

**TOWARD FUTURE DEVELOPMENT**  
**-Pros and cons of ironmaking and steelmaking slags and mold fluxes-**

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Abstract

Rationalization of the physical and chemical properties of ironmaking and steelmaking slags and mold fluxes helps optimize integrated steel production processes. Increased potential of the slags and fluxes can bring about improved products at increased productivity. Waste slag evolution and energy consumption can also be decreased greatly. Important interactions between the slags/fluxes and processes in advanced steelmaking system are critically reviewed for future improvement, depicting key technological problems. Present state of the fundamental understanding of the above properties of the slags and fluxes is discussed, and future work is suggested to solve the problems.

**Introduction**

Steel industry in the world utilizes silicate slags of the order of *300 million ton per year*. The compositions of the slags and fluxes are near neutral to basic. They include those from the smelting of sinter, pellet and ore in BF, hot metal pretreatment (HMPT), blowing of the hot metal in BOF, melting of scrap and DRI in EAF, secondary refining of the steel melt, and mold flux for continuous casting. Each of the slags calls for application-specific physical and chemical properties. The requirements for the slag properties have changed as the quality of raw materials decreased, the productivity of the steelmaking processes increased, the quality of steel products improved and process modification progressed [1]. At the same time, environmental and cost concerns have demanded the minimization of the generation of waste slags. It is the aim of this paper to review pros and cons of ironmaking and steelmaking slags and mold fluxes based on recent information, and suggest possible direction of the future

research and development of these materials with emphasis placed on both fundamentals and applications.

### **Trend of Development in Ironmaking, Steelmaking and Continuous Casting**

To keep up the competitiveness in cost and quality in international arena is the top priority for the long term survival of any steel company. Minimizing the consumption of energy, emission of greenhouse gases, dioxins, NO<sub>x</sub>, SO<sub>x</sub> and particulate and the evolution of waste slags is of equal importance for the survival [2]. Toward these moving targets, the following slag-related measures will be addressed with more emphasis in process metallurgical area:

1. Increased use of iron ores containing more water and gangue materials for sintering,
2. Injection of non-coking coal up to 300kg/ton-hot metal into BF to replace coke,
3. Implementation of smelting reduction to supplement the mainstay steelmaking route,
4. Increased scrap recirculation and DRI production,
5. Proliferation of hot metal pretreatment processes for BF-BOF plants,
6. High speed blowing of BOF with minimized slag,
7. Implementation of large EAF with O<sub>2</sub> injection and scrap preheating by post combustion of off-gas,
8. Increased rate of secondary refining, and
9. High speed continuous casting for conventional and thin slab continuous casting.

Development of these processes and associated slags has been directed toward increasing the rate of smelting, blowing, refining and casting while decreasing impurities for improving steel qualities and process upsets at lower cost. Such efforts should continue as the targets are moving to be more demanding. In addition, minimization of the evolution of waste slags has become a crucial issue for steel industry. To meet these requirements, the followings require serious and long term attention:

1. Improve the utilization efficiency of slag components effective for refining,
2. Find ways to utilize HMPT slags, and
3. Increase the rate of internal recycling and external application of BOF and EAF slags.

In addition, steel industry is contributing to local community by applying their high temperature technologies to the incineration of civil garbage and industrial wastes. Acidic slags and metals from the incineration plants are in need of similar consideration.

### **Important Subjects of Development Related to the Slags**

Subjects of importance that closely relate to the slags under the above mentioned circumstances will be discussed in the following:

#### **1. BF Slag**

BF slag occurs about 310kg/ton-hot metal. Majority (70%) of the BF slag has been utilized as a raw material for cement and concrete for a long time. It has been industrially used for rock wool and fertilizer, but in a small scale. The balance of the slag has been applied only to civil engineering, road and port construction. More sensible mass application should be explored, with modification of chemistry if necessary. Cost imposes, however, heavy burden.

In addition, sensible heat of the slag melt is dissipated for no use. Attempts to utilize the heat were made extensively, without any industrial success. Difficulties inherent to the chemistry modification and heat recovery arise from the fact that the slag gets quite viscous as it cools. Some measures need to be worked out to keep the slag fluid until the chemistry modification is homogeneously done and dissipating heat recovered. Constraint is once again the cost for mass processing,

There is not much to do on the chemistry of BF slag as its composition is largely determined by gangue materials in the ore and ash in the coke. In the past, basicity was increased just a bit within a narrow margin due to process requirements. Integrated review of cost, raw materials and energy consumption all across the mining, dressing, sintering/pelletizing and smelting in BF may open up some room for a better optimization.

## 2. Hot Metal Pretreatment Slags

The HMPT for removing Si, P and S prior to decarburization in BOF has been confirmed to be an advantageous avenue for steelmaking via BF-BOF route. HMTP serves to increase steel yield and hit rates of aim temperature and carbon, and decreases eruption and blowing time. Use of Mn-ore in place of costly Mn-alloys is favorably practiced in BOF with the pretreated hot metal. Refractory wear is also decreased. In addition to the increased productivity, evolution of BOF slag is reduced. Two typical ways have been in operation to optimize the total production system for decreasing the evolution of waste BOF slag:

One way is to recycle the BOF slag to sintering. This naturally causes the increase of P in hot metal beyond the dephosphorizing capability of BOF, and hence implementation of HMTP for dephosphorization is mandatory. Kitagawa [3] showed in **Fig. 1** that the increase in hot metal P could be kept below 0.14% even at 100% recycle of BOF slag, provided that 85% or more of hot metal was dephosphorized at HMPT to 0.04%. Utilizing the process steps shown in **Fig. 2**, 85% (today 100%) of hot metal was desiliconized at the trough and tilting tundish in BF shop, dephosphorized and desulfurized in sequence by injecting the fluxes in the desiliconized hot metal in torpedo cars at the pretreatment center (PTC), and blown in BOF. Total slag evolution in steelmaking sector decreased, as shown in **Fig. 3**, from 138 to 121kg/ton-steel. BOF slag itself decreased substantially from 92 to 42kg/ton-steel, but a part of the decrease was off-set by the increased evolution of HMPT slags. Evolution of waste slag should be around 70kg/ton-steel, as all the BOF slag is recycled and silica rich slag from desiliconizing operation is also recycled as a silica source in the steel plants.

The other way to minimize the BOF slag without recycling is to reduce Si in hot metal to a minimum. According to Tanaka, Kohira, Watanabe, Matsuno, Isawa and Shirayama [4], Si in hot metal at tap from BFs was reduced to a low 0.20%. The hot metal was desiliconized ( to  $\leq 0.1\% \text{Si}$  ), desulfurized and dephosphorized with somewhat different processes shown in **Fig. 4**. The pretreated hot metal was blown in BOF with zero addition of slag materials. Total amount of slag in steelmaking sector was much reduced from the previous figure of 130kg/ton-steel for a conventional BOF shop to 60kg/ton-steel with the new system. BOF slag itself was reduced to 10kg/ton-steel only. This reduction is shown in **Fig. 5**.

In both cases, however, the slags after dephosphorization ( $\% \text{CaO}/\% \text{SiO}_2 \leq 2$ ,  $\text{Fe} \cong 10\%$ ,  $\text{P}_2\text{O}_5$  3- 4%) and desulfurization ( $\text{C/S} > 3$ ,  $\text{Fe} \leq 1\%$ , some S and F, and/or Na) are only little recycled, considerable portion being disposed for landfill at some expenses. As mentioned earlier, effective utilization of dephosphorizing (fertilizer?) and desulfurizing slags is the

crucial issue for further success of HMPT.

