The Laboratory Study of Metallurgical Slags and the Reality

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1. Introduction

An important target for research within the field of process metallurgy is to lay a solid foundation for steel industry to improve the process performance in terms of environmental impact, quality level, and product consistency. As steel is one of the most commonly used materials worldwide, an increase in production efficiency or improvement of product performance has the potential to yield great savings in resources and reduced environmental impact. However, applying academic results in full industrial scale comes with some challenges, namely, 1) The experimental design and related theoretical concept must allow for a realistic transformation of the results to the industrial practice, and 2) the actual parameters of the industrial process must be known to such extent, so that a useful implementation of the academic results is possible.

As metallurgical phenomena involving slag and metal are of a very complicated multivariate, time-dependent, and nonlinear nature with significant edge effects when being scaled, the above-mentioned challenges must be carefully addressed. If any link in this applied research value chain fails, real improvements to the industrial process are impossible. This article shows that frequent mistakes have been made in laboratory measurements of the important slag properties, for example, sulfide capacity, phosphate capacity, apparent viscosity, and apparent interfacial tension.

Given the challenges, the aim of this review article is to address how to make reliable laboratory measurements on slag properties and study the slag interfacial phenomena relevant to laboratory measurements of the important slag properties, for example, sulfide and phosphate capacities and interfacial tension.

To help a sensible discussion, some specially designed experiments are conducted to support the argument. The review is focused on slag properties (namely, sulfide capacity, phosphate capacity, apparent viscosity, and apparent interfacial tension) and studies of interfacial slag phenomena.

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the industrial reality. Aspects on how to use the results in industrial reality are also discussed. The article focuses on the slag properties: sulfide capacity, phosphate capacity, apparent viscosity, and apparent interfacial tension and the link to the industrial procedures involving sulfur and phosphorus refining, slag foaming, and inclusion removal. Some remarks on relevant properties, experimental conditions, and fundamental principles are given.

Removing of sulfur and phosphorous during steelmaking is important, as these elements strongly affect the mechanical properties of the steel product. The concepts of sulfide capacity and phosphate capacity of slags are widely used to predict the potential outcome of the refining processes. However, recent results show that the sulfide capacity itself may, under certain circumstances, also be strongly dependent on the oxygen potential of the system. This is also true in the case of phosphate capacity, as illustrated by the novel results presented in this article. The literature review along with the present experimental results and theoretical consideration intend to emphasize the importance of well-controlled experimental conditions, especially the oxygen potential when conducting the measurements and the importance of reporting them along with the results.

In real industrial practices, the “slag” very often consists of not only liquid phase but also some other phases. Different models have been used to simulate the flow of the multiphase mixture. A careful examination needs to be made based on both literature survey and experimental results, to gain an insight into the viscous behavior of the slag containing solid particles or/and gas bubbles or/and second liquid.

Considerable amount of data has been published for surface and interfacial tensions of slags. To use the data in a scientific manner, it is essential to know whether the data are measurable in a nonequilibrium system. An in-depth discussion is given in this review to address the data reported for nonequilibrium systems and the uncertainties when using them in industrial practices.

Slag foaming increases productivity and efficiency in electric arc furnace (EAF) steelmaking and, on the other hand, may cause harmful slopping in basic oxygen furnace (BOF) steelmaking. Hence, slag foaming should be controlled and optimized. Predicting foaming behavior based on a few key parameters such as slag viscosity and slag-gas interfacial tensions is common. However, recent results reveal that the slag foam itself shows a non-Newtonian behavior, and the published models are not common to describe the slag foaming in a realistic manner. Even the models predicting the movement of solid particles and liquid droplets are subjected to questioning. A literature survey along with experimental results obtained in both cold models and real slags at steelmaking temperature would be useful to understand the behavior of real foam in industrial practices.

The removal of nonmetallic inclusions from the steel to the top slag through the slag-metals interface is critical to meet the demands on steel cleanliness. Even though physically sound inclusion removal models exist, the model outcome might be invalid both due to principally wrong measurements of the interfacial tensions, and also due to the evolution of the system itself when the slag and steel successively approach equilibrium during the process, inevitably causing the interfacial and thermodynamic properties to vary over time. This aspect has not been carefully discussed in the literature.

To help the discussion by illustrating the possible mistakes made in laboratory studies causing misleading information, this article also includes some novel results from carefully designed experiments by the present group. In fact, this is not a traditional review article. The main objective is to discuss how to obtain high-quality and useful laboratory results that can be used in the industrial practices. It should be mentioned that no attempt will be made to cover all the previous works in the vast research areas under consideration. Only the publications most relevant to the discussion are included. To help the readers, all the references are provided in the corresponding sections of discussion, but not in the introduction.

2. Slag Properties

First, the slag properties subjected to questioning are discussed. It includes both thermochemical properties (e.g., sulfide capacity and phosphate capacity) and thermophysical properties (interfacial tension and viscosity).

2.1. Sulfide Capacity and Phosphate Capacity

The removals of sulfur and phosphorus have been studied extensively for many decades. A large focus has been put on measuring the sulfide and phosphate capacities of slags. A truly impressive amount of work has been done, and it has helped to both broaden and deepen our knowledge of sulfur and phosphorus behavior in slags. In fact, there are too many references for all of them to be included here. Therefore, only the references most relevant to the discussion are mentioned.

Richardson and Fincham\(^{[1,2]}\) introduced the sulfate capacity and sulfide capacity concepts, the latter being relevant for steelmaking operations. It is based on the following reaction.

\[
\frac{1}{2} S_2(g) + O^{2-} = S^{2-} + \frac{1}{2} O_2(g)
\]  

The sulfide capacity is expressed by the following equation.

\[
C_S = (\text{wt} \% S)_{\text{slag}} \times \frac{P_{O_2}}{P_{S_2}}^{1/2} \times K_1 \times \frac{a_{O^{2-}}}{f_{S^{2-}}}
\]

In the equation, \(P_{O_2}\) is the partial pressure of oxygen, \(P_{S_2}\) is the partial pressure of sulfur, \(a_{O^{2-}}\) is the activity of oxygen ions, and \(f_{S^{2-}}\) is the activity coefficient for sulfide ions. \(K_1\) is the hypothetical equilibrium constant of reaction (1), which would be a function of temperature.

Richardson and Fincham found that the sulfide capacity only depends on composition and temperature of the melt over certain oxygen and sulfur potential ranges.\(^{[3]}\) This is of considerable convenience for several reasons. First, the results from measurements of different slag compositions made at the same temperature but under different oxygen and sulfur potentials can directly be compared with one another. Second, measurements can be carried out at potentials different from those prevailing in the industrial reactor. Third, from the sulfide capacity the sulfur partition, \(L_S\), between slag and metal can be calculated if the
masses of metal and slag are known. $L_S$ calculated using $C_S$ is, thus, valuable for estimating the final sulfur content of the steel.

