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 refining potential of the slags and fluxes can bring about improved quality at increased productivity of products. 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, and key technological problems are depicted. The 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

The world's steel industry utilizes and produces silicate slags of the order of over **300 million ton per year**, the compositions of which are near neutral to basic. They come from blast furnace (BF)-, hot metal pretreatment (HMPT)-, basic oxygen furnace (BOF)-, electric arc furnace (EAF)-, ladle furnace (LF)- and continuous casting (CC)-operation. The slags call for application-specific physical and chemical properties that have been changing with (1) degrading raw materials, (2) increasing productivity of ironmaking and steelmaking processes, (3) improving quality of steel products, and (4) progress of process modification /1/. Also, environmental and cost concerns have demanded minimization of waste slag generation.

It is the aim of this paper to review the pros and cons of ironmaking and steelmaking slags and mold fluxes and suggest possible direction of the future research and development of these materials with emphasis placed on both fundamentals and applications.

TREND OF DEVELOPMENTS IN IRONMAKING, STEELMAKING AND CONTINUOUS CASTING

Maintaining competitiveness in cost, productivity and quality in the international arena is the top priority for the survival of steel companies. Thus, the utilization of downgraded raw materials will proceed. The through-put rate of unit processes involved and the availability of corresponding equipment will be increased further. The decrease in the impurities will be pushed forward to reduce process upsets and improve product properties, as the demands for the properties become more stringent. Minimizing the consumption of energy,

emission of greenhouse gases, dioxins, NO_x, SO_x and particulates, and evolution of slags is of equal importance for survival /2/. To meet these requirements, the following measures have been put in place and will continue:

(1) Increased use of sintering of less expensive iron ores containing more water and gangues,

(2) Injection of non-coking coal up to 300kg/ton-hot metal (HM) into BF to replace coke,

(3) Proliferation of hot metal pretreatment processes for large scale BF-BOF plants,

(4) Industrialization of smelting reduction to supplement the mainstay BF-BOF / scrap-EAF,

(5) Further enhancement of high speed blowing of BOF with minimized slag,

(6) Increase in scrap recycling and production of direct reduced, hot briquette iron (DRI/HBI),

(7) Further improvement in the productivity and energy consumption of large EAF with more O_2 injection and scrap preheating by post combustion of off-gas,

(8) Increased rate of secondary refining, and

(9) High speed casting for conventional and thin slab continuous casting to catch up the productivity of BOF + hot rolling mill (HRM) and large scale EAF + HRM.

The process metallurgical and environmental developments that involve slags should place more emphasis on minimizing the slag evolution and better utilization of the evolved slags.

To meet these moving targets, the following slag related issues require serious attention:

(1) Improve the utilization efficiency of slag components that are effective for refining,

(2) Find ways to stabilize the external use of BF slag and utilize HMPT slags with modifications, and

(3) Increase the rate of internal recycling and external application of BOF and EAF slags.

In addition, the steel industry is contributing to local communities by applying their high temperature technologies to the incineration of civil garbage and

industrial wastes. This activity will expand further in the near future, and hence another issue requiring attention is:

(4) Find utilization of acidic slags and metals occurring from the incineration plants.

IMPORTANT DEVELOPMENTS RELATED TO SLAGS

1. BF Slag

BF slag (near neutral quasi ternary 40-45%CaO-5%MgO-35-40%SiO_2-20%Al_2O_3) occurs typically around **310kg/ton-HM**, although some BFs are operating at 200kg/ton-HM or less with ores containing less gangue materials and impurities. The majority of the BF slag (~70%) has been utilized for cement and concrete for a long time. This has reduced energy consumed for calcining limestone, resulting in a considerable decrease in CO_2 evolution. Instability in this application exists, however, as challenged by recycled concrete arising from demolished buildings. Some measures are needed to minimize the instability by finding alternative better applications of the slag. The slag has also been industrially converted to rock wool and fertilizer, but on a small scale. The balance has found only low-end application to civil engineering, road and port construction. More sensible mass application should be explored, with modification of chemistry if necessary. Cost imposes, however, heavy limitations.

Sensible heat of the slag melt is dissipated uselessly. Attempts to utilize the heat were made extensively, without much industrial success. Difficulties inherent to the chemistry modification and heat recovery arise from the fact that the slag melt surface becomes too viscous as it cools to allow any sensible heat- or mass-transfer. Measures need to be worked out to keep the slag fluid until the chemistry modification is homogenously done and dissipating heat recovered. Constraints are once again the size of the possible market for such heat and slag and the cost incurred for mass processing. However, within these limitations the resulting slag should find reasonable application.

In this context, reduction of the slag evolution seems to be one of the most promising measures. Gangue materials in the ore and ash in the coke and coal, together with additives to sinter and pellet to fulfill process thermodynamic and kinetic requirements, determine the chemistry of BF slag. One recent notable improvement under increasing pulverized coal injection (PCI) up to 230kg/ton-hot metal is that the BF slag has