Many efforts have been paid to find fluxes with greater sulfide and phosphate capacities. Fluxes containing high fraction of  $\text{Na}_2\text{CO}_3$ ,  $\text{NaF}$  and/or  $\text{CaF}_2$  were tried and some of them were industrialized for a long time. These flux components have, however, their own cost and environmental drawbacks. After more than a decade of industrial campaign, therefore, the compositions of the fluxes seem to have converged into (1) ore/sinter +  $\text{O}_2$  for desiliconizing, (2) sinter/scale + lime (+ limited amount of fluospar and/or  $\text{Na}_2\text{CO}_3$ ) for dephosphorizing, and (3) lime + limited amount of fluospar and/or  $\text{Na}_2\text{CO}_3$  or  $\text{Mg}$  + lime for desulfurizing. The desiliconizing fluxes are applied by top addition with  $\text{O}_2$  injection. The dephosphorizing fluxes are injected into hot metal transfer vessel with  $\text{O}_2$  or added from the top in BOF type vessel. The desulfurizing fluxes are either injected with  $\text{N}_2$  into or mixed with hot metal by mechanical or gas stirring in hot metal transfer/charging vessels. Either pre-mixed or post-mixed fluxes are used, but post mixing seems to have advantages in cost and dynamic control.

In all cases, optimization between increasing cost with expensive fluxes and increasing slag evolution with less expensive fluxes seems to have been still in progress. The optimization for desiliconization is whether to rationalize sintering and BF operations for lowest possible hot metal Si at tap or intensify HMPT for minimizing hot metal Si after tap. Similarly for dephosphorization and desulfurization, it is either to maximize the sulfide and phosphate capacities by improving flux compositions at extra cost or dilute the impurities transferred into the slag by increasing flux consumption at extra slag evolution. Such optimization will further develop as the demand will grow for increased mass processing of steel with improved qualities for better life cycle assessment. The quality improvement will be met in one way by reducing impurities to extra low concentrations at high speed refining as detailed by Emi [1].

Generally speaking, utilization ratio in units of the phosphate and sulfide capacities of the fluxes in practice would be at best somewhere around 50%, perhaps less. The utilization ratio depends on the operation, usually lower for injection processing. In addition to the process thermodynamic considerations, there are some rooms left for improving the utilization ratio of the fluxes by enhancing process kinetics. Key issues are (a) to enhance the formation of slag toward designed composition at the point of injection into or addition to the melt, and (b) promote mass transfer of the impurities into the bulk phase of the slag during transitory and/or permanent reaction modes in the vessel.

These circumstances challenge us to interesting R & D of the slags. For the case (a), it is essential to transform fine lime powder into  $\text{CaO}$ -saturated liquid slag particles instantaneously at the point of addition to achieve highest possible phosphate or sulfide capacity. This should be done with minimum amount of fluxing components that are recyclable. Spreading/wetting of the liquid fluxing components on  $\text{CaO}$  particles, penetration of the liquid into the particles, and dissolution of  $\text{CaO}$  particles into the liquid to saturation would be a conceivable sequence. More insight into the dynamics of these sequential steps should be rewarding, and requires attention. Residence time and interfacial area of slag/metal contact should be made longer and larger by proper emulsification. This also calls for further investigation on the dynamics of the interfacial phenomena.

### 3. BOF and EAF Slags

In BOF, function of slag has changed for blowing the pretreated hot metal. The slag is made quite basic, but not expected to either dephosphorize or desulfurize. Instead, it serves

for protecting the metal bath from excessive generation of fume at the point of impingement of  $O_2$  jet. Smelting reduction of Mn-ore becomes easier due to the reduced amount of slag, resulting in considerable cutback of Fe-Mn alloy addition. Also, the slag is utilized to coat the vessel wall with MgO to prolong the vessel life. At the end of the blow of BOF with pretreated hot metal, sequential control of slag properties, first for slag splash coating and second for stiffening to prevent slag carry over into ladle, would leave some room for further rationalization. Remaining slag has been recycled mostly to sintering and partly to HMPT. Small fraction of BOF slag has been used as a supplemental raw material for cement. Otherwise, use is limited for the time being to landfill and gravel for temporary path.

If hot metal is not pretreated, BOF slag is in need of retaining high phosphate and sulfide capacities by adding considerable amount of lime. The addition causes the dissolution of substantial amount of iron oxide and MgO, respectively, from metal bath and vessel lining into the slag, resulting in iron loss and refractory wear. Control of slag-foaming is also one of the problems in the early stage of the blowing as it causes the eruption of slag and metal from the vessel mouth. The eruption is known to occur when high rate evolution of CO meets viscous slags. The viscous slags arise when silica content is relatively high, temperature low, and the dissolution of raw materials added for slag formation is incomplete. These factors help to stabilize the foam by making the drainage of slag film between the bubbles slow and superficial strength of the film increased.

Whether hot metal is pretreated or not, carry-over of highly oxidizing BOF slag into ladle should be avoided to prevent reoxidation of deoxidized melt. For this objective, mechanical flow control devices for stopping slag outflow have been employed at the tap hole of BOF. In addition, stiffening of the slag with the addition of MgO is a popular practice to increase the melting point of the slag and the volume fraction of suspending solid phase in the slag.

In EAF, submerged short-arc melting is a common practice. Foamy slag during melting protects furnace wall from side arcing, melt surface from heat dissipation, and electrode from oxidation. Today, the foaming seems to be well under control. EAF's have been operating largely for melting and oxidizing with single slag practice, leaving refining on the secondary refining furnaces. Energy content of the slag is in the range of 65-80kWh/ton-steel. Thus, although there are not much issues specific to EAF slag left, further reduction in the slag volume is still necessary to reduce the electricity consumption as discussed by Scheele [5].

Carry-over of BOF and EAF slags from ladle to tundish, and finally into continuous casting mold is one of the major origins of macro inclusions that cause downstream process upsets and impair product qualities. The carry-over of ladle slag containing FeO and MnO is detrimental even if they are diluted to a few %. The carry over occurs due to vortexing of the top slag during drainage of steel melt from ladle and tundish. Mechanical countermeasures based on fluid dynamic considerations are in place, but not satisfactory in transient operation. Detection of the slag flow out from ladle nozzle is practiced for which optical or electromagnetic properties of liquid slag are required.

#### 4. Secondary Refining Slags

Secondary refining calls for a variety of slag compositions to meet product requirements. Finishing desulfurization and modification and removal of inclusions are commonly done with the secondary refining slags. Increased sulfide capacity with proper viscosity is the first requisite for the desulfurization. As the requirement for steels containing single ppm S is not

uncommon, slags nearly saturated with CaO is often used with fluxing components such as  $\text{CaF}_2$  and  $\text{Al}_2\text{O}_3$ . Composition ranges suited for the combination of improved sulfide capacity and reasonable viscosity have been explored for numbers of slag systems. As an example, Mannesman index was proposed and utilized to estimate the favorable combination in CaO-base flux systems. For the modification of inclusions, chemical composition of the slag is tailored to yield, depending on the application, silicate- or aluminate-type inclusions with reasonable relative deformability on hot rolling. For inclusion removal, good wettability and fluidity are required for the slag to enhance the assimilation and dissolution of oxide inclusions from slag/metal interface into the bulk of the slag. For these secondary refining slags, oxygen potential should always be minimized.