Due to its versatility and usefulness, a substantial amount of work has been carried out, measuring the sulfide capacity for a large number of slag systems.\cite{1,1-29} Only the references relevant to the discussion are included here. Recently, based on literature data, Kang and Pelton compiled a database to calculate sulfide capacity for slag systems, including the oxides $\text{Al}_2\text{O}_3$, $\text{CaO}$, $\text{FeO}$, $\text{Fe}_2\text{O}_3$, $\text{MgO}$, $\text{MnO}_x$, $\text{SiO}_2$, and $\text{TiO}_x$, which covers the majority of earlier works.\cite{30} In their publication, the authors also include an excellent list of references. Systems containing other oxides have been studied as well.\cite{31}

The capacity concept has been adopted for several impurity elements, among them phosphorus.\cite{32} Wagner introduced the phosphate capacity based on the description of ionic reactions between liquid steel and liquid slags containing phosphorus reported by Herasymenko.\cite{33} The phosphate capacity is expressed by

$$\text{C}_p = K_4 \frac{a_{\text{O}_{2}^{-}}}{f_{\text{PO}_{4}^{3-}}}$$  (3)

where $a_{\text{O}_{2}^{-}}$ is the activity of free oxygen anions, $f_{\text{PO}_{4}^{3-}}$ is the activity coefficient of phosphate anions in the slag phase, and $K_4$ is the hypothetical equilibrium constant of reaction (4), which would be a function of temperature.

$$\frac{1}{2} P_{2}(g) + \frac{3}{2} O_{2}^{-} + \frac{5}{4} O_{2}(g) \leftrightarrow \text{PO}_{4}^{3-}$$  (4)

After the introduction of the phosphate concept, many studies have been carried out.\cite{34-58} A constraint of the capacity concept is that the slag structure should be independent of oxygen potential. In the case of sulfide capacity, the term $\frac{a_{\text{O}_{2}^{-}}}{f_{\text{SO}_{2}^{2-}}}$ should remain constant over the oxygen potential range of interest. For slags containing stable oxides, such as $\text{CaO}$, $\text{MgO}$, and $\text{SiO}_2$ this is true, as being initially shown by Richardson and Fincham.\cite{31}

Similarly, the term $\frac{a_{\text{O}_{2}^{-}}}{f_{\text{PO}_{4}^{3-}}}$ needs to be constant for the phosphate capacity to remain constant when altering the oxygen potential. However, for slag systems containing transition metal oxides, such as $\text{FeO}_x$, $\text{TiO}_x$, and $\text{V}_2\text{O}_5$, this may no longer be the case. A change in oxygen potential will cause a change of the slag structure.\cite{33} It is likely that the capacity of the slag also will change due to the change in structure. Unfortunately, it has often been assumed that the capacity (sulfide or phosphate) is independent of the oxygen potential, even when systems contain multivalent species. Measurements for systems that contain multivalent species have, therefore, been carried out over a wide oxygen potential range typically from $1 \times 10^{-12}$ to $1 \times 10^{-6}$ atm for phosphate capacity measurements\cite{34-46} and $1 \times 10^{-12}$ to $1 \times 10^{-5}$ atm for sulfide capacity measurements.\cite{1,1-29} On the other hand, the oxygen potentials prevailing in the reactors only partly coincide with these ranges. The oxygen potentials in the industrial reactors are usually measured using an oxygen sensor, very common Celox sensor designed by Heraeus Electro-Nite is used. The Celox sensor contains a Cr/Cr$_2$O$_3$ electrode as the reference. As a complement, the total oxygen contents in the steel samples are usually determined by chemical analysis. The oxygen partial pressures are usually in the range of $1 \times 10^{-15}$–$1 \times 10^{-9}$ atm for secondary steelmaking and in the range of $1 \times 10^{-9}$–$1 \times 10^{-7}$ atm in BOF. A recent work indicates that the relevant upper limit may be as high as 0.21 even 1 atm,\cite{59} because at some locations, the slag is sometime exposed to air and the oxygen jet.

### 2.1.1. Structure of Silicate Melts with Transitional Species

The structure of silicate slag melts is determined by the slag composition, particularly the molar ratio of network-forming oxides to network-breaking oxides. As the molar ratio of network-breaking to network-forming oxides increases from 0 (full polymerization of the network) to 2, no network polymerization would be present. However, when multivalent oxide species exist, the structure of the slag will also depend on the oxygen potential, due to the variation of the species with different valences and their differing effect on the network.

Free oxygen anions are formed by basic oxides through the dissociation reaction (5) and (6).\cite{33,60}

$$\text{MO} \leftrightarrow M^{2+} + O^{2-}$$  (5)

$$\text{(Si - O - Si)} + \text{MO} \leftrightarrow 2(\text{Si} - \text{O}^{-}) + M^{2+}$$  (6)

The activity of the free oxygen anion will increase, as the molar ratio of basic oxide to acidic oxide increases. Oxygen anions may also be produced by the increase in valence state of multivalent species, such as iron and vanadium ions. By increasing the oxygen potential, the production of oxygen anions would occur according to reaction (7) and the activity of the free oxygen anion would increase.

$$\text{Fe}^{2+} + \frac{1}{4} O_{2}(g) \leftrightarrow \text{Fe}^{3+} + \frac{1}{2} O^{2-}$$  (7)

The iron species produced by reaction (7) is amphoteric and would, therefore, either participate in the network or act as a network breaker depending on the activity of free oxygen anions. In environments with low free oxygen activity, $\text{Fe}^{3+}$ would mainly function to increase the free oxygen activity, while the opposite effect is expected in an environment with higher free oxygen anion activity.

It is commonly understood that different cations modify the structure of silicate slags to different extents. In particular, it is the ionic radii and the charge of the cations that determine the contribution. Cations carrying a larger radius exert a lesser Coulomb’s force on the ion of opposite charge, compared with those of smaller radii. The ionic radius would decrease with an increase in oxidative state, $\text{Fe}^{2+}$ compared with $\text{Fe}^{3+}$.\cite{50,61} It was recently shown that a change in valence of Fe cations has a strong effect on the structure of silicate slags.\cite{62} This structure variation with oxygen potential would likely lead to the variation of thermophysical properties, e.g., viscosity, as well as the thermochemical properties of the slag.\cite{63-65} As a matter of fact, great controversy has been noticed when comparing the literature data for $C_F$ or phosphorus partition in the $\text{CaO}-\text{SiO}_2-\text{MgO}-\text{FeO}_x$ system at 1873 K.\cite{34-40} To the best of authors knowledge, the variation of thermophysical and thermochemical properties with oxygen potential for steelmaking slags has not been studied systematically. A systematic study of the
dependence of the properties of slags containing multivalence species, e.g., iron oxides, vanadium oxides, and titanium oxides on the oxygen potential would be greatly needed.

Usually, similar experimental setups have been used for the “equilibrium” study.\cite{34-46} In these studies, magnesia crucibles have often been used, and an open system with a protective atmosphere of argon gas has been used. Instead of using an open system, Huss et al.\cite{40} used a closed one.

The use of different oxygen potentials above the slag in different laboratories could be one of the reasons for this disagreement. In fact, using open systems in the study of phosphate capacity or phosphorus partition would result in uncertainties with respect to oxygen potential. The oxygen potential would vary from the slag-metal (iron) interface to the slag surface, where the oxygen partial pressure is a function of the geometry of the crucible and the argon flow and even time. This could, in turn, lead to great uncertainties when studying slags with multivalent species, e.g., Fe^{2+} and Fe^{3+}. Although in some of these studies\cite{34,38,41,42,55-57} only the phosphorus partition data are reported, and the same discussion would also apply to $L_P$. Nevertheless, the measured $L_P$ for systems containing multivalent oxide species can only be applied to the reactor when oxygen potential is almost the same as in the laboratory study.

