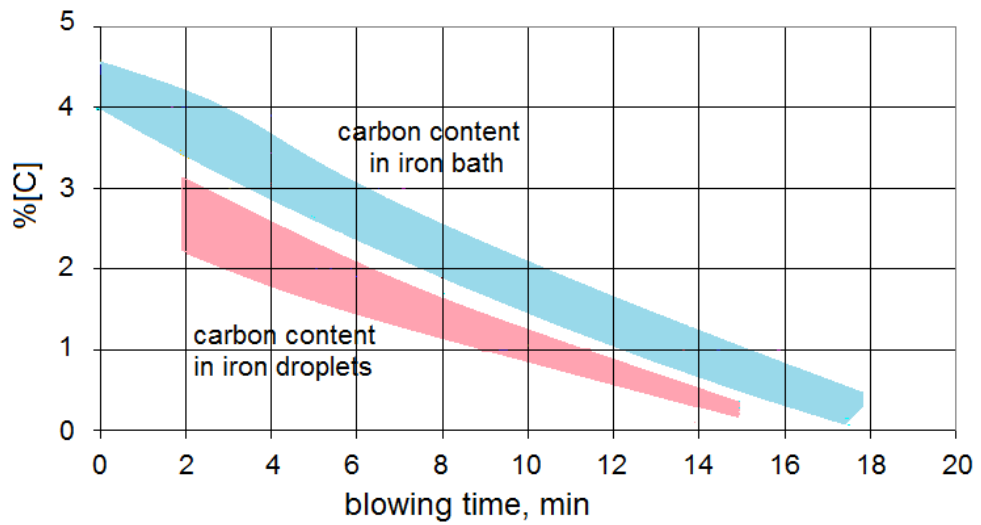


Fig. 17 Carbon content in droplets recycling in slag compared with average carbon content in iron bath in five test runs at Koverhar steelworks 1975 [33]

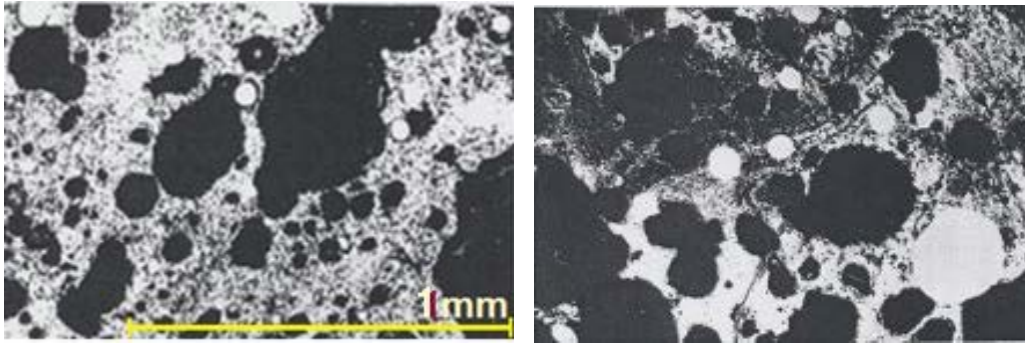


Fig. 18 Foamy slag emulsion with large gas bubbles and iron droplets after 2 min and 5 min from the start of the blow [33]

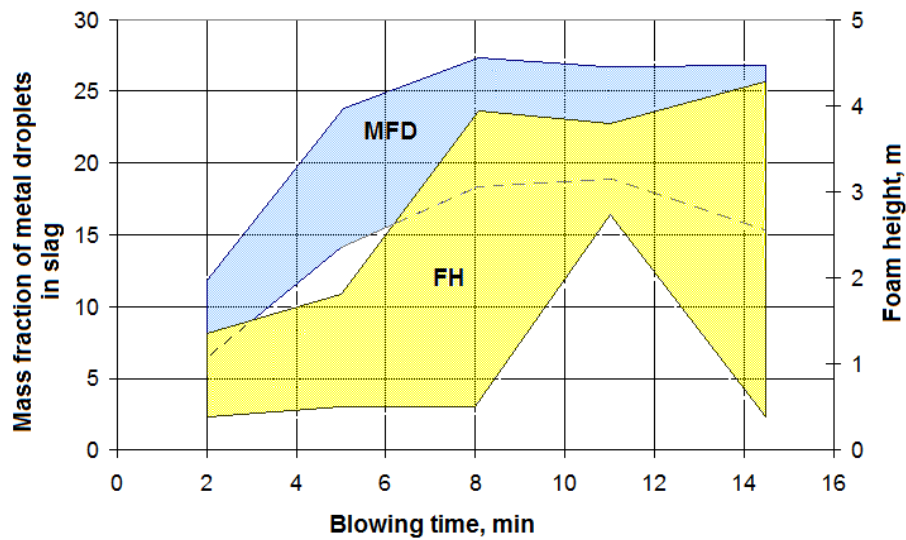


Fig. 19 Mass fraction of iron droplets suspended in slag and the foam height in five test runs at Koverhar steelworks 1975 [33]). The distance from the iron bath surface to converter mouth was to 5 m.