## 5. Mold fluxes

Mold fluxes are applied to continuous casting in the shape of powder, granules or hollow spheres. The fluxes are to fulfill so many functions at a time in the mold. At the meniscus of steel melt in continuous casting mold, it should spread over evenly, melt at a designed rate to supply sufficient but not excessive amount of liquid flux of designed uniform composition onto the meniscus. Yet unmelted original solid layer and sintered layer are to thermally blanket the surface of steel melt to prevent crust formation. The liquid flux layer should be thick enough not to expose steel melt surface at the swell caused by deflected circulating flow of steel melt from the narrow face of the mold. The liquid flux layer should be quick in dissolving inclusions that ascend to the meniscus..

Fluid dynamic turbulence could occur at the boundary of liquid flux layer and steel melt meniscus particularly at high rate casting when sub-meniscus flow speed gets high. As shown in **Fig. 6**, the turbulence is enhanced by asymmetric melt flow out from submerged entry nozzle (SEN) in the mold, and includes: (1) vortex formation near SEN, (2) excessive wave motion of the deflected sub-meniscus steel flow and/or (3) break up of Ar gas bubbles injected into SEN. These events induce the entrainment and emulsification of the liquid flux into steel melt, causing exogenous macro inclusions that are harmful for steel qualities.

The entrainment and emulsification at the flux/steel boundary involve the following sequential activation processes (in addition to the Marangoni instability): The turbulent sub-meniscus flow gives rise to (1) the initial stretching of a part of liquid flux from the bulk in stringy droplet shape, followed by (2) the rupture of the stringy portion to separate the droplet. Energy supplied by the flow should overcome the increase in interfacial energy and viscous drag energy arising from the above deformation. Both the flux/metal interfacial tension and the viscosity of the flux come into play. Cramb, Chung, Harman, Sharan and Jimbo [6] did extensive investigation on the interfacial tension. In reality, the window for changing the interfacial energy is narrow unless the steel is resulfurized, and hence the entrainment has been prevented by increasing the flux viscosity as shown by Watanabe, Suzuki, Nakada, Suzuki and Sakai [7] in **Figs. 7 and 8**.

The liquid flux should infiltrate uniformly into solidifying shell/mold boundary, and lubricate the boundary for the oscillating motion of the mold. The liquid flux layer should be capable of supplying liquid flux film of certain thickness evenly into the shell/mold gap. It should not develop thick flux rim along the periphery of the meniscus of the steel melt. The flux film is subject to steep temperature gradient, and hence mold wall side of the flux film is solidified in glassy and crystalline state. When the mold is oscillating, shell side of the film exhibits non-Arrhenius behavior. Dynamic shear force distribution across the flux film needs

to be clarified to control the friction imposed on thin, hot, and hence fragile solid steel shell in contact. Here, we need the knowledge of the flux viscosities not limited to liquid temperatures but also at temperatures slightly lower.

The film should also provide the shell with proper resistance to the heat transfer to the mold to avoid the occurrence of excessive thermal stress and cracks on the shell. Control of the radiative and conductive heat transfers across the film has been discussed. For high speed casting of medium carbon peritectic steels, slower cooling is required in mold to prevent the crack formation. The reduction in the heat transfer is practiced by increasing the thermal resistance at solidified flux film/mold wall interface and decreasing the radiation across the film. This is done by increasing the roughness of the film surface at mold wall as a consequence of the crystallization of that side of the film. The crystallization also helps reducing radiative heat transfer, causing the reflection at the crystal grain boundaries. Thus, continuous cooling transformation (CCT) and time temperature transformation (TTT) diagrams need to be investigated to reveal dynamic crystallization of the film during rapid cooling in the gap between the shell and mold.

## 6. Smelting Reduction Slag

Slag plays dominant role in iron bath smelting. Fruehan [8] showed that the reduction reactions of FeO dissolved in the slag occur at the boundary between Fe-C drops, coal char and the slag. Control of the slag foaming in the reactor is another important factor for the bath smelting as it determines the rate of production. The foaming height is proportional to the viscosity and inversely proportional to the square root of the interfacial tension of the slag under otherwise identical condition of gas evolution.

In all of the above metallurgical operations, process thermodynamics and process kinetics/mass transfer are essential tools for further improvement and innovation. Considerable progress has been made in the past years to generate relevant data and develop theories for the slags. There still remains, however, an extending area of fundamental understanding that requires further exploration. Some of the topics that call for our attention in this area will be depicted in the following, referring to recent investigations.

### Topics on the Fundamentals of Slags and Fluxes

#### 1. Structure of the silicate melt

Three dimensional structure of liquid slags and fluxes influences their physico-chemical properties. Unfortunately, however, progress in this area of research during 90's was rather scarce. In a recent critical review of the investigations on the structure of the slags, Gaskell [9] concluded that the results of trimethylsilylation are more credible than the interpretation of Raman spectra. In the system CaO-SiO<sub>2</sub>, orthosilicate anions, SiO<sub>4</sub><sup>4-</sup>, are the dominant species in basic composition range where the ratio (Non Bridging Oxygen, NBO)/Si is greater than 4. As the ratio decreases, fraction of polymer ions, possibly Si<sub>2</sub>O<sub>7</sub><sup>6-</sup>, Si<sub>3</sub>O<sub>10</sub><sup>8-</sup> and Si<sub>4</sub>O<sub>12</sub><sup>8-</sup>, will increase. However, their fraction and mode of polymerization are quite ambiguous. Slags of interest in iron and steelmaking are largely in the range of NBO/Si = 2 and above. Constitution of the melt near the ratio of 2 is still unknown. When the 3<sup>rd</sup> component, CaF<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, or Fe<sub>x</sub>O, is contained, virtually nothing is clear about the structure of such melts. Waseda and Toguri [10] stated on the basis of their extensive X-ray investigations as follows: "The SiO<sub>4</sub><sup>4-</sup> tetrahedral unit has been quantitatively confirmed from the in-situ X-ray

measurements as the fundamental local ordering unit of silicate melts and this unit structure was found to be insensitive to both temperature and composition. In the silica dilute region, the  $\text{SiO}_4^{4-}$  tetrahedra exist individually and their polymerization is quite likely to start as the silica content increases. However, the available X-ray diffraction results quantitatively confirm only the formation of the  $\text{Si}_2\text{O}_7^{6-}$  type simple chain. Quantitative determination of polymerized silicate anions in silicate melts is still far from complete”.

Regarding  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions in slags, neither the structure of their tetrahedral (occasionally octahedral, depending on the circumstances) coordination with respect to oxygen anion nor the role of these ions in the network has been made clear. An attempt to clarify the above ambiguity was made recently with Raman spectroscopy by Sasaki, Suyama, Mohri and Ishii [11]. A band arising at  $900\text{cm}^{-1}$  for iron-bearing sodium silicate melts at high oxygen partial pressure indicated that the 3-D network structure formed by  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions could be different from each other.

In spite of these ambiguities, the structural knowledge is essential in understanding the physical properties of the slags and the nature of slag-metal reactions. It also has to do with reaction sites in the slags for removing impurities, such as S and P, from steel melt in contact. We hope that future investigations by means of EXAFS (Extended X-ray Absorption Fine Structure), AXS (Anomalous X-ray Scattering) and Raman spectra, supplemented with relevant property measurements, shed more light on the structure of the slag melts.