As most of the slags in BOF and EAF contain both Fe^{2+} and Fe^{3+}, whether the capacity data determined under different oxygen partial pressures in the laboratory can be used in industrial practices requires a careful examination. To illustrate the importance of the dependence of the capacities on oxygen potential, experiments were specifically designed and carried out.

### 2.1.2. Experimental Evidence to Support the Theoretical Consideration

The experimental setup was described in detail in previous publications.\cite{40,46} Only the salient features are presented here to orientate the reader. A vertical graphite resistance furnace with an alumina reaction tube was used. The reaction tube was closed in the lower end by a water-cooled aluminum cap and in the upper end by an interconnected water-cooled chamber made of aluminum. The setup featured a lifting system, able to move the samples vertically from the even temperature zone to the cooling chamber in seconds for rapid cooling to terminate the reaction.

A molybdenum holder was used to hold the crucibles. In the case of very low oxygen partial pressures, i.e., $1 \times 10^{-16}$ atm, a graphite holder was used instead. The holder was connected to the lifting system by a molybdenum, or graphite, tube. The whole system was sealed using O-rings, except for the lifting unit, which was sealed by a radial lip.

Reaction gases were introduced into the furnace through an inlet situated at the lower aluminum cap, whereas the outlet was placed in the upper part of the aluminum cooling chamber. A separate argon gas inlet was positioned in the cooling chamber to force convection onto the samples for rapid cooling inside the cooling chamber.

The weighed in compositions is shown in **Table 1**. As both phosphate and sulfide capacities were measured over a large range of oxygen partial pressures, the experimental setup with respect to reaction gas and crucible materials had to be adjusted.

In the determination of phosphate capacities, after thorough mixing of the oxides, the powder mixture was pressed into two cylindrical pellets. The samples were placed in dense sintered magnesia crucibles (17 mm $Ø \times 53$ mm height). First, a thin layer of copper powder (<0.5 g) was added, covering the bottom of the crucible. The two slag pellets were placed in the middle of the crucible. The gap between the crucible wall and the slag pellets was filled with copper powder. This arrangement was expected to minimize the reaction between the slag phase and the crucible wall during heating. In the study of sulfide capacity, Cu and Cu$_2$S were thoroughly mixed and put in the bottom of the molybdenum crucible. The oxides were thoroughly mixed and put on the top.

The samples were inserted into the sample holder, lowered to the even temperature zone, and the furnace was sealed. The reaction chamber was evacuated for 10 min and then back filled with argon gas (99.999%). This process was repeated three times. The reaction chamber was evacuated one additional time before the reaction gas was introduced into the reaction chamber. The flow of reaction gas was lowered to 0.1–0.2 L min$^{-1}$, which was kept throughout the whole equilibrating period. The sample was then heated to 1873 K and kept at that temperature for 24 h. After equilibration, the samples were rapidly moved to the cooling chamber in about 2 s. After the samples had been moved to the cooling chamber, the flow of reaction gas was terminated. At the same time, a high flow of argon gas was forced onto the samples to promote rapid cooling. After cooling of the furnace, the samples were taken out.

The slag composition was analyzed by X-ray fluorescence (XRF). For analyzing phosphorus in copper, the copper was

| No. | Al$_2$O$_3$ | CaO | SiO$_2$ | $"V_2O_5"$ |
|-----|----------|-----|---------|------------|
| S-1 | 3.7      | 28.4 | 59.1    | 8.8        |
| S-2 | 8.4      | 25.2 | 58.6    | 7.8        |
| S-3 | 24.3     | 24.4 | 47.2    | 4          |
| S-4 | 3.7      | 28.4 | 59.1    | 8.8        |
| S-5 | 8.4      | 25.2 | 58.6    | 7.8        |
| S-6 | 24.3     | 24.4 | 47.2    | 4          |
| S-7 | 3.7      | 28.4 | 59.1    | 8.8        |
| S-8 | 8.4      | 25.2 | 58.6    | 7.8        |
| S-9 | 24.3     | 24.4 | 47.2    | 4          |
| S-10| 24.3     | 24.4 | 47.2    | 4          |

| No. | MgO | SiO$_2$ | $"V_2O_5"$ | $"P_2O_5"$ |
|-----|-----|---------|-------------|-------------|
| P-1 | 29.58 | 58.72   | 8.03        | 3.68        |
| P-2 | 29.44 | 58.84   | 7.99        | 3.73        |
| P-3 | 28.95 | 59.04   | 7.87        | 4.14        |
| P-4 | 29.43 | 59.01   | 7.85        | 3.72        |
| P-5 | 30.02 | 60.02   | 8.11        | 1.85        |

### Table 1. Weighed in slag compositions.

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*Note: The table includes the weighed in compositions of various samples.*

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dissolved in HNO₃, and the solution was subsequently analyzed by inductively coupled plasma-sector field mass spectrometry (ICP-SFMS). For analyzing sulfur in slag and copper, a combustion method using LECO CS-600 was used.

The normalized experimental results are presented in Table 2. The equilibrated slag compositions are given together with the corresponding phosphorus or sulfur concentrations. Please note, the amount of vanadium oxide is given as if it was only in one valence state, viz., V²⁺, because it is the major type of species. Although the coexistence of multiple valence states in liquid slags is likely under the present equilibrium conditions,[67–73] no effort was made to determine their fractions. The imposed oxygen partial pressures were calculated from thermodynamic literature data[74–77] and are included in the table.

Worth mentioning is that serious efforts were made to study the phosphate and sulfide capacities with a system containing iron oxide, which is more relevant to the steelmaking processes. Several attempts were made with different experimental setups, but without satisfactory and reproducible results, mostly due to the difficulties in controlling the slag-refractory reaction, which affected the slag composition. This initial approach was abandoned, and instead, a slag system containing vanadium together with liquid copper was chosen. This experimental setup yielded satisfactory results, as is described in more detail later. The main purpose of this study was not to report \( C_p \) and \( C_s \) values for the present slag systems, but to illustrate the effect of oxygen potential when the slag contains multivalent elements. Hence, the exact valences of vanadium were not determined.

As already mentioned, the oxygen potentials in steelmaking processes cover a big range. Though it would be valuable to make measurements in the whole range of oxygen potentials, the great difficulties in finding suitable crucibles have made this attempt impossible. Also, it is practically very difficult to keep the same slag composition in a wider range of oxygen potentials. As the main objective of the experimental work is to verify the effect of oxygen potential on the capacities of slags with multivalent species, no extensive experimental study has been conducted.

### 2.1.3. The Effect of Multivalent Species on the Sulfide and Phosphate Capacities

It is reasonable to expect that when vanadium is present in the slag, the amount of free oxygen ions would increase with an increase in oxygen partial pressure similar to a slag containing iron species. An example of the possible reactions illustrating this effect is given in the following equation.

\[
V^{2+} + \frac{1}{2} O_2(g) \leftrightarrow V^{4+} + \frac{1}{2} O^{2-} \tag{8}
\]

It has previously been reported that vanadium can adopt valence states of +2, +3, +4, and +5 in slags.[67–72] In a previous work by some of the authors, it was found that the majority of vanadium is present as \( V^{3+} \) and \( V^{4+} \) for a related slag at an oxygen partial pressure of about 1 \( \times 10^{-12} \) atm.[68] However, how the slag structure is changed exactly has not been studied in detail in this work.