been successfully decreased from 280-350 to 265-300kg/ton-hot metal without impairing BF operation, as shown in Fig. 1 /3, 4, 5/, by reducing the addition of SiO_2 sources to sintering, i.e., by reducing SiO_2 content in sinter from ca. 4.9-5.8% to 4.2-4.9%. Integrated revision of cost, raw materials and energy consumption all across the mining-, dressing-, sintering/pelletizing- and smelting-sectors would offer a better optimization.
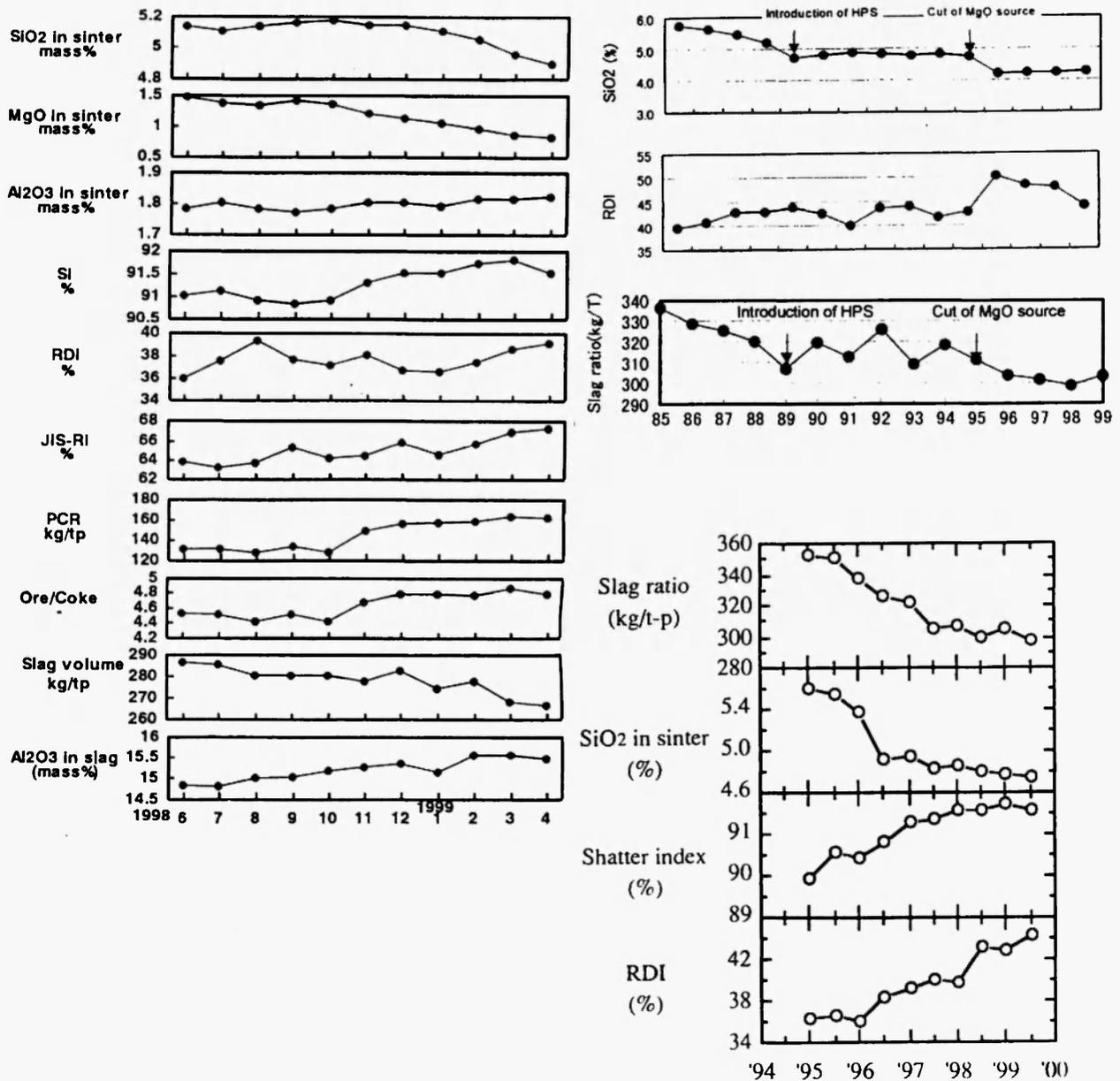

Fig. 1: Reduction of BF slag evolution with the decrease in SiO_2 content of sinter (left column: Tobata, Nippon Steel /4/, upper right: Fukuyama, NKK /3/, lower right: Mizushima, Kawasaki Steel /5/).

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 the BF-BOF route. HMTP serves to increase steel yield and hit rates of aim temperature and carbon, and decreases eruption and blowing time. The 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, the evolution of BOF slag, including slags from desiliconization and HMPT, is reduced.

Two typical methods have been in operation to optimize the total production system for decreasing the evolution of waste BOF slag:

One method 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 /6/ showed (Fig. 2) that the increase of P in HM 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. 3, today 100% of hot metal is desiliconized at the trough and tilting tundish in the BF shop, dephosphorized and desulfurized in sequence by injecting post-mixed fluxes
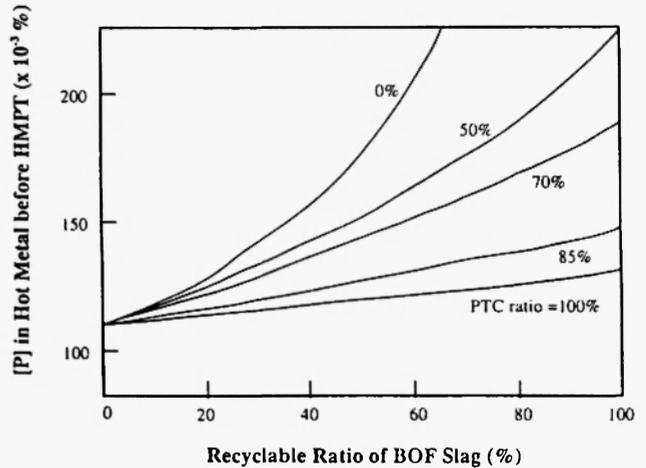
Fig. 2: Recyclable upper limit of BOF slag as a function of hot metal pretreatment (HMPT) ratio at pretreatment center (PTC) and initial P in hot metal before HMPT /6/.
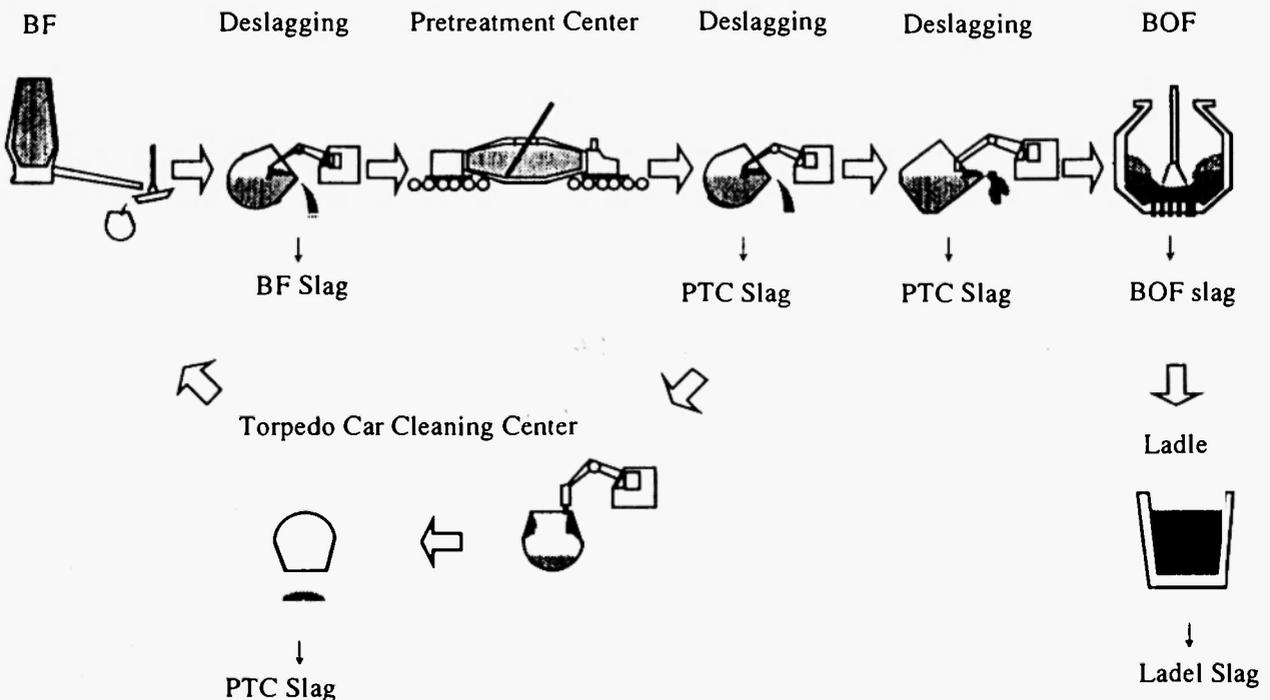
Fig. 3: Process route for 100% recycling of BOF slag to sinter/BF by treating 100% of hot metal at PTC for HMPT to remove [Si], [P] and [S] /6/.

into the desiliconized hot metal in torpedo cars at the pretreatment center (PTC), and blown in BOF. Total slag evolution in the steelmaking sector decreased, as shown in Fig. 4, from 138 to 121kg/ton-steel. BOF slag itself decreased substantially from 92 to 43kg/ton-steel, but a part of the decrease was offset by the increased evolution of HMPT slags. Consequently, evolution of waste slag should have decreased to about 70kg/ton-steel, about 50% of 138kg/ton-steel, since all the BOF slag is recycled and silica rich slag (included in "Other"

in Fig. 4) from desiliconizing operation is also recycled as a silica source within 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 *et al.* /7/, Si in hot metal at tap from BFs was reduced to a low 0. 2%. The hot metal was desiliconized (to < 0.1%Si), desulfurized and dephosphorized with somewhat different processes shown in Fig. 5. The pretreated hot metal was blown in BOF with zero addition of slag materials. Slag evolution
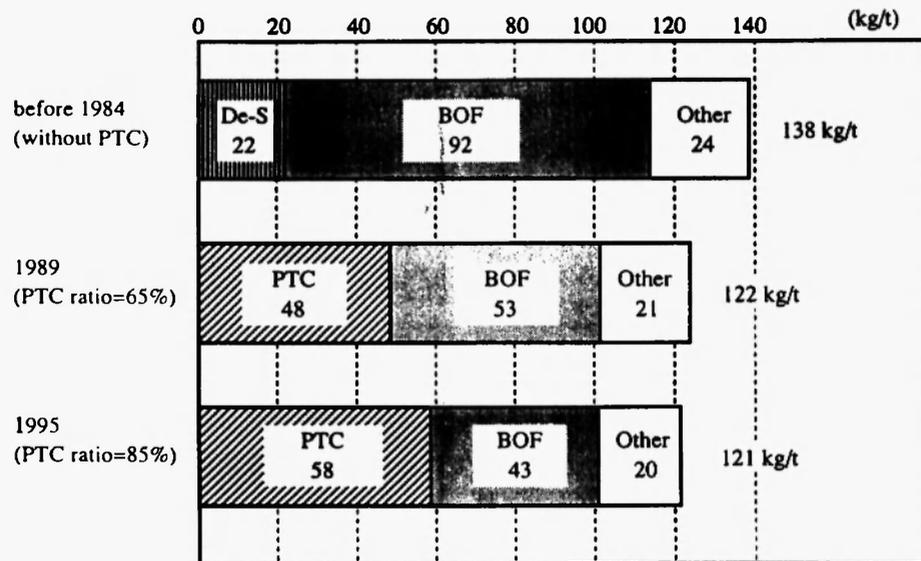