## 2. Physical Properties of slags

The viscosity and interfacial tension are two of the most important physical properties of the slags for bath smelting and refining and mold fluxes for continuous casting. Mass transfer in the slag phase of impurities from steel melt is in some cases controlling the rate of purification refining. To promote the refining, volumetric coefficient of the mass transfer should be increased. The diffusivity of impurities in the slags is usually inversely proportional to the viscosity, and hence fluid slags are preferred. There are, however, limitations to decrease the viscosity. They come from, e.g., (1) compositional constraint of the thermodynamic capacities required for the refining, (2) pollution by fluxing components such as  $\text{NaF}$ ,  $\text{CaF}_2$  or  $\text{B}_2\text{O}_3$ , (3) temperature range available, (4) heat loss across the slag layer, (5) wear of vessel refractories, and (6) reoxidation of steel melt by air through the slags. Optimization of the viscosity are being made within these limitations.

Beyond that, efforts have been paid to increase the slag/metal interfacial area by enhancing the stirring of the slag and metal. Emulsification of top slag into metal and vice versa, and injection of slags into metal are typical examples. In these cases, slag/metal interfacial tension comes into play. Interfacial tension, contact angle, work of adhesion and spreading coefficient between inclusion and steel melt or between inclusion and slag melt have been shown to play important role for the agglomeration or modification and assimilation into slag of inclusions. For mold fluxes, control of the two properties has been crucial to secure good surface quality of the cast strand. The viscosity and interfacial tension are also the key parameters in successful bath smelting as discussed before.

### (1) Viscosity

In the limited range of near neutral to basic composition of the slags utilized in ironmaking, steelmaking, ladle refining and continuous casting, the viscosity of the slags is controlled by



the cooperative motion of silicate anion flow units. Experimental data on many liquid metallurgical slags and fluxes have been made available and compiled for our convenience (cf. Mills [12]). Riboud and Urbain separately proposed empirical equations to estimate the viscosity of multi-component slag melts as a function of the concentration of component oxides (see [12]). In this category of approach, recently reported equations by Iida, Sakai, Kita and Shigeno [13] appear to give better estimate of the viscosities of multi-component slag melts with broader range of compositions (up to 37%TiO<sub>2</sub> or 60%SiO<sub>2</sub>). However, variation from observed viscosities is still large for slags with high concentrations of amphoteric oxides or more than two kind of amphoteric oxides. Also, the reliability of the estimation is not satisfactory for sensitive applications of fluid slags, such as mold fluxes for high speed casting.

At this moment, empirical equations are still inadequate to predict the viscosity for those practical applications where the accuracy of the estimated viscosity is seriously questioned. This is particularly so when slags are to be used in viscous two phase range where solid phase persists. Viscosity of liquid slags/fluxes containing solid particles is of great practical importance to explain the dynamics of slag formation at the injection of CaO-particles, the behavior of slag in the cohesive zone in BF or the motion of mold flux film with crystallized phase. In this connection, it is interesting to see the experimental result of Wright, Zhang, Sun and Jahanshahi [14]. They confirmed that the Einstein-Roscoe equation stands for CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melt containing up to 20% of spinel particles. or slightly above the softening temperatures. Viscosity near the softening temperatures is also important as it relate to the lubrication by the flux film in continuous casting mold. At this moment, however, data base is not adequate to allow our access to the viscosity of the slags that contain solid phase or are in rheological domain. Only way to solve these inadequacies is still limited to the direct measurement of the viscosity. Accumulation of precisely measured viscosity data for the slags and fluxes under the above conditions is definitely required.

More rationalized interpretation of the viscosity of molten ternary slags was attempted successfully by Seetharaman and Sichen [15] in terms of an Eyring type expression coupled with excess Gibbs energy of mixing. Agreement between their own observed and estimated viscosities of the melts in the system CaO-Fe<sub>n</sub>O-SiO<sub>2</sub>, CaO-MgO-SiO<sub>2</sub>, CaO-MnO-SiO<sub>2</sub> and MgO-Fe<sub>n</sub>O-SiO<sub>2</sub> is remarkably good for near neutral to basic composition as shown in **Fig. 9**. The success may stem from the fact that the size and shape of the flow units would be rather small and regular with limited distribution, and cation-anion interactions would be not too much different within the composition range investigated. Extrapolation of this approach to acidic range and lower temperatures may require additional considerations.

Haida and Emi [16] critically reviewed the mechanisms and theories of viscous flow of silicate melt that were proposed on the basis of the ionic structure of the melt. Since that time, there seems to be not much progress in the theory that reflects the change of the size, shape and charge of flow unit anions and cation-anion interactions with temperatures and compositions. Investigations on the structure of the slag melt is again required to support the progress in this area.

## (2) Interfacial/Surface Tension, Contact Angle and Work of Adhesion

Compilation was extensively done by Keene [17] that provides us with handy reference to interfacial and surface tensions, contact angles and work of adhesion. These quantities are sensitive to contamination by surfactants. Further addition of data, acquired under well

defined experimental conditions for relevant systems, and revision of available data are awaited for improved reliability and decreased scatter (cf. Keene, **Fig. 10** on the interfacial tension between  $\text{Fe}_n\text{O}$ -containing slags and Fe melts, Poirier, Yin, Suzuki and Emi, **Fig. 11** on the contact angle between  $\text{Al}_2\text{O}_3$  and Fe-O-S melts [18] ).

For empirical estimation of the surface tension, Tanaka and Hara [19] extended Butler equation with numbers of assumptions to  $\text{CaO-SiO}_2$ ,  $\text{FeO-Fe}_2\text{O}_3$  and  $\text{CaO-SiO}_2\text{-Fe}_x\text{O}$  melts, and obtained reasonable agreement with experimental data. Cramb and Jimbo [20] estimated the interfacial tension between the slag and steel melt from the surface tensions of the slag and steel by use of Girifalco-Good equation. This approach was followed recently by Tanaka and Hara [19], resulting in good agreement with observed interfacial tension between liquid steel and  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_x\text{O}$  melt.

In practice, dynamic interfacial phenomena in transition are sometimes more important than static ones in equilibrium. When slag melt is brought into contact with liquid metal, the two are neither in thermal nor in chemical equilibrium. Accordingly, heat and mass transfers take place at the slag/metal interface, generating Marangoni flow. The flow can be quite aggressive, emulsifying slag and metal concurrently across the interface. X-ray observation of this phenomenon was reported first time by Kozakevitch in mid 1950's, followed by Ooi, Nozaki and Yoshii, and Ogino and Hara in mid 1970's and by Riboud, Lucas, Gaye and Olette in early 1980's. Recently, Chung, Jimbo, Sharan, Kolbeinsen, Byrne and Cramb [21] carried out more detailed study trying to quantitatively describe the interfacial turbulence. It was suggested that local variations in slag viscosity near the slag/metal interface control the reaction rate, the velocity of fluid flow and the onset of emulsification.

Coupling among the chemical reaction, heat and mass transfer, temperature and concentration gradient and fluid flow takes place non-uniformly over the interface. This is one of the typical subjects to be addressed by the science of complexity which is as yet in its infancy. Quantitative clarification of such complex dynamic phenomena is a difficult problem to tackle. As it has much relevance to the development of future refining process, however, further investigations, e.g., those by Cramb's group [6], [21] and Seetharaman's group [22], are much encouraged. In this connection, Mukai's group has been developing extensive study on slag/metal system with emphasis placed on Marangoni instability [36].

Wetting and spreading of inclusions by slag are also important in the modification of inclusions. Yin, Shibata, Emi and Kim [23] exhibited dynamic process of inclusion morphology change caused by the spreading of CaO rich liquid on  $\text{Al}_2\text{O}_3$  clusters. Inclusion engineering by modification, as a key element of quality steel production, will find more application. Such dynamics of the inclusion-slag melt interaction requires more attention.