For calculating the phosphate capacities of the present slags, Equation (9) can be used.

\[
C_p = K_p \frac{f_{\text{po}^{\text{4+}}}}{f_{\text{p}} \times \text{wt} \% P_40_{\text{slag}}} = \left( \frac{\text{wt} \% P_40_{\text{slag}}}{} \right) \times K_p \tag{9}
\]

where \( f_p \) is the activity coefficient of phosphorus in the metal, \( P_{40_{\text{slag}}} \) is the partial pressure of oxygen, and \( K_p \) stands for the equilibrium constant of reaction (10).

\[
\frac{1}{2} P_2(g) \leftrightarrow [P]_{\text{wt} \% \text{Cu}} \ \Delta G^\circ = -125000 + 0.54 T \text{ J mole}^{-1} \tag{10}
\]

The subscript “1 wt% in Cu” in Equation (9) and (10) denotes the standard state of dissolved phosphorus in copper. The standard Gibbs energy change for Equation (10) has been reported by Ikeda et al.[78] The data for activity coefficient of phosphorus dissolved in copper are taken from the study given by Kaida et al.[79] The calculated phosphate capacities for the respective samples are presented in Table 2.

A certain difference between the weighed in and the analyzed slag compositions is noticed when comparing Table 1 and 2. The concentrations of vanadium (III) oxide and silica decreased while the concentration of magnesium oxide increased. Furthermore, phosphorus was transferred from the slag phase to the metal phase, the extent of which increased with a decrease in the applied partial pressure of oxygen. However, the difference between the weighed in and the analyzed slag compositions (except phosphorus) is expected to have no appreciable effect on the discussion of the impact of oxygen potential. This aspect will be further discussed later.

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**Table 2. Normalized experimental results and gas phase conditions.**

| Slag Composition | Phosphate Capacities | Sulfide Capacities |
|------------------|----------------------|-------------------|
|                  | MgO | SiO₂ | “V₂O₃” | P₂O₅ | [P]_Cu | P_{O₂} | CO₂ | C₉ | w% | w% | w% | ppm | atm | at% | × 10⁻³⁵ |
| P-1              | 48.52 | 46.88 | 4.55 | 0.05 | 4390 | 1.73 | 1.33 | 1.73 x 10⁻¹³ | 1 | 7.69 |
| P-2              | 44.76 | 49.75 | 5.08 | 0.41 | 4640 | 1.73 | 1.10 | 3.1 | 3.28 |
| P-3              | 46.44 | 47.59 | 4.83 | 1.14 | 3920 | 1.05 | 1.09 | 7.3 | 1.12 |
| P-4              | 45.29 | 47.40 | 4.89 | 2.43 | 450 | 1.72 | 1.08 | 24.2 | 0.63 |
| P-5              | 45.34 | 48.39 | 4.89 | 1.38 | 240 | 1.72 | 1.08 | 24.2 | 0.67 |

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To ensure the reliability of the experiments for phosphate capacity, two separate experiments, P-4 and P-5, were conducted. The experiments were carried out using the same procedure and under the same oxygen partial pressure. Pyrophosphate, however, was added in different amounts to the samples, as shown in Table 1. Table 2 reveals that the difference of \( C_p \) between these two experiments (P-4 and P-5) is small. It implies that even the amounts of phosphorus are different, and the phosphate capacities are in good agreement, showing satisfactory reliability of the experiments. The agreement between the data for experiments P-4 and P-5 would also suggest that the difference in \( C_p \) obtained at different oxygen partial pressures is so profound, it cannot be due to the experimental uncertainty. Also, the difference in the slag composition shown in Table 2 is not expected to affect the discussion. In the case of sulfide capacity measurement, to check the reproducibility, a repeating run was made with identical conditions (see sample S-9 and S-10 in Table 2). As seen, the results are reasonably reproducible.

To illustrate the effect of oxygen potential on the experimentally determined \( C_p \), the phosphate capacity is plotted as a function of the partial pressures of oxygen in Figure 1a. To help the discussion in later section, Figure 1b shows the effect of oxygen potential on the phosphorus partition between the slag and the metal. The phosphorus partition is defined by the following equation:

\[
L_p = \frac{f_p \times M_p \times P_{O_2}^{5/4}}{M_{P2O_5} \times K_9} \tag{11}
\]

As shown in Figure 1a, an inverse relation between phosphate capacity and oxygen partial pressure is evident. For the same slag composition, the phosphate capacity differed one order of magnitude over the investigated range of oxygen partial pressure, viz., decreasing from \( 7.69 \times 10^{-15} \) to \( 6.27 \times 10^{-14} \) with an increase in the oxygen partial pressure from \( 1.73 \times 10^{-11} \) to \( 1.72 \times 10^{-8} \) atm.

Free oxygen anions are of importance for the removal of phosphorus from metals. An increase in the activity of the free oxygen anion would shift the dephosphorization reaction, Equation (12), to the right-hand side, as free oxygen ions are consumed.

\[
\begin{align*}
[P]_{1\text{wt\%}} & + \frac{3}{2} \text{O}_2^- + \frac{5}{4} \text{O}_2(g) \leftrightarrow \text{PO}_4^{3-} \\
& \tag{12}
\end{align*}
\]

The dephosphorization reaction may also shift to the right-hand side by an increase in the partial pressure of oxygen. However, a production of phosphate anions would consume free oxygen ions accounting to Equation (12).

The assumption of the phosphate capacity being independent of oxygen potential implies that the quotient \( \frac{a_{\text{O}_2^-}^{1/2}}{f_{\text{O}_2}} \) is constant over an oxygen partial pressure range. However, the present reasoning reveals that the assumption of phosphate capacity being independent of oxygen potential may not be the case for slags containing multivalent slag species.

In line with the above-mentioned theoretical consideration, Figure 1a shows a clear decrease in phosphate capacity with increasing oxygen potentials, whereas the slag composition is nearly constant. As previously discussed, an increase in the activity of the oxygen anions is expected with increasing oxygen potentials, Equation (8). An increase in the activity of the phosphate anion is also expected with increasing oxygen potentials, Equation (12). Although both activities have increased, the net result has been a decrease in the ratio of \( \frac{a_{\text{O}_2^-}^{1/2}}{f_{\text{O}_2}} \). This means that the activity of the phosphate anion has increased more than the activity of the free oxygen anion has. This is understandable, as oxygen anions are consumed in the process of increasing the phosphate anion activity. The present experimental results along with the above-mentioned theoretical discussion have evidently shown that the partial pressure of oxygen has a significant influence on the phosphate capacities of multivalent slags. The assumption that phosphate capacity is independent of oxygen potential cannot be applied to slags containing multivalent species. In some of the publications,\(^{[34–38,41,42,55–57]}\) only the phosphorus partitions are reported. However, either the reported \( C_p \) or \( L_p \) would only be valid in the oxygen potential range used in the laboratory experiments. It is well known that high oxygen potential favors dephosphorization, as indicated by Equation (4) and (12). This common knowledge is not in contradiction with the present discussion and the experimental result shown in Figure 1a. The same experimental data in Figure 1b evidently reveal that higher

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**Figure 1.** a) Phosphate capacities as a function of imposed oxygen partial pressures for comparable slag compositions. b) Phosphorus partition as a function of oxygen partial pressure.
oxygen potential does result in higher phosphorus partition \( L_p \) between the slag and the liquid metal, when the slag composition is fixed. Although higher oxygen potential will definitely lead to higher \( L_p \) for any slag, the phosphate capacity \( C_p \) decreases with the experimental oxygen potential (see Figure 1a).