Fig. 4: Decrease in the amount of the evolution of total slags and waste slags with increased application of hot metal pretreatment (HMPT) /6/.
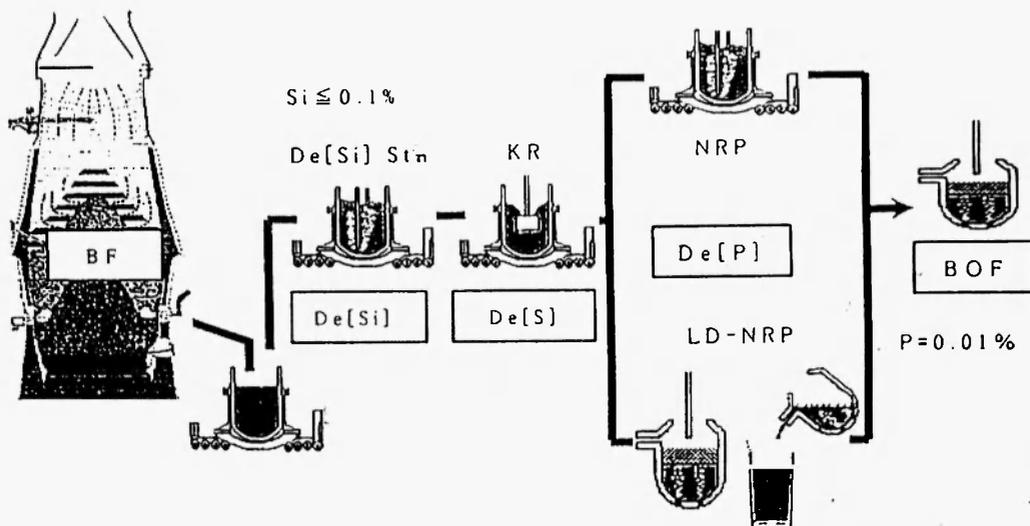

Fig. 5: Process route for near zero evolution of BOF slag by decreasing |Si| in hot metal to 0.10% with improved operation of BF and supplemental desiliconization of hot metal at HMTP /7/.

in the steelmaking sector was much reduced from the previous figure of 130kg/ ton-steel for a conventional BOF shop to 60kg/ton-steel, less than 50%, with the new system. BOF slag itself was reduced to only 10kg/ton-steel. This reduction is shown in Fig. 6.
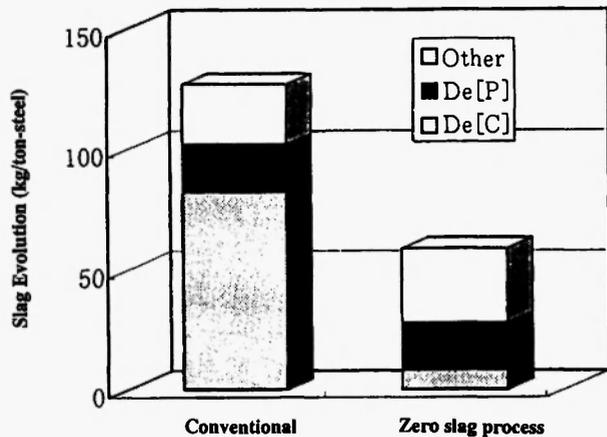

Fig. 6: Reduced evolution of steelmaking slag by the implementation of Zero Slag Process (Bottom segment of the columns indicates slag arising from BOF) /7/.

In both cases, however, the slags after dephosphorization (%CaO/%SiO$_2$ < 2, Fe ≅ 10%, P$_2$O$_5$ 3- 4%) and desulfurization (C/S > 3, Fe <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 the dephosphorizing and desulfurizing slags is the crucial issue for further success/maturation of HMPT.

For more efficient refining with less slag, many efforts have been paid to find fluxes with greater sulfide and phosphate capacities. Fluxes containing high fraction of Na$_2$CO$_3$, NaF and/or 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 + O$_2$ for desiliconizing,

(2) sinter/scale + lime (+ small amount of fluospar and/or Na$_2$CO$_3$) for dephosphorizing, and

(3) lime + small amount of fluospar and/or Na$_2$CO$_3$ or Mg + lime for desulfurizing.

The desiliconizing fluxes are applied by top addition with O$_2$ injection. The dephosphorizing fluxes are injected into hot metal transfer vessel with O$_2$ or added from the top in BOF type vessel. Utilization of spare BOF for HMPT is becoming popular where surplus steelmaking capacity is available, although greenfield installation of HMPT with BOF type vessel may not be economical. The desulfurizing fluxes are either injected with 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-mixed ones seem to have advantages in terms of cost and dynamic control of the process.

In all cases, optmization between "increasing cost with expensive but less amount of 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 to dilute the impurities transferred into the slag by increasing flux consumption at extra slag evolution. Such optimization will 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/. Such improvement can be advantageously achieved by practicing HMPT. One obvious obstacle to implementing HMPT is the decrease in the use of scrap in BOF while the scrap has cost advantage. One way to overcome the obstacle is to integrate BOF shop, operating predominantly on hot metal, and EAF shop, based mostly on scrap but with hot heeling by hot metal, into one steel works that has BFs/2/.

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 either 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 subjects of R & D of the slags. For case (a), it is essential to transform fine lime powder into CaO-saturated liquid slag particles instantaneously at the point of addition to achieve highest possible phosphate or sulfide capacity. This should be done with the minimum amount of fluxing components that are recyclable. Spreading/ wetting of the liquid fluxing components on CaO particles, penetration of the liquid into the particles, and dissolution of 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, including substantial contribution of the Marangoni effect in the early stage of slag/metal contact to the emulsification.

3. BOF AND EAF SLAGS

In BOF, the function of slag has changed for blowing the pretreated hot metal. The slag is made quite basic, but is not expected either to 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. The remaining slag has been recycled mostly to sintering and partly to HMPT. A small fraction of BOF slag has been used as a supplemental

raw material for cement. Otherwise, use is limited to landfill and gravel for a temporary road.

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 amounts of iron oxide from the metal bath into the slag, resulting in iron loss even when bottom gas stirring is practiced. 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 the superficial strength of the film high. Under such conditions, the eruption is difficult to avoid completely, and keeping up as high a hit rate of end carbon and temperature as with pretreated HM is also impossible with normal HM in BOF practice.

In EAF, submerged short-arc melting is a common practice. Foamy slag during melting protects furnace walls from side arcing and radiation, melt surfaces from heat dissipation, and electrodes 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 many issues specific to EAF slag left, further reduction in the slag volume is still necessary to reduce the electricity consumption as discussed by Scheele /8/.