### (3). Thermal Diffusivity and Absorption/Extinction Coefficient of Mold Fluxes

It was discussed in the above that the heat transfer from liquid steel to continuous casting mold determines initial solidification of steel shell formation in the mold. To control the heat transfer rate within a narrow acceptable window, mold flux film which flows into the slit between the mold and shell plays a decisive role. It controls conductive and radiative heat transfers and resistance to heat transfer at the flux film/mold interface. However, reliable data on the thermal diffusivity and absorption and extinction coefficients of mold fluxes are limited. Also, factors influencing the roughness at the mold side surface of the flux film, that determines the interfacial resistance, are hardly available.

Shibata, Cho, Emi and Suzuki measured as partly shown in **Fig. 12** the thermal diffusivities and absorption and extinction coefficients [24], [25] and the interfacial resistances [26] for a number of mold fluxes. On the basis of these data, they determined relative contribution of conductive and radiative heat transfer and interfacial thermal resistance, and discussed the influence of the properties of the mold flux on these quantities [27]. Due to the existence of radiation-shielding solid layer on the mold wall side of the flux film, the heat transfer was largely due to conduction. The conductive heat transfer was, however, reduced considerably by the superficial air gap at the flux/mold interface that was created by the surface roughness of the film. In 1999, laser flash method has been developed so much that it is now capable of determining in 10ms the conductive component separately from radiative one with high precision for liquid slags. Measurement of the thermal and optical properties with advanced devices is necessary to accumulate meaningful data.

Dynamic crystallization behavior of liquid flux film and CCT and TTT characteristics were investigated by Orrling, Tillander, Kashiwaya and Cramb [28]. Also, Tsutsumi, Nagasaka and Hino [29] investigated interesting correlation between the film surface roughness and crystallization on cooling of mold fluxes. These dynamic measurements are important, and need to be carried out for a wide range of the fluxes to control the initial solidification of steels that are sensitive to surface cracks (cf. medium carbon peritectic steels) at high casting speed.

#### 4. Thermodynamic Properties of Slag

Phase diagrams of, and activities and solubilities of component oxides in ironmaking and steelmaking slags have been determined extensively and compiled (cf. Slag Atlas, 2<sup>nd</sup> Edition). Similarly, the capacities have been made available (cf. **Fig. 13** for phosphate capacity by Tsukihashi and Sano, cited in Sano [30] ). Variations occasionally observed in these data have been converging. In addition to conventional slag systems, efforts to measure these quantities were extended in recent years to slag systems including exotic oxides ( $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{S}$ ,  $\text{BaO}$ ,  $\text{ZrO}_2$  etc), since the oxides were supposed to improve the refining or casting function of the slags and fluxes. As the multi-component slag systems are quite diversified in composition, there are shortfalls in the coverage of the compositions by experiments. Accordingly, attempts were made to predict these thermodynamic quantities on the basis of models and databases.

The optical basicity has been proposed to exhibit reasonable proportionality to sulfide capacities of slags containing little amount of  $\text{FeO}$  and  $\text{MnO}$ . It reflects the ability to provide  $\text{O}^{2-}$  ions involved in the reactions for the removal of the impurities. Other capacities, solubilities and activities of constituents of slags have also been determined for a variety of slag systems with fair to reasonable proportionality to the optical basicity as elaborated in the review by Mills[31]. The optical basicity has been useful to estimate the sulfide capacities in view of relative simplicity of the calculation involved and reasonable amount of necessary data available, as reported by Mitchell, Sleeman, Duffy, Ingram and Young [32]. One of the difficulties with this approach is that the variation in the calculated sulfide capacities for a given optical basicity is sometimes too large to allow for reliable estimation for a stringent demand. Another difficulty is that the best-fit optical basicity value for  $\text{FeO}$  for the sulfide capacities (0.97) differs from that for phosphate capacities (0.35). In former times, different values were also claimed, ranging from 0.51 to 1.0 as summarized in [31]. In depth clarification on the origin of the difference should be worked out on the basis of structural

understanding and reaction mechanism.

Gaye and Lehman [33] was, however, successful in calculating the sulfide capacities of multi-component slags in the system  $\text{SiO}_2\text{-TiO}_2\text{-Ti}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-CrO-FeO-MgO-MnO-CaO}$  containing up to 10-20% $\text{CaF}_2$  and a few %S. This was done by improving statistical thermodynamic IRSID model. The structure of the slags in the improved model is described by cells each consisting of a central anion with two adjacent cations and a shell of 6 arbitrarily taken nearest neighbor anions. Two sublattices, an anionic sublattice occupied by divalent anions and a cationic sublattice filled with various cations, are considered. Parameters are used that were made to fit experimentally determined phase diagrams. As shown in **Fig. 14**, the sulfide capacities ( $-\log C_s = 1$  to 5) were calculated for a variety of compositions in the  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MnO-MgO-CaO}$  system, exhibiting very good agreement with experimental ones. Phase diagram calculated with this model for  $\text{FeO-FeS-MnO-MnS}$  also agreed well with observed one. Phosphate-, nitride- and hydroxyl-capacities etc have been defined similarly, determined for some slags, and shown useful in practical application. Regular solution model by Banya and Hino was capable of predicting these capacities with reasonable agreement (cf. [33], [34] ). Basically, their model should be valid for slags in basic composition range.

Development of any model should be directed toward user friendly one. It should contain minimum number of adjustable parameters, while consistently reproducing thermodynamic quantities with minimum deviation over wide range of compositions and temperatures. We look forward to further interactive development of experimental determination and model prediction of the relevant thermodynamic quantities.

## Summary

Important functions of slags and fluxes in advanced ironmaking, steelmaking and casting processes are reviewed covering BF, hot metal pretreatment, BOF, EAF, secondary refining and continuous casting. Emphasis is placed on hot metal pretreatment and continuous casting processes where the improvement in the design and application of slag/flux can trigger major rationalization of the processes and total optimization of the integrated system for steel production. Current state of understanding of the fundamental aspect of the slags and fluxes is also reviewed with reference to possible direction of future research to help the designing of the slags and fluxes to be utilized in the processes. Further investigations are needed on the structure of the slag/flux and dynamic phenomena of coupled heat and mass transfer at the slag, flux/metal interface.

## Acknowledgments

The author wish to thank Professor S. Seetharaman, Royal Institute of Technology, Sweden for his kind support to this work while the author was with RIT and to Mr. T. Sakuraya and Mr. S. Takeuchi, Kawasaki Steel Corp, Japan for their valuable comments and discussions.