#### 4. Concluding comments

The role of ionic melts, slags, fluxes and molten electrolytes is very important in various stages in metals processing ranging from primary smelting of raw materials to the final pyrometallurgical stages of metals refining and casting. The optimal properties of the ionic melts and optimal processing conditions in various stages is a very complex question that is depending not only on the optimal properties with relation to the process itself, but also on the aggressiveness of the melt to the furnace lining and the recyclability of the melts, especially slags from various metallurgical smelting, converting and refining processes.

If we look at the two examples presented here, 1) substitution of traditional iron silicate slag in matte converting or direct blister making by calcium ferrite slag (or sodium - calcium carbonate melt that is also an alternative for effective impurity removal) and 2) role of slag and its relation to blowing practice in oxygen converter process, can we say that all available knowledge is collected, analyzed and used for process development related to the properties of ionic melts playing important role in these processes?

There is very large amount of knowledge available in literature concerning the thermodynamic and physical properties of slags and fluxes, their role in the various metallurgical processes and various processing stages, ranging from specified experimental data and analysis of role of ionic melts in individual process steps to comprehensive models for processes including the role of ionic melts, slags and fluxes. Would it be useful to establish a wide international project for collection and critical analysis on all available knowledge concerning the properties of ionic melts and their role in various metallurgical processes, including the optimal choice of furnace lining?

## References

- [1] L. Coududier, D.W. Hopkins, I. Wilkomirsky, *Fundamentals of Metallurgical Processes*, 2<sup>nd</sup> Edition, Pergamon Press, 1985. p. 216.
- [2] *Slag Atlas*, 2<sup>nd</sup> Edition. Verlag Stahleisen, Düsseldorf 1995, p. 230
- [3] G.Lambotte, P.Chartrand, Thermodynamic optimization of the (Na<sub>2</sub>O-SiO<sub>2</sub>-NaF-SiF<sub>4</sub>) reciprocal system using Modified Quasichemical Model in the Quadruplet Approximation. *J. Chem. Thermodynamics* 43 (2011), p.1678
- [4] L. Hongjie, A.E. Morris, D.G.C. Robertson, Thermodynamic Model for MnO-Containing Slags and Gas-Slag-Metal Equilibrium in Ferromanganese Smelting. *Metallurgical and Materials Transactions B*, vol. 29B, 1998, p. 1181
- [5] D. Gaskell, *Introduction to the Thermodynamics of Materials*. *Taylor and Francis Books*, 2003, p. 549
- [6] M. Svinerton, The influence of slag evolution on BOF dephosphorisation. University of Wollongong Thesis Collection 2005
- [7] B. Björkman, Properties of blast furnace slag with high MgO content: Evaluation of sulphur distribution and alkali yield to slag from plant data. *Proceedings of the Fifth Japan-Nordic Countries Joint Symposium on Science and Technology of Process Metallurgy*. 1992, Helsinki Finland, p. 23
- [8] D.R. Gaskell, Structural Aspects of Slags. *Proceedings of the 5th International Conference on Molten Slags, Fluxes and Salts '97*, Sydney Australia 1997. p. 11
- [9] J. Muller, M. Erwee, Blast furnace control using slag viscosities and liquidus temperatures with phase equilibria calculations. *Southern African Pyrometallurgy 2011* (Eds. R.T. Jones and P. sen Hoed) Southern African Institute of Mining and Metallurgy, Johannesburg, p. 309
- [10] S. Wright, L. Zhang, S. Sun, S. Jahanshahi, Viscosities of calcium ferrite slags and calcium alumino-silicate slags containing spinel particles. *Journal of Non-Crystalline Solids* 282 (2001), p.15
- [11] S. Sukenaga, Yo. Gonda, Sh. Yoshimura, N. Saitoi, K. Nakashima, Viscosity Measurement of Calcium Ferrite Based Slags during Structural Relaxation Process. *ISIJ International*, Vol. 50 (2010), No. 2, p. 195
- [12] A.Vartiainen, Viscosity of iron-silicate slags at copper smelting conditions. *Sulfide Smelting '98* (eds. J. A. Asteljoki, R.L. Stephens. TMS, Warrendale, P.A. (1998), p. 363
- [13] K.C. Mills, B.J. Keene, Physical Properties of BOS slags, *International materials Reviews* 1987, 32, No. 1-2