Carry-over of highly oxidizing BOF and EAF slags from ladle to tundish, and finally into CC 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 weight percents. The carry-over occurs due to vortexing of the top slag during drainage of steel melt from ladle and tundish. In EAF, eccentric bottom tapping has been effective to solve this problem. In BOF, 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 MgO phase in the slag. Mechanical countermeasures based on fluid dynamic considerations are also in place to stop the outflow with electromagnetic or optical sensors, but are not yet satisfactory in transient operation.

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 has become not uncommon, slags nearly saturated with CaO are often used with fluxing components such as CaF_2 and Al_2O_3. Composition ranges, suited for the favorable combination of sulfide capacity and viscosity, have been explored for numbers of slag systems. As an example, the Mannesman index was proposed and utilized to estimate the favorable combination in $CaO-SiO_2-Al_2O_3$ 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

Process development was driven in the past largely by the demands for productivity. It will be driven more by demands for product quality. Mold fluxes have great influence on the quality of continuous cast strands, in particular at high speed casting that is the ongoing direction of the development of CC technology. The fluxes are applied to CC molds in the shape of powder, granules or hollow spheres. They serve to fulfill many functions at a time in the mold. At the meniscus of steel

melt in CC-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 serve to thermally blanket the surface of steel melt to prevent metal crust formation. The liquid flux layer should be thicker than the amplitude of mold oscillation, and 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. 7, 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.
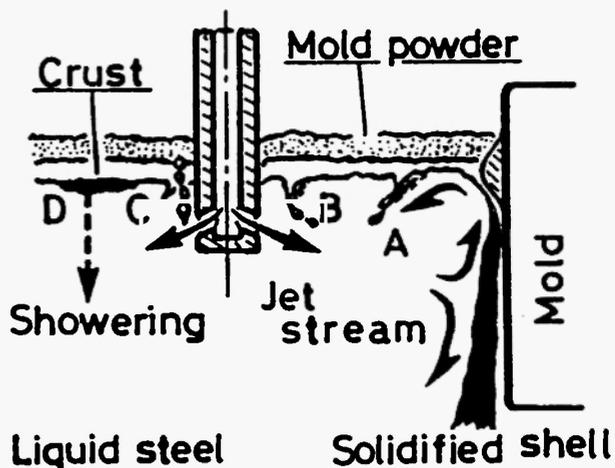

Fig. 7: Four modes of mold flux entrainment at the flux/steel melt boundary (Mode A: by the turbulence caused by melt flow, Mode B: by vortexing, Mode C: by the turbulence caused by ascending motion and break up of Argon bubbles, Mode D: by the sedimentation of metal crust formed by excessive heat loss at the meniscus)

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 *et al.* /9/ 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 *et al.* /10/ in Fig. 8.

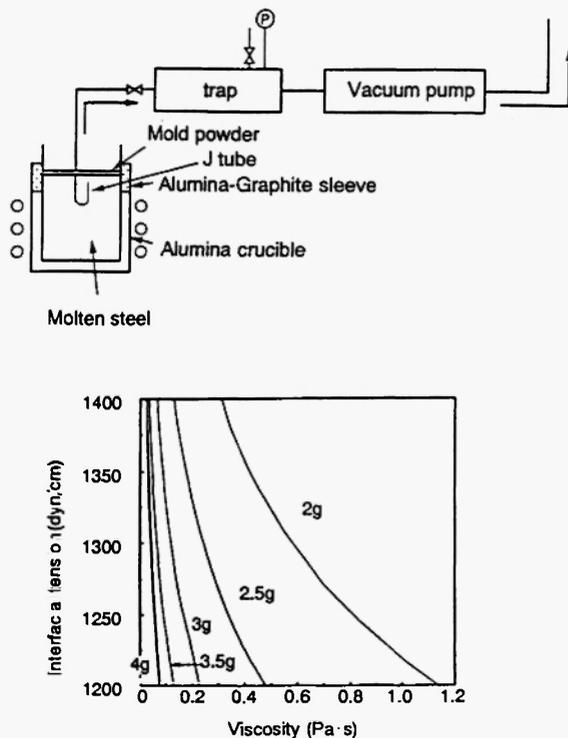The liquid flux should also infiltrate uniformly into solidifying shell/mold boundary, and lubricate the

Fig. 8: Weight of the mold flux entrainment in samples (in gram) sucked into the J tube shown above in hot model experiment and the effects of viscosity (η) & interfacial tension (γ) of mold flux on the entrainment of the flux by vortexing (weight of entrained flux is proportional to $\eta^{-1/4} \gamma^{-2}$) /10/.

boundary for the oscillating motion of the mold. The liquid flux layer should be capable of supplying liquid flux film of a certain thickness evenly into the boundary. It should not develop thick semi-solid flux rim along the periphery of the meniscus of the steel melt. The flux film is subject to a steep temperature gradient, and hence mold wall side of the flux film is solidified in strata of glassy and crystalline layers. When the mold is oscillating, the 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 force imposed on the 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 practiced. For high speed casting of peritectic carbon steels, slower cooling near the meniscus in the mold is particularly required to prevent the crack formation. This has been achieved by increasing the roughness of the film surface at the mold wall caused by the crystallization of that side of the film by use of slightly basic fluxes. The roughness increases the thermal resistance at the interface of solidified flux film and mold wall, and decreases the conductive heat transfer. Radiation heat transfer across the film also decreases due to the reflection at the grain boundaries of flux crystals. Thus, continuous cooling transformation (CCT) and time temperature transformation (TTT) diagrams of the fluxes in relevant cooling rate regimes will help reveal dynamic crystallization of the film in the shell/mold wall interface near the meniscus.