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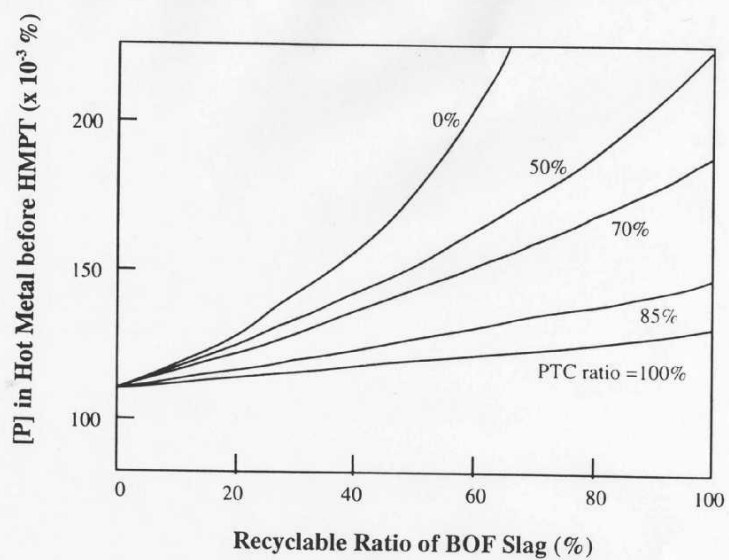


Fig. 1 Recyclable upper limit of BOF slag as a function of hot metal pretreatment (HMPT) ratio at pretreatment center(PTC) and initial P before HMPT, [3]

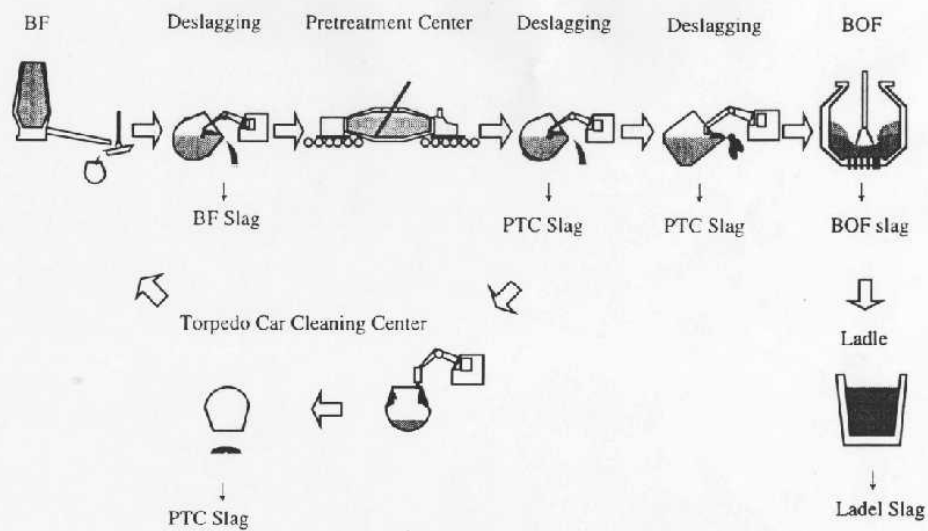
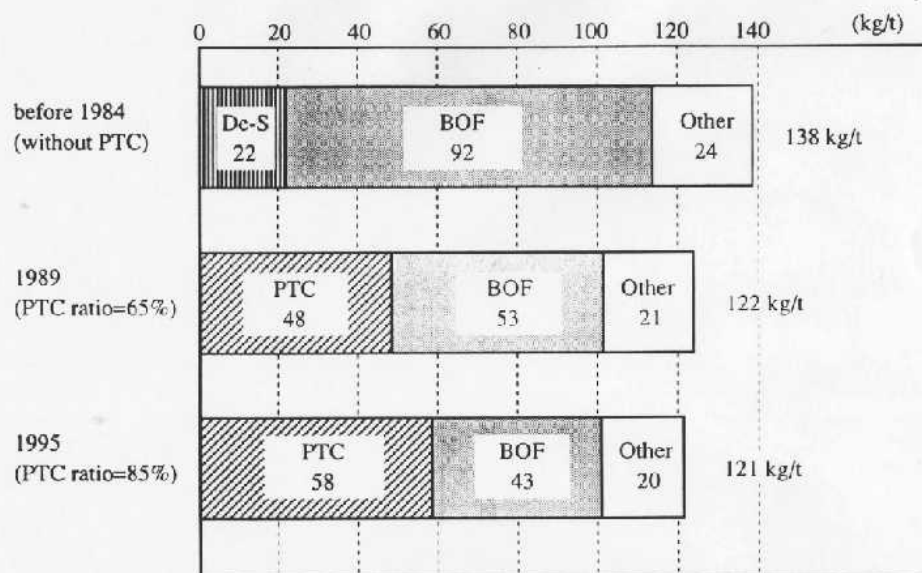
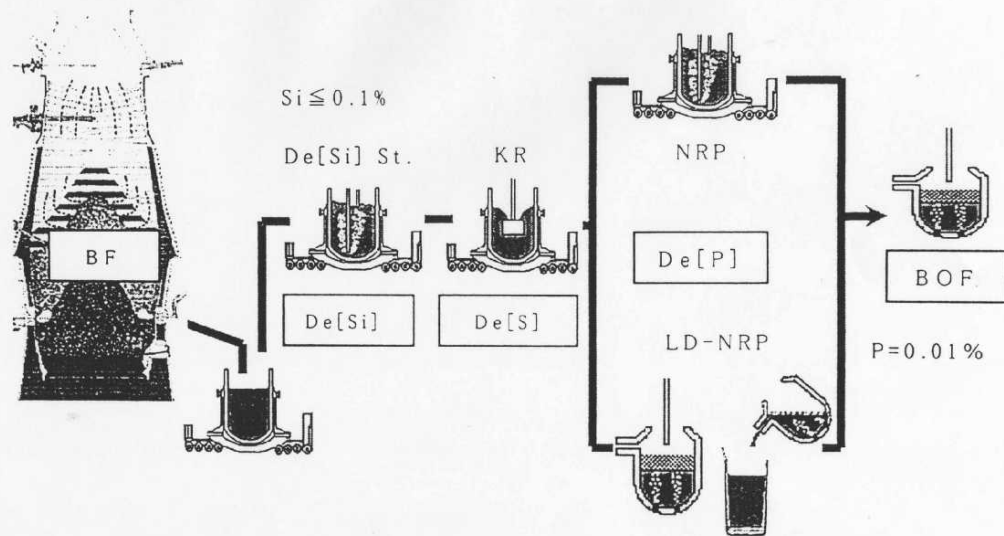


Fig. 2 Process route for 100% recycling of BOF slag to sinter/BF by treating 100% of hot metal at PTC for HMPT for removing [Si], [P] and [S], [3]

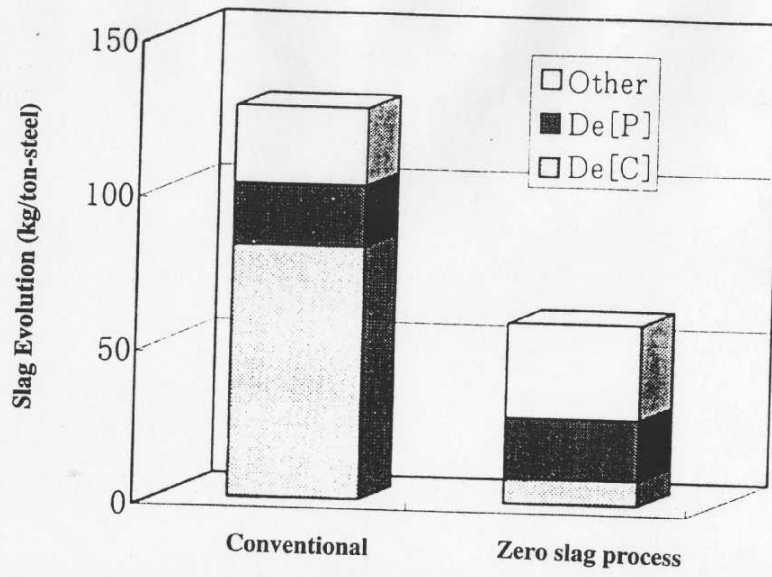




**Fig. 3 Decrease in the evolution of total slag and waste slag with increased application of hot metal pretreatment(HMPT) , [3]**



**Fig. 4 Process route for near zero evolution of BOF slag by decreasing [Si] in hot metal to 0.10% by improved BF operation and [Si] removal at HMTP, [4]**