The sulfide capacity was calculated according to Equation (2), and the results are included in Table 2. The corresponding sulfide partial pressure was calculated from the activity of sulfur in liquid copper, according to the following equation.

\[
\frac{1}{2} S_2(g) = S_{20} Cu, \quad \Delta G^o = -120000 + 25.2T J \text{ mole}^{-1} \quad (13)
\]

The activity coefficient data for sulfur in liquid copper were taken from Sigworth and Elliott and extrapolated to the experimental temperature.

From Table 2, it is evident that the sulfide capacity increases greatly when the oxygen partial pressure is increased. The sulfide capacity is increased \( \approx 500 \) times when the oxygen partial pressure is increased from about \( 1 \times 10^{-16} \) to \( 1 \times 10^{-11} \) atm. This change is much greater than the variation due to slag composition at a fixed oxygen partial pressure. It is also worth noting that the sulfur concentration in this slag changes very little with the oxygen partial pressure. If \( C_S \) would be constant over the oxygen range studied, there would be a much greater change in the sulfur concentration of the slag.

Similar as the case of phosphate capacity, it is evident that the sulfide capacity is dependent on the oxygen potential, when the slag contains multivalent species. Unfortunately, a large amount of sulfide capacity measurements have been carried out with slags containing, e.g., iron, chromium, and titanium without considering the impact of oxygen potential. In fact, two of the works were carried out by one of the present authors. This must be told to the industries to avoid misusing of the data. The values may only be true under the same conditions, as the experiments were carried out.

For industrial application, engineers often use the \( C_P \) and \( C_S \) values to calculate the partitions between slag and metal, because the mass ratios between metal and slag always vary. The phosphorus partition has been given in Equation (11). Sulfur partition is expressed in the following equation.

\[
L_S = C_S \times \frac{f_2}{P_{O_2}} \times K_{12} \quad (14)
\]

As shown by this article, without good control and knowledge of oxygen potential in the experiment of \( C_P \) measurement, it is impossible to obtain reliable \( C_P \) or \( L_P \) data. It is evident that the same slag would have different \( C_P \) values and, therefore, different \( L_P \) values according to Table 2. It is the researchers’ duty to report the oxygen partial pressure used in their measurement. As both BOF and EAF slags contain more than 20% FeO, the use of literature \( C_P \) must be extremely careful. Using the literature data for BOF or EAF without consideration of the oxygen potential would possibly lead to very doubtful conclusion. In the development of dynamic model, the oxygen potential varies not only with time but also with the position in the slag. It would be a great challenge to consider these variations when modeling the dephosphorization process dynamically.

It is commonly understood that some solid oxide phases are stable under steelmaking conditions. In this case, the phosphate capacity cannot be used, as the concept would only apply to fully liquid slags. In the presence of solid phase, the use of phosphate capacity would be greatly misleading, as dephosphorization by solid phases depends greatly on the kinetic condition, e.g., mass transfer in the liquid phase and the diffusion in the solid phase. Unfortunately, a careful examination reveals that many phosphate capacity data have been reported for slag containing solid phase, the weight percentages of the solid phase being as high as 25–60%. In addition, the phase diagrams for the systems containing FeO are strongly dependent on the oxygen potential. A detailed discussion regarding the dependence of the phase diagram on the oxygen potential can be found in the publication by Khadhraoui et al. Without a good knowledge of the experimental oxygen potential, one would have great difficulties to use a correct phase diagram and to make sure that the reported phosphate capacities are for the slags containing only liquid.

Sulfur is removed in the torpedo and during ladle treatment. Here, only the latter process is discussed. The composition of ladle slag used for refining varies substantially with the steel grades. In the case of steel killed by aluminum, the slag consists mainly of CaO, Al₂O₃, SiO₂, and MgO. These oxides are stable over a large range of oxygen partial pressures, and the sulfide capacity will remain constant. It is well known that slag is sometimes carried over during tapping from the previous process step; in those cases, the resulting ladle slag might contain 5–10% FeO, even 20% FeO. For steel grades that are heavily alloyed with, e.g., vanadium and titanium, some of their oxides will also be present in the slag. When a slag contains the species having variable valency, the \( C_S \) value can no longer be considered independent of the oxygen partial pressure, and great caution must be taken when using literature data.

Many attempts to model the phosphate capacity have also been made. However, as pointed out by the above-mentioned discussion, to model the phosphate capacity for multivalent slag systems, the term \( \frac{a_{\text{Fe}}^{1/2}}{a_{\text{Mg}}^{0.8}} \) needs to be also considered as a function of the oxygen potential, but not only the slag composition.

### 2.2. Physical Properties

Physical properties, e.g., viscosity and the interfacial tensions between slag and metal as well as between slag and refractory have been frequently used in process development. Although many data for these properties can be found in the handbooks and databases, the suitability of the data and how to use the same need great attention.

#### 2.2.1. Apparent Viscosity

In real industrial practices, the “slag” very often consists of not only liquid phase but also some other phases. It is well known that in the BOF process, the slag usually contains different solid phases, such as undissolved lime particles and precipitated solids, e.g., calcium silicate. When slag foaming takes place in BOF, the slag consists of also gas phase and even iron droplets. Another example of two-phase mixture is the gas plume in an
argon stirred ladle. Hence, the viscosity data for liquid containing second phase are frequently needed in the modeling and optimization of the processes. Very often, a simple model based on the lever rule is used in process simulation. A publication wherein one of the present authors was involved using lever rule in the modeling of sulfur refining in ladle treatment can be used as an example to illustrate this aspect.

Besides the lever-rule model, a number of models have also been developed. Some of these models have a semi-empirical nature based on experimental data. However, the majority of the experimental data has been obtained using aqueous solutions. The huge difference in viscosities between slag (usually > 0.1 Pa s) and aqueous solution limits greatly the application of any of these models to slag system.

Only a few reports on viscosities of solid-slag mixtures are available. Kondratiev and Jak calculated the fractions of solid phase using thermodynamic software for some reported slags and applied Roscoe model to the two-phase mixtures. The comparison of the experimental data with the model prediction does not seem to give a clear conclusion. Wright et al. measured the viscosities of slag with either Al₂O₃-MgO particles or Fe₂O₃ particles.

A careful experimental study on the viscosity of slag-solid mixture was carried out in the present laboratory. In this study, the size and fraction of the precipitated solid phase were measured and reported. The apparent viscosity of the two-phase mixture was found to increase with the increase in the fraction of the solid particles (the particle sizes are in the range of 50-100 µm). As an example, Figure 2 presents the variation of viscosity as a function of the 2CaO·SiO₂ particles in an Al₂O₃-CaO-MgO-SiO₂ slag. As shown in the figure, the Einstein–Roscoe model could be used for the two-phase mixtures up to about 10 vol% of solid phase.

Both the studies by Wu et al. as well as Wright et al. point out that the reproducibility of the results becomes very poor when the fraction of solid particles reaches a certain level, indicating thereby that the liquid has become non-Newtonian at such high fraction of second phase. While Wright et al. find that the viscosity depends greatly on rotation speed when the fraction of particles is above 0.04, Wu et al. report a limit of solid fraction of 0.1, above which the measurements are not possible.