6. SMELTING REDUCTION SLAG

Slag plays a dominant role in iron bath smelting. Fruehan /11/ 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 conditions 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 recent 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 RELEVANT TO STEELMAKING

1. Structure of Silicate Melts

The three-dimensional structure of liquid slags and fluxes influences their physico-chemical properties. Unfortunately, however, progress in this area of research during the 90's was rather sparse. In a recent critical review of the investigations on the structure of the slags, Gaskell /12/ concluded that the results of trimethylsilylation are more credible than the interpretation of Raman spectra. In the system CaO-SiO_2, orthosilicate anions, SiO_4^{4-}, 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 $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$ and $Si_4O_{12}^{8-}$, 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 3rd component, CaF_2, Al_2O_3, or Fe_xO, is contained, virtually nothing is clear about the structure of such melts. Waseda and Toguri /13/ stated on the basis of their extensive X-ray investigations as follows: "The SiO_4^{4-} 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 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 $Si_2O_7^{6-}$ type simple chain. Quantitative determination of polymerized silicate anions in silicate melts is still far from complete".

Regarding Fe^{3+} and 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 *et al.* /14/. A band arising at 900cm^{-1} for iron-bearing sodium silicate melts at high oxygen partial pressure indicated that the 3-D network structure formed by Fe^{3+} and 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, will shed 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 sintering, smelting, refining and mold fluxes for continuous casting. Sintering of iron ores for better reducibility and optimized high temperature strength depend very much on the spreading of and bond formation by iron oxide containing CaO-MgO-SiO_2-Al_2O_3 liquid between the ore grains. Similar is the case for the cohesive zone in BF. 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 that come from, e.g., (1) compositional constraint on the thermodynamic capacities required for the refining, (2) pollution caused by fluxing components such as NaF, CaF_2 or B_2O_3, (3) liquid 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 should be 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 an important role in 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 earlier.

(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 influenced by associated cations. Experimental data on many liquid metallurgical slags and fluxes have been made available and compiled for our convenience (cf. Mills /15/). 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 /15/). In this category of heuristic approach, recently reported equations by Iida *et al.* /16/ appear to give a better estimate of the viscosities of multi-component slag melts with broader range of compositions (up to 37%TiO_2 or 60%SiO_2). However, variation from observed viscosities is still large for slags with high concentrations of amphoteric oxides or those containing more than two kinds of amphoteric oxides. At this moment, empirical equations are still inadequate to predict reliably the viscosity for such applications where the accuracy of the estimated viscosity is seriously questioned as mold fluxes for high speed CC.

This is particularly so when slags are to be used in a viscous two phase range where solid phase persists in liquid. 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 CaO saturated slags, the same in the cohesive zone in BF, stiffening of BOF slag with MgO particles or the motion of mold flux film with crystallized phase. In this connection, it is interesting to see the experimental results of Wright *et al.* /17/. They confirmed that the Einstein-Roscoe equation stands for CaO-MgO-Al_2O_3-SiO_2 melt containing up to 20% of spinel particles or slightly above the softening temperatures. Viscosity near the softening temperatures is also important as it relates to the sintering of iron ores and lubrication by the flux film in continuous casting mold. At this moment, however, database is not adequate to allow our access to the viscosity of the slags that contain solid phase or are in the rheological domain. The 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.

A more rationalized interpretation of the viscosity of molten ternary slags was attempted successfully by Seetharaman and Sichen /18/ 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_nO-SiO_2, CaO-MgO-SiO_2, CaO-MnO-SiO_2 and MgO-Fe_nO-SiO_2 is remarkably good for near neutral to basic composition as shown in Fig. 9. This 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 consideration.

Haida and Emi /19/ critically reviewed the mechanisms and theories of viscous flow of silicate melt
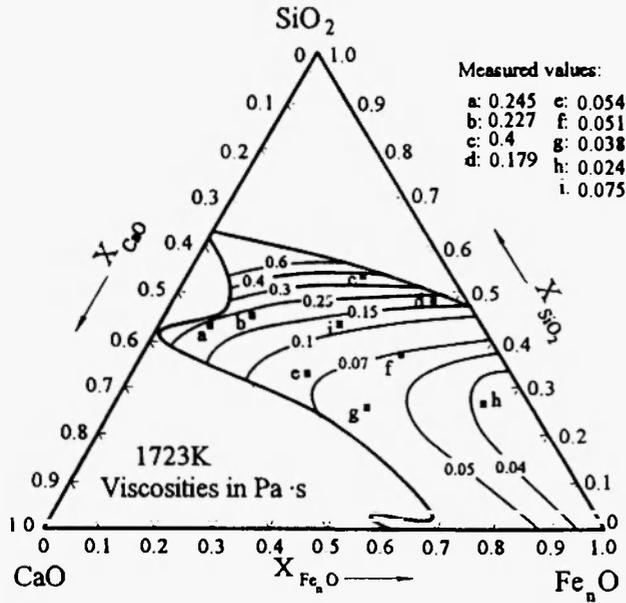
Fig. 9: Calculated vs. observed viscosities of CaO-SiO$_2$-Fe$_n$O melts at 1723K /18/.

Fig. 10: Compilation of literature data for the interfacial tension between iron and slags containing Fe$_x$O [in ref. 20].

that were proposed on the basis of the ionic structure of the melt. Since that time, there does not seem to be 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 are again required to support the progress in this area.

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

An extensive compilation was carried out by Keene /20/ that provides us with handy reference to interfacial and surface tensions, contact angles and work of adhesion. These quantities are sensitive to con-tamination 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 Fe$_n$O-containing slags and Fe melts, and Poirier *et al.*, Fig. 11, on the contact angle between Al$_2$O$_3$ and Fe-O-S melts /21/).