**Fig. 5 Reduced evolution of steelmaking slag by implementing Zero Slag Process**  
(Bottom of the columns indicates slag arising from BOF), [4]

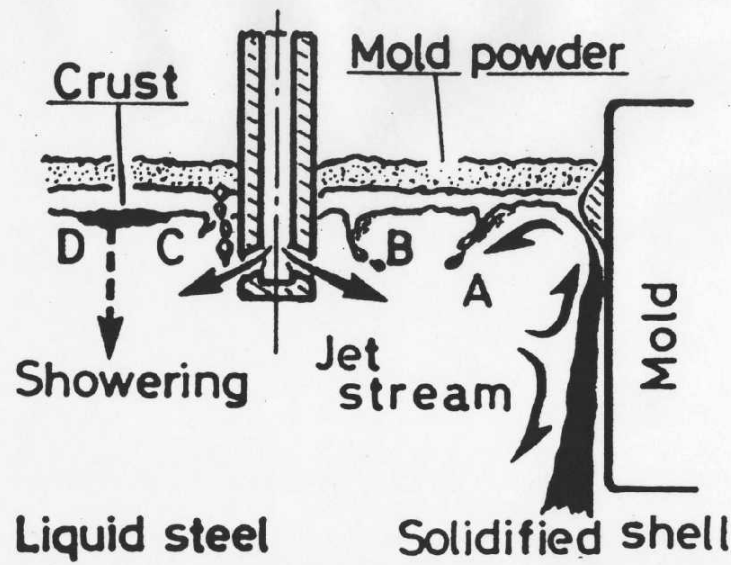
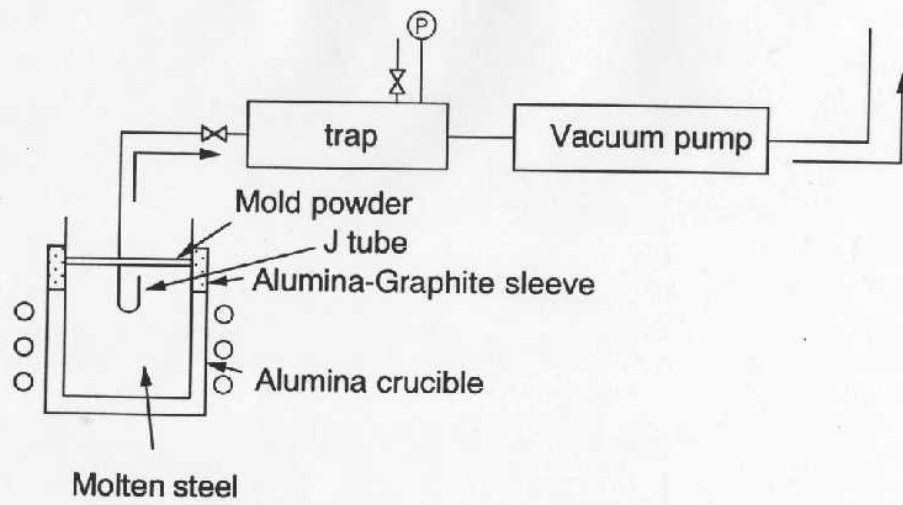
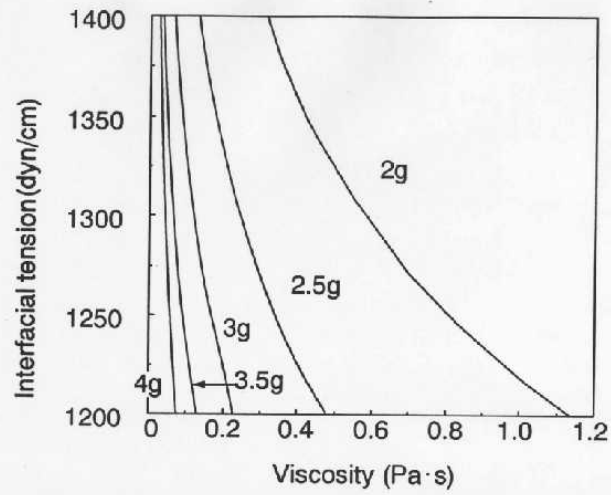


Fig. 6 Four modes of mold flux entrainment at the flux/steel melt boundary  
 (A: by turbulence caused by melt flow, B: by vortexing, C: by turbulence caused by Argon bubbles, D: by sedimenting crust caused by excessive heat loss)



**Fig. 7 Sampling for mold flux entrainment caused by vortexing in laboratory Simulator, [7]**



**Fig. 8 Effects of viscosity( $\eta$ ) and interfacial tension( $\gamma$ ) of mold flux on the entrapment of the flux by vortexing ( Weight of entrapped flux is proportional to  $\eta^{-1/4} \gamma^2$ ), [7]**

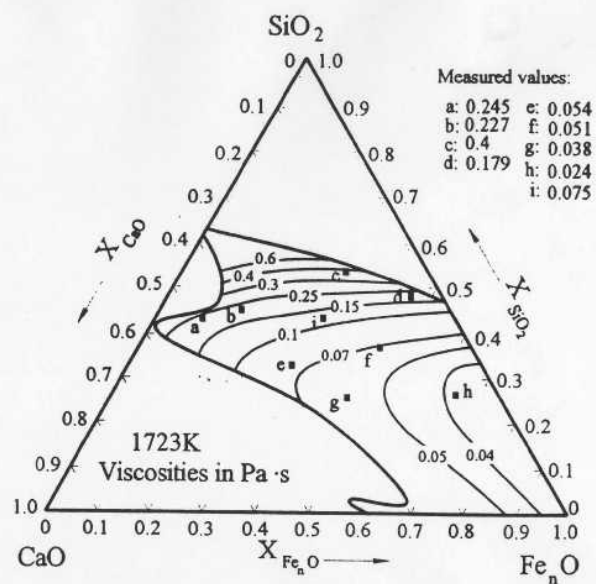
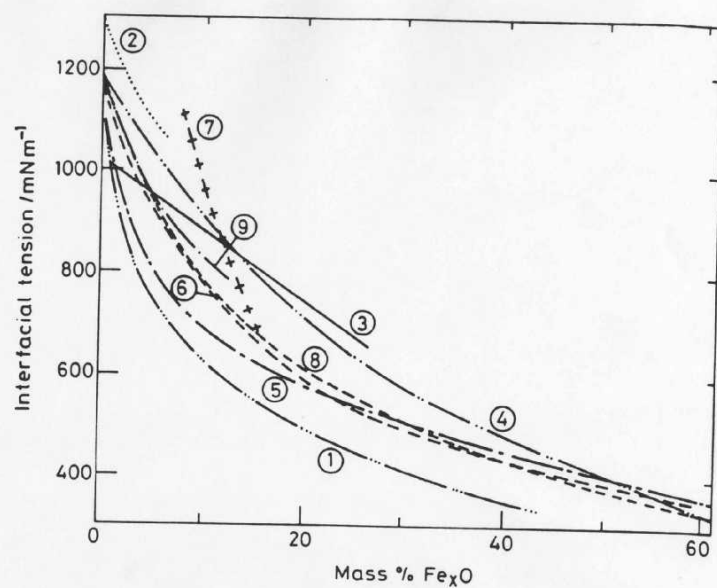
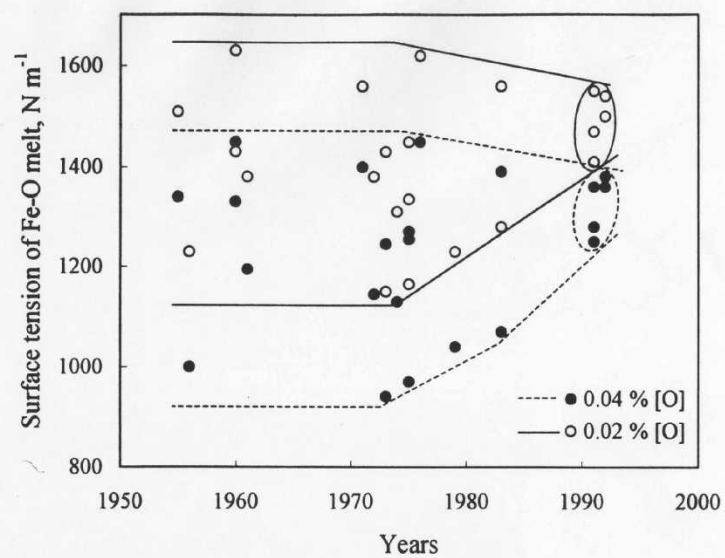