The considerable difference could be due to the types and sizes of the particles used and even their shapes.

The apparent viscosity depends on the particle size of the second phase. It is common knowledge that the same weight (or volume) fraction of the solid particles could lead to very different two-phase mixtures. For example, a mixture with particles having size of a few centimeters would have completely different viscosity compared with a mixture with particles of a few micrometers. The experimental results obtained in the present laboratory in Figure 3 evidently show that the particle size has profound impact on the apparent viscosity of the charcoal–silicon oil mixtures. The results in Figure 3 indicate that using thermodynamic calculation to purely calculate the fraction of the solid phase without the knowledge of the particle size and shape would not provide reliable information to the industrial engineers. In fact, the reported information could even mislead the industry.

In the case of a liquid with another liquid as the second phase or a liquid with gas as the second phase, the situation would be even more complicated. In such cases, the apparent viscosities would involve the energy required to deform the second phase. Besides the lever-rule model, a number of models have also been developed. Some of these models have a semi-empirical nature based on experimental data. However, the majority of the experimental data has been obtained using aqueous solutions. The huge difference in viscosities between slag (usually > 0.1 Pa s) and aqueous solution limits greatly the application of any of these models to slag system.

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In a previous work carried out in the present group, the apparent viscosities of foams formed by both gas–silicon oil and gas–slag have been experimentally measured. For the sake of brevity, only the viscosity measurements of slag–gas mixture are described in this article. To study the apparent viscosities of foaming slag, an induction furnace with a water cooled copper coil was used. The experimental details can be found in a previous publication. The rotation cylinder method with a Brookfield RVDV-II + Pro unit was adopted. Graphite crucibles with 30 mm inner diameter and an inner height of 130 mm were used. In view of the uncertainty introduced using graphite components in viscosity measurement for liquid slags, molybdenum crucibles were used to determine the viscosity of the liquid slag without foaming. For each foaming experiment, 7 g of hot metal (consisting of 3.9 wt% carbon) and 1 g of graphite powder were put in the bottom of the crucibles, before 67 g of the prepared slag was put above them. The slag composition was chosen based on an Linz-Donawitz (LD)-converter slag, namely, CaO(43 wt%)-SiO₂(32 wt%)-FeO(25 wt%). Foaming started about 4 min after the induction was started.

### Figure 2
Variation of viscosity with the fraction of 2CaO·SiO₂ particles and model predictions. Adapted with permission. Copyright 2011, Wiley-VCH GmbH.

### Figure 3
Variation of viscosity with the fraction of charcoal particles with different sizes.
The foam was found to be relatively stable for ≈2 min. The viscosity measurement was started immediately when foaming was observed. While different rotation speeds were used, only one rotation speed was used in each experiment to minimize the effect of slag composition change on the measurement. The reproducibility of the experiments was found to be reasonably good.

Both silicon–oil and slag foams reveal viscosities four to five times higher than the pure liquids. Figure 4 presents the apparent viscosities of gas–slag mixtures (in fact, foaming slags).

The results of the viscosity measurements in Figure 4 show that the foam does not act as a Newtonian fluid. Instead, a shear-thinning non-Newtonian behavior is observed, where the apparent viscosity is lower at higher spindle rotation speed.

It must be mentioned that the results are very likely to vary with the experimental setup and conditions, because the wall effects and type as well as dimensions of the spindle would all have important impacts on the apparent viscosity of a liquid having non-Newtonian behavior. Nevertheless, Figure 4 evidently reveals an increase in apparent viscosity in the foam compared with the pure liquid slag. The apparent viscosity is measured in the range of 0.3–0.5 Pa s in the foam, whereas the viscosity of the pure liquid slag was determined to be only 0.095 Pa s, which is in accordance with the literature. It was also found that even a few volume percent of gas would increase the viscosity dramatically (never decrease). The use of the lever rule would result in great uncertainties in a model calculation to predict the flow, especially in the case wherein the flow is not too turbulent. For example, when simulating the gas plume in a gas stirred ladle, choosing the viscosity value would impose a challenge.

The above-mentioned discussion reveals that using the lever rule to predict the apparent viscosity of a two-phase mixture is far from reality. The viscosity of a two-phase mixture greatly depends on the shape and the size of the particles (or liquid droplets). Without the information about the particles (as some published works did), any model predictions must be used with great caution. The reported apparent viscosities in literature must also be used with great caution, because the two-phase mixtures are likely to deviate from Newtonian behavior, and the measured values could be dependent on the experimental setup.

2.2.2. Apparent Interfacial Tension

In view of the nature of heterogeneous reaction of many materials processes, great attention has been paid to the reaction interfaces. Usually, the interfacial tension is given the foremost importance in the study of interfaces, in general, and slag–metal reactions, in particular. As examples, the dependencies of entrainment of ladle slag into liquid steel and the removal of inclusions to the slag on interfacial tension have been the topic of many researchers. Because of this importance, many studies on the determination of interfacial tensions have been carried out. While a long list of these studies can be found in Slag-Atlas,[115] the present review would not repeat this list. Instead, the references are given when the data are used in the discussion.

To determine the surface tension of a liquid or interfacial tension between liquid and solid or even between two liquids, the sessile drop technique is often used. Measuring the contact angle between the liquid and the substrate plays an essential role in this kind of measurement. To make the discussion brief, this article would mostly focus on the measurements of the contact angle.

The variation of the contact angle between two phases that are not in equilibrium is well reported and documented.[116–121] As such variation is inevitable in a nonequilibrium system, the present focus is not given to this kind of variation. Instead, a discussion regarding the reliability of the measurement and the applicability of the data is given. For this purpose, it is essential to have an in-depth understanding of the dynamic nature of wetting behavior.

Figure 4. Apparent viscosity of foaming slag. Reproduced under the terms of the CC-BY license,[114,176] Copyright 2016, J. Martinsson, B. Glaser, D. Sichen, published by Springer Nature.

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The following theoretical discussion is based on a liquid–solid system, whereas it should also apply to the interfaces between other phases. When a liquid is put on the solid surface, the Gibbs energy change between the two states can be described as

\[ \Delta G_{\text{Tot}} = \Delta G_{\text{Reaction}} + \gamma_{\text{LS}} \times A \]  

(15)

where \( \Delta G_{\text{Reaction}} \) is the Gibbs energy of the reaction for a nonequilibrium system, viz., the reaction between the liquid and solid; \( \gamma_{\text{LS}} \) is the interfacial energy between liquid and solid, and \( A \) represents the interfacial area. The Gibbs energy of the system, \( \Delta G_{\text{Tot}} \), will try to approach zero, because, initially, the liquid phase and solid phase are not in thermodynamic equilibrium.