For empirical estimation of the surface tension, Tanaka and Hara /23/ extended Butler's equation with numbers of assumptions to CaO-SiO$_2$, FeO-Fe$_2$O$_3$ and
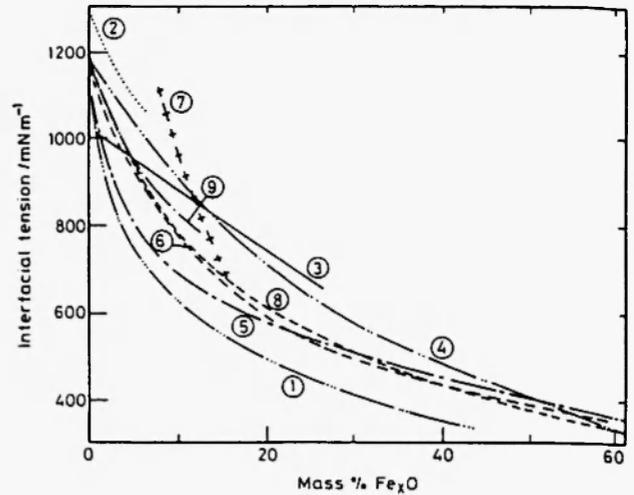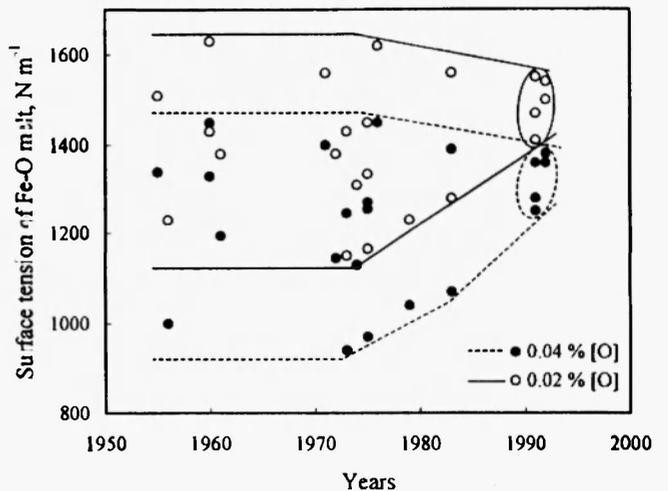

Fig. 11: Chronological change of observed surface tension of Fe-O melts by various researchers /21/.

CaO-SiO$_2$-Fe$_x$O melts, and obtained reasonable agreement with experimental data. Cramb and Jimbo /22/ 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. The latter approach was recently followed by Tanaka and Hara /23/, resulting in good agreement with observed interfacial tension between liquid steel and CaO-SiO$_2$-Al$_2$O$_3$-Fe$_x$O melt.

In practice, dynamic interfacial phenomena in transition are sometimes more important than static ones in equilibrium. When a slag melt is brought into contact with liquid metal, the two are neither in thermal nor in chemical equilibrium. Accordingly, heat and mass transfer takes 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 *et al.* and Ogino and Hara in mid 1970's and by Riboud *et al.* in early 1980's. Recently, Chung *et al.* /24/ carried out 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. Contribution of such interfacial turbulence to the rate of impurity removal may not be great, limited only to the very beginning of the removal, in permanent reactors where the ratio of slag/metal interface to metal volume is small. However, the contribution will be substantial in injection processes and film reactors where the ratio is large, suggesting a way for better utilization of slag.

Coupling among the chemical reactions, heat and mass transfer, temperature and concentration gradient and fluid flow occurs non-uniformly over the interface. This is one of the typical subjects to be addressed by the science of complexity that 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 /9, 24/ and Seetharaman's group /25/, are to be much encouraged. In this connection, Mukai's group has been developing extensive study on slag/metal system with emphasis placed on Marangoni instability /26/.

Wetting and spreading of slag on inclusions are also important in the modification of inclusions. Yin *et al.* /27/ exhibited the dynamic process of inclusion morphology change caused by the spreading of CaO rich liquid on Al_2O_3 clusters. Inclusion engineering by such modification, as a key element of quality steel production, will find more application. Such dynamic interaction between inclusion and slag melt requires more attention to push forward the inclusion engineering.

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

It was discussed in Section 5 that optimized heat transfer from liquid steel to continuous casting mold determines sound initial solidification of steel shell in the mold. To control the heat transfer rate within a narrow acceptable operating window, mold flux film that flows into the boundary between the mold and shell plays a decisive role. It controls conductive and radiative heat transfer, and resistance to heat transfer across the boundary. However, reliable data on the thermal diffusivities 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 well defined.

Shibata *et al.* measured, as partly shown in Fig. 12, the thermal diffusivities and absorption and extinction coefficients /28, 29/ and the interfacial resistances /30/ for a number of mold fluxes. On the basis of these data, they determined the 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 /31/. 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, the laser flash method has been developed so much that it is now capable of determining in 10ms the conductive component separately from the radiative one with high precision for liquid slags. Measurement of the thermal and optical properties with such an advanced device is necessary to accumulate meaningful data.