Fig. 9 Calculated vs. observed viscosities of CaO-SiO<sub>2</sub>-Fe<sub>n</sub>O melt at 1723K, [15]

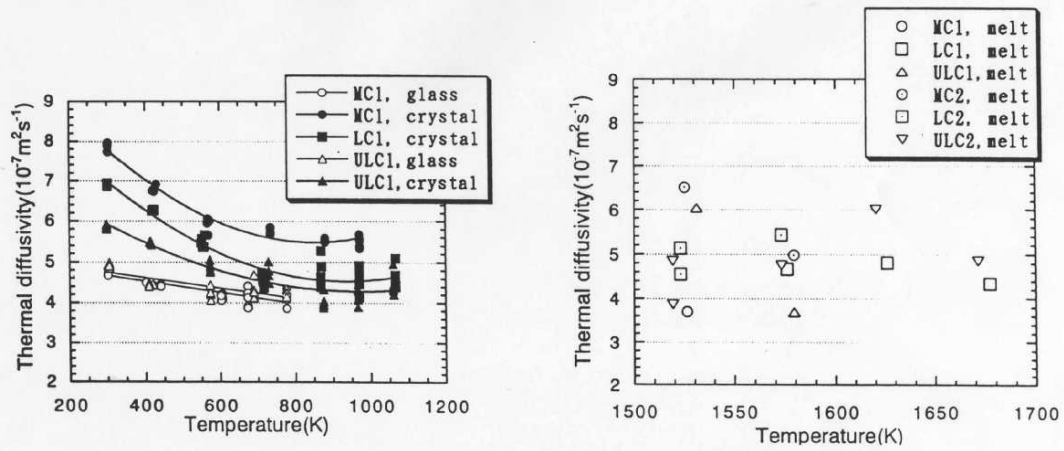


**Fig. 10** Compilation of literature data for the interfacial tension between iron and slags containing  $\text{Fe}_x\text{O}$ , [in ref. 17]

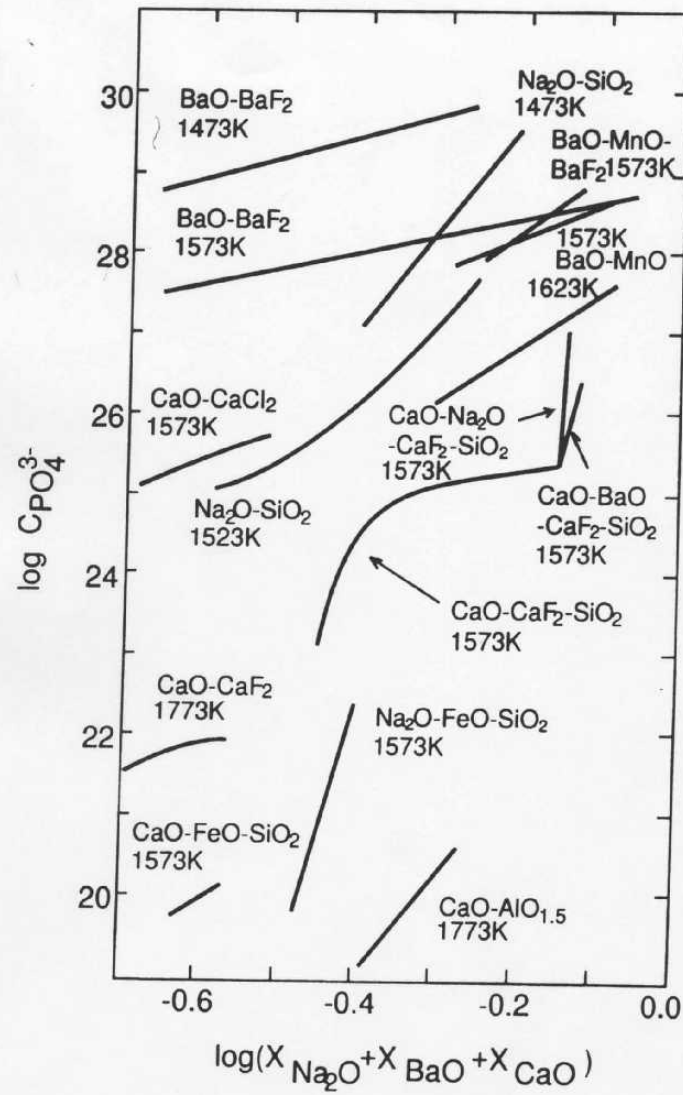




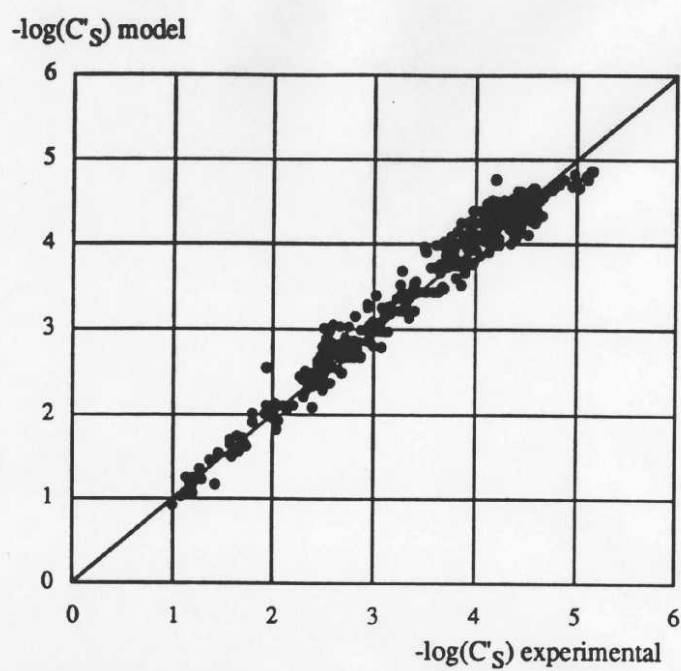
**Fig. 11** Chronological change of observed surface tension of Fe-O melts by various Researchers, [18]



**Fig. 12 Thermal diffusivity of liquid (right figure) and solid (left figure) mold fluxes in commercial use ( note that glassy fluxes show lower diffusivity than crystalline ones, but both come close at elevated temperatures. Also, extrapolation of the solid diffusivities to liquid temperatures exhibit reasonable agreement with liquid diffusivities), [24]**



**Fig. 13 Phosphate capacities of various flux systems, [25]**



**Fig. 14** Calculated vs. observed sulfide capacities in the system CaO-MgO-MnO-  
Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, [33]