As the first step of discussion, one could assume that \( \gamma_{\text{LS}} \) did have a value and was constant. In such case, for \( \Delta G_{\text{Tot}} \) to reach zero, the area \( A \) must change to compensate the inevitable change of \( \Delta G_{\text{Reaction}} \) in a nonequilibrium system. The variation of interfacial area \( A \) would consequently result in the variation of the contact angle. Hence, the wetting angle must change with time if liquid and solid are not initially in equilibrium. To
illustrate the inevitable variation of the wetting angle with time, a series of carefully designed experiments were conducted in the present laboratory.\cite{124,128} In this study, the variation of contact angles between different graphite substrates and liquid silicon was studied. The initial apparent contact angle between liquid silicon and graphite depends substantially on the type of graphite, the difference being more than 100%. Irrespective of the types of the graphite, a fast variation of the contact angle with time was observed. The rate of spreading of the Si droplet was found to depend on the heating history as well as the type of graphite substrate.

The variation of the contact angle with time is, in fact, a kinetic factor, depending on the kinetic conditions, for example, the porosity and surface properties of the solid substrate. Indeed, the variation rate of the contact angle in some way represents the reaction rate of the chemical reaction. For the researcher doing the measurement, the moment when the value is taken would be very arbitrary and would also depend on the individuals. At low temperatures (e.g., room temperature), the chemical reactions are usually very slow. Therefore, it is not too difficult to get a stable value for the contact angle. Fortunately, in the processes at low temperatures, the chemical reaction would also be extremely slow. Hence, the reported wet angle (or the surface energy) can be very valuable for engineering. On the other hand, chemical reactions are so fast at steelmaking temperature. The reaction rate greatly depends on the kinetic conditions in the reactor. Whether the interfacial energies obtained somehow arbitrarily in the laboratory with very different kinetic conditions could be used in a real reactor would be a serious question.

In the second step of the discussion, one could assume that the researcher has waited enough long time before taking the value for the contact angle. Usually, a researcher would prepare the solid sample (e.g., refractory) and slag with desired composition before the experiment. To simplify the discussion, one could denote the slag composition as \( \text{Slag}_1 \) and the refractory composition as \( \text{Solid}_1 \). In this situation, the interface will change from the initial state, as the reaction between \( \text{Slag}_1 \) and \( \text{Solid}_1 \) is taking place. When the contact angle does not vary with time substantially, the slag and refractory would very likely have reached a state very close to equilibrium at the interface. However, common sense tells us that there will be concentration gradients in the slag and even in the refractory. The slag at the interface would have a very different composition, \( \text{Slag}_2 \). Similarly, the composition of refractory at the interface would have become \( \text{Solid}_2 \). Unfortunately, the reported values are usually addressed to the system of \( \text{Slag}_1 - \text{Solid}_1 \), but not \( \text{Slag}_2 - \text{Solid}_2 \). Also, considering the concentration gradients in the two phases in contact and the difficulties in chemical analysis at the interface to report the values for \( \text{Slag}_2 - \text{Solid}_2 \) would be technically very difficult. Also note that the systems of interest to the engineering team are usually the systems far from equilibrium. The misuse of data obtained for system very close to equilibrium, e.g., \( \text{Slag}_2 - \text{Solid}_2 \) for the intended system, e.g., \( \text{Slag}_1 - \text{Solid}_1 \) would greatly mislead the process optimization. In fact, this situation does happen in many studies on inclusion removal. A discussion about this will be given in the later section of the communication.

As the third step of the discussion, the authors would point out that the definition of the “interfacial tension” in a nonequilibrium system is in great doubt. One can only measure the chemical potentials in a system at equilibrium, for example, slag–metal equilibrium. The same would apply to interfacial tension, because the value cannot be measured between two phases that are not in equilibrium. Even when the term “apparent” is used, one should still be cautious, because adoption of the data requires a careful examination of both the kinetic conditions in the reality and the experimental conditions in the laboratory. Moreover, in a nonequilibrium system, both \( \Delta G_{\text{reaction}} \) and the interfacial area \( A \) will change simultaneously. In addition, even the term of \( \gamma_{\text{LS}} \) would vary with the variation of the slag and solid compositions. The apparent interfacial tension would depend on all these variations. It is indeed a kinetic description. How to treat the published values of apparent interfacial tensions poses a great challenge.

3. Some Slag Phenomena

3.1. Slag Foaming

Foaming slag plays an important role in the BOF and EAF steelmaking processes. Foam enhances the reactions between the steel and the slag: it protects the furnace lining as well as isolates the heat significantly.\cite{124} The phenomenon has, therefore, been studied since its first breakthrough during the 1950th.\cite{124–128} Foaming slag is complex by nature. It is a mixture of gaseous, liquid, and solid phases, which interact both physically and chemically during the processes.\cite{128,129} The slag is, therefore, constantly changing its physical and material properties, making it difficult to model and predict.

Due to the complexity, it is difficult to conduct relevant and reliable experiments on foaming slag. Many parameters will interfere with the results, and to interpret, the results can be very challenging. A combination of large industrial trials and carefully designed laboratory experiments where parameters can be isolated is perhaps the best strategy to better understand this phenomenon.

3.1.1. Structure of Foaming Slag

Today, many researchers, including the present authors,\cite{112,110,131} design and conduct cold model experiments to imitate the foaming phenomena. Although using a cold model can be very helpful and efficient, the results in cold model studies should be used with caution. It is not possible to directly transfer the results obtained in cold model study to a foaming slag.

While the foam structure in cold model study, e.g., foams of silicon oil–gas mixtures are well known, the structure of foam of slag has been studied very little. In a previous article by the present authors, high-temperature experiments were conducted to study the structure of foaming slag, using slags of different compositions in the CaO–SiO₂–MgO–FeO system. The different slag compositions led to different viscosities.\cite{132} An induction furnace was used, in which a graphite crucible filled with a CaO–SiO₂–MgO–FeO slag and 7 g of pig iron containing 3.9 wt% C was heated. The slag and iron were melted already after \( \approx 4 \) min, at which point the foaming started by the reduction of FeO. When the foam was fully built up, the induction furnace was turned off. The slag then froze in a few seconds, maintaining
the structure of a foaming slag. Thereafter, the crucible was immediately filled with a transparent epoxy before being cut both horizontally and vertically. An example of the results is shown in Figure 5, where Figure 5a shows the foam of a slag with dynamic viscosity of 100 cP, 150 cP (Figure 5b), and 200 cP (Figure 5c). The surface tension of the different slags was relatively constant around 200 mN m$^{-1}$.

One can see that the structures of the different foams are far away from the common cold models based on, for example, silicone oil. In reality, the foam has a larger variation and is much more complex. Note that the slag in Figure 5a has the lowest viscosity, and the slag in Figure 5b has higher viscosity, whereas the slag in Figure 5c has the highest viscosity. As shown in Figure 5a, many small gas bubbles are kept in the slag, forming a foam that has much lower gas fraction in comparison with silicon foam. Figure 5b shows a foam consisting of both small bubbles and bigger gas bubbles. On the other hand, slag shown in Figure 5c cannot really be classified as a foam. In this slag, gas forms channels, but not small gas bubbles. A simple comparison between the slag foam and the silicon foam evidently indicates that although cold model experiment can be a good tool to study qualitatively the foaming behavior, direct application of the cold model results to slag at steelmaking temperature must be done with great caution.

3.1.2. Behavior of Foaming Slag

There are today still many questions regarding foaming slag. The gap between the industrial reality and academic studies is considerably large. Many academic models have been developed, both empirically and theoretically. Due to the lack of knowledge of the nature of foaming slags, the quality of the model description about the real slag foam needs careful evaluation.