- [14] K.C. Mills, S. Sridhar, Viscosities of ironmaking and steelmaking slags. *Ironmaking & Steelmaking* , vol 6, no. 4 1999, p. 262
- [15] L. Forsbacka, Experimental study and modelling of viscosity of chromium containing slags. *Doctoral Thesis. TKK-MT-196*. Helsinki University of Technology, Espoo 2007
- [16] F. T. Firdu. Kinetics of copper reduction from molten slag. *Master of Science Thesis in Engineering*, Helsinki University of Technology, Department of Materials Science and Engineering 2009
- [17] S-H. Seok, S-M. Jung, Y-S. Lee, D-J. Min, Viscosity of highly basic slags. *ISIJ International*, Vol. 47 (2007), No. 8, p. 1090
- [18] H.W. Kilau, V.R. Spironello, W.M. Mahan, Viscosity of BOF slags fluidized with fluorspar, colemanite, and fused boric acid. *Investigative Report no. 8292*. US Bureau of Mines, 1978, p. 1
- [19] J.M. Font, M. Hino, K- Itagaki, Thermodynamic evaluation of arsenic and antimony on the Bessemer matte and calcium ferrite slag. *Yazawa International symposium, Metallurgical and Materials Processing: Principles and Technologies*, vol 1 (eds. F. Kongoli, K. Itagaki, C. Yamauchi, H.Y. Sohn) TMS 2003 p. 307
- [20] A. Yazawa, S. Nakazawa, Yo. Takeda, Distribution behaviour of various elements in copper smelting systems. *Advances in Sulfide Smelting*, vol 1. *Proceedings of the 1983 Sulfide Smelting Symposium* (eds. H.Y. Sohn, D.B. George, A.D. Zunkel). AIME, Warrendal 1983, p. 99
- [21] S. Jahanshahi, S. Sun. Some aspects of calcium ferrite slags. *Yazawa International symposium, Metallurgical and Materials Processing: Principles and Technologies*, vol 1 (eds. F. Kongoli, K. Itagaki, C. Yamauchi, H.Y. Sohn) TMS 2003, p. 227
- [22] J.M. Font, , M. Hino, K- Itagaki, Phase equilibrium and minor-element distribution between Ni<sub>3</sub>S<sub>2</sub>-FeS matte and calcium ferrite slag under high partial pressures of SO<sub>2</sub>. *Metallurgical and Materials Transactions B*, vol 31B, 2000, p. 1231
- [23] K. Mills, The estimation of slag properties. *Short Course presented at South African Pyrometallurgy 2011*
- [24] M. Liukkonen, L. E. K. Holappa, D. Mu, Interfacial Energy between CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag and Iron in equilibrium and reaction conditions. *Molten Slags, Fluxes and Salts '97*, ISS Warrendale PA 1997, p. 163
- [25] A. Yazawa, Y. Takeda, Y. Waseda, Thermodynamic properties and structure of ferrite slags and their process implications. *Can. Met. Quart.*, vol 20, No. 2 1981, p. 129
- [26] K. Itagaki, Distribution of minor element in sulphide smelting. *Proceedings of Yazawa International Symposium, Metallurgical and Materials Processing*:vol 1. (Edited by F. Gongoli, C. Yamauchi and H.Y. Sohn), TMS 2003. p.293
- [27] S. Nikolov, *Licentiate Thesis*. Helsinki University of Technology, Faculty Process Engineering and Materials Science 1993
- [28] S. Nikolov, H. Jalkanen, M. Kytö, Distribution of some impurity elements between high grade copper matte and calcium ferrite slag. *Proceedings of 4<sup>th</sup> International Conference on Molten Slags and Fluxes*. Sendai Japan, ISIJ 1992, p.560
- [29] K.W. Lange, Verfahrenstechnik, ein Schlüssel zum Verständniss der Technischen Hochtemperaturprozesse. *Archiv für das Eisenhüttenwesen*, vol 43, no. 22. 1972, p. 93
- [30] A. Chatterjee, N. O Lindfors, J. O. Wester, Process metallurgy of LD steelmaking, *Ironmaking and Steelmaking* 1976, no 1, p. 21
- [31] H. Jalkanen, L. Holappa, On the Role of Slag in Oxygen Converter Process, *Proceedings of the VII International Conference on Molten Slags Fluxes and Salts*, Cape Town, South Africa, 25 – 28 January 2004, p. 71

- [32] M. Huitu, The control of slag path in the LD process. (in Finnish), *MSc Thesis*, Helsinki University of Technology, Espoo 1974
- [33] R. Väinölä, Investigation of combustion mechanism in LD-converter. (in Finnish), *MSc Thesis*, Helsinki University of Technology, Espoo 1975