Dynamic crystallization behavior of liquid flux film and CCT and TTT characteristics were investigated by Orrling *et al.* /32/. Also, Tsutsumi *et al.* /33/ investigated an interesting correlation between the film surface roughness and crystallization on cooling of mold fluxes. These dynamic measurements are
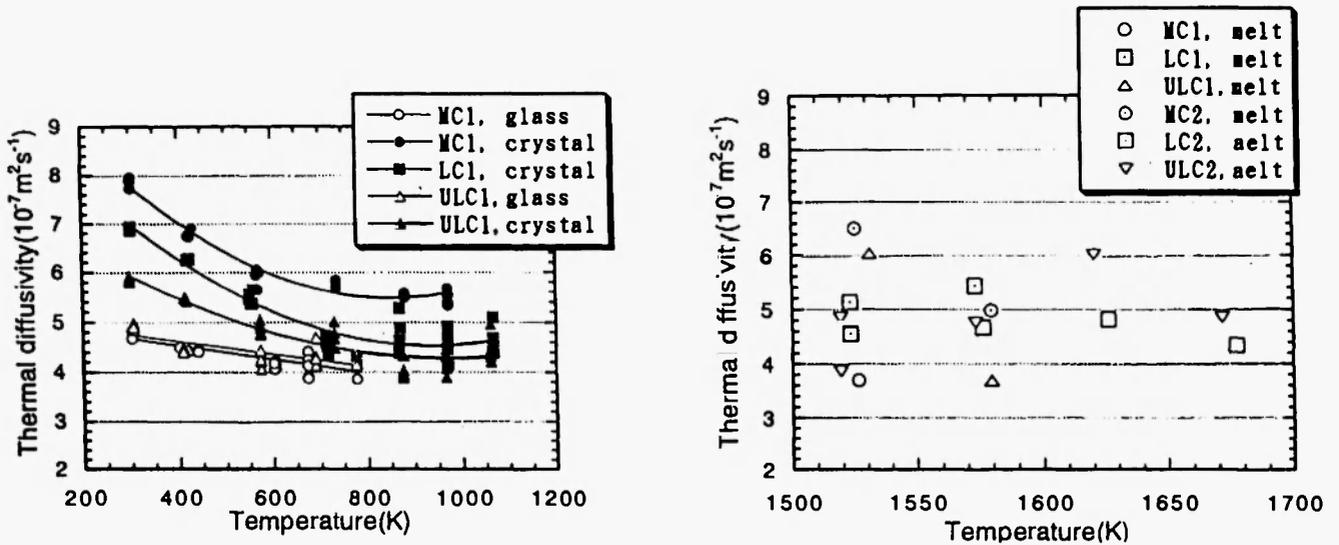
Fig. 12: Thermal diffusivity of liquid (right figure)- and solid (left figure)-mold fluxes in commercial use (note that glassy fluxes show lower diffusivities than crystalline ones, but both come close at elevated temperatures. Also, extrapolation of the diffusivities from solid to liquid temperatures exhibits reasonable agreement with liquid diffusivities). Details of composition and other characteristics of fluxes for ultra-low carbon (ULC), low carbon (LC) and medium carbon (MC) steels are given in ref. 28.

important, and need to be carried out for a wide range of the fluxes to minimize erratic initial solidification of steels that causes surface cracks (cf. peritectic steels) at high casting speed.

3. 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, 2nd Edition, VDEh). Similarly, the capacities have been made available (cf. Fig. 13 for phosphate capacity by Tsukihashi and Sano, cited in Sano /34/). 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 (Li$_2$O, Na$_2$S, BaO, 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
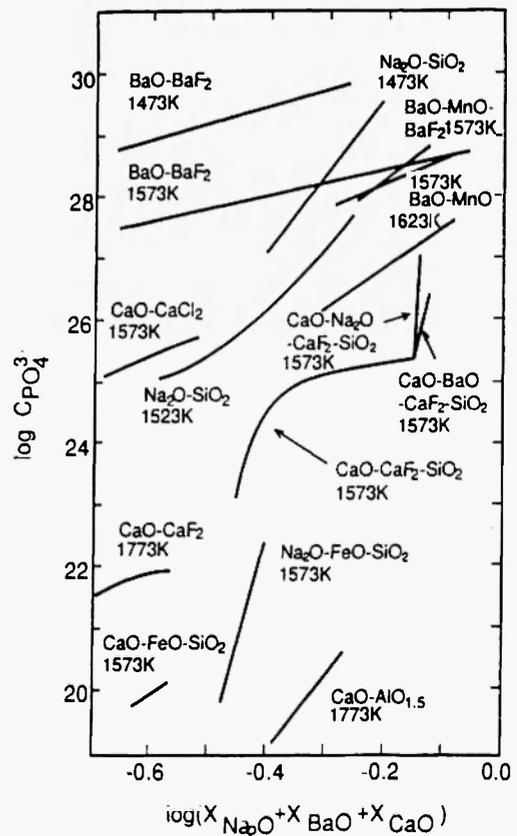

Fig. 13: Phosphate capacities of various flux systems /34/.

the basis of models and databases.

The optical basicity has been proposed to exhibit reasonable proportionality to sulfide capacities of slags containing a small amount of FeO and MnO. It reflects the ability to provide 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 /35/. 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 *et al.* /36/. 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 sensitive demand. Another difficulty is that the best-fit optical basicity value for 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 /35/. 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 /37/ were, however, successful in calculating the sulfide capacities of multi-component slags in the system SiO_2-TiO_2-Ti_2O_3-Cr_2O_3-Al_2O_3-Fe_2O_3-CrO-FeO-MgO-MnO-CaO containing up to 10-20% CaF_2 and a few percent of 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 SiO_2-Al_2O_3-MnO-MgO-CaO system, exhibiting very good agreement with experimental ones. Phase diagram calculated with this model for the system FeO-FeS-MnO-MnS also agreed well with observed one. Phosphate-, nitride- and hydroxyl-capacities etc have been defined similarly,
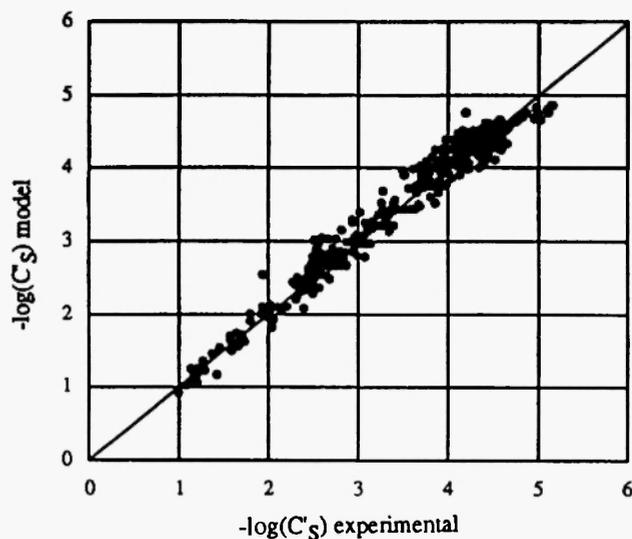

Fig. 14: Calculated vs. observed sulfide capacities in the system CaO-MgO-MnO- Al_2O_3-SiO_2 /37/.

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. /38, 39/). Basically, however, their model should be valid for slags in the basic composition range.

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

state of understanding of the fundamental aspects 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

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