The height of a foam is considered the most important characteristics. Due to its simplicity, the foaming index, $\Sigma$, is widely used to express the foaming height of a specific slag, accepted both in the academy and in the industry. It was first defined with Equation (16), where the foaming height $\Delta h$ is expressed by superficial gas velocity, liquid viscosity, density, and surface tension.$^{[133,134]}$

$$\Sigma = \frac{\Delta h}{\Delta V_g} \to 5.7 \times 10^2 \frac{\mu}{\sqrt{\rho \sigma}}$$

The relevance of the foaming index has although been challenged.$^{[130,139,152-155]}$ According to the index, the foaming height will continuously increase with increasing viscosity. However, room temperature experiments conducted in the present laboratory$^{[160]}$ have demonstrated that the foaming height only increases with increasing viscosity to a certain maximum value, after which the foam height decreases with increasing viscosity.

Similar results were also seen in the high-temperature experiments conducted in the induction furnace mentioned earlier; see result in Figure 6. When the viscosity was relatively low, as the slag shown in Figure 6a, the foam was well developed with a high stable foaming height, and it was possible to see bubbles leaving the slag continuously. When the viscosity was increased, the foaming height started to decrease, and bigger bubbles could be seen escaping from the top of slag, as shown in Figure 6b. When viscosity was too high, on the other hand, as shown in Figure 6c, the gas accumulated in the bottom of the crucible and at the interface between the slag and the pig iron, before leaving the slag as a long gas plume, pushing the entire slag aside.

Also, as described in Section 2.2.1, a foam behaves as a shear-thinning non-Newtonian fluid.$^{[112,114,156-159]}$ In a foam, any movement would need additional energy to deform the bubbles and the foam. This means that when a foam has been established, the new generated bubbles will interact differently with the foam dependent on the bubble size. Small bubbles may be trapped in the foam, whereas bigger ones just pass through it. The foaming index concept seems to be too simple to describe the real slag foaming in the reactor.

Even though some sophisticated attempts have been made to predict the foaming height of laboratory and industrial trials with satisfying result,$^{[144,145]}$ Computational fluid dynamics (CFD) still has a long way to go before the models can describe a general foaming process. The computational tools used today to describe the flow of a foam often use, for example, the Einstein–Roscoe equation to describe the apparent viscosity of the foam and use the Navier–Stokes equations to calculate the movement.$^{[160]}$ The Navier–Stokes equations are proved to be acceptable for Newtonian single-phase fluids. It is although not ideal for describing a foaming slag. In fact, assuming Einstein–Roscoe equation and Navier–Stokes equations could be used to foam is subjected to great question. A slag containing about 10% of second phase is hardly to be Newtonian. Several computational models from the last decades have resulted in movies and figures of foaming slag behavior or slag flow in LD converters where the
slag is in the form of foam in most time period of the process.\textsuperscript{[141,142,161–168]} The flow of foaming slag predicted by the CFD model must be carefully examined. Some experiments have been conducted in the present laboratory. The results reveal confidently (on the contrary to many models) that foam does not actually flow at all. Instead, when a gas plume moves through a foam, only the area very close to the plume is affected.\textsuperscript{[112]} Further laboratory research is definitely needed to improve the foundation to better understand the movement and behavior of foaming slags.

3.1.3. Particle and Droplet Movement in Foam

The movement of particles and droplets in foaming slag is of interest to understand the reaction mechanisms in the BOF furnace. There are several models to describe the velocity of a falling particle or droplet in a fluid. The simple equation Stokes law can be seen in Equation (17), where $v$ is the terminal velocity of the particle, $\rho_{\text{particle}}$ and $\rho_{\text{fluid}}$ are the densities of the particle and fluid, $\mu$ is the viscosity of the fluid, $g$ is the gravity, and $R$ is the radius of the falling particle. It is well known and proved applicable for ideal systems where a spherical particle falls through a Newtonian single-phase fluid.

$$
 v = \frac{2}{9} \frac{(\rho_{\text{particle}} - \rho_{\text{fluid}})}{\mu} g R^2 
$$

To check how well the Stokes law can describe the velocity of falling particles in non-Newtonian fluid, the residence times and velocities of different solid particles (different densities and sizes) were measured while they were falling in different foams by the present group.\textsuperscript{[133]} The specific experimental settings and conditions can be found in the earlier publication. It was found that the surface tension plays a significant role in the residence time, which is, of course, not considered in Stokes law (see Equation (17)). Higher surface tension of the liquid phase would lead to lower velocity and longer residence time of the falling particle. This is in accordance with the theory that it is more energy consuming to deform a liquid surface, compared with a liquid bulk.\textsuperscript{[113]} A foam is indeed a two-phase fluid built up by surfaces. In the same article, a semiempirical model of the particle velocity was developed by regression to fit the experimental results; see Equation (18). In the equation, $v$ is the apparent velocity of the falling particle, $d_{\text{particle}}$ is the particle diameter, $g$ is the gravity, $\rho_{\text{particle}}$ and $\rho_{\text{foam}}$ are the density of particle and foam, $\sigma_{\text{liquid}}$ is the liquid surface tension, $d_{\text{bubble}}$ is the bubble diameter, $\mu_{\text{liquid}}$ is the dynamic viscosity of the liquid phase, and $a$–$c$ are the parameters to fit the model.

$$
 v = \frac{\left(\frac{2}{9} \times d_{\text{particle}}^2 \times g \times (a \times \rho_{\text{particle}} - b \times \rho_{\text{foam}})\right) - c \times \left(\frac{\sigma_{\text{liquid}}}{d_{\text{bubble}}}\right)}{3 \times \mu_{\text{liquid}} \times \pi}
$$

As shown in Figure 7, the particle velocity calculated by Stokes law is up to ten times higher than the measured velocities as well as the velocities calculated by Equation (18). The main difference between the semiempirical model, namely, Equation (18) and Stokes law is that the semiempirical model also includes the energy needed to deform and push the bubbles aside during the fall.
Both the model predictions and experimental results evidently reveal that the common equation used today may not be the best choice to describe the movement of particles in a foam.

It should be mentioned that some of the current decarbonization and dephenorization models in BOF include the function of iron droplets in the slag foam, for example, the works of Brooks et al., Dogan et al., and Rout et al. Based on the work by Brooks et al. in 2005, the referred models have been continuously developed throughout the years, including reactions in the oxygen jet impact zone, the metal bath–slag interface, and in the emulsion between metal droplets and slag and gas. It is interesting to see that these models are in good direction and are getting improved with time. The residence time is indeed an important parameter for understanding the kinetics of reaction in the process and must be included to obtain sound models.

The slow movement of particles in the foam would indeed suggest new consideration of the process models for BOF and EAF, because the long residence time of the droplets would make the contribution of the droplet-slag reaction more profound than what researchers have believed.

### 3.2. Interfacial Phenomena in Inclusion Removal

The increasing demand on the quality of steel makes the cleanliness of steel substantially crucial. An efficient removal of inclusions to the top slag in ladle treatment has, therefore, become an important task for the engineers and researchers. A number of models have been developed to describe the separation of nonmetallic inclusion to the slag. In the early stage, the models assumed that all inclusions reaching the interface between the steel and the slag would be removed immediately from the steel. The importance of both interfacial energy and the existence of a liquid metal film has been later realized. The later models have a sound physical description of the phenomena of inclusions crossing the slag–metal interface.

The focus of the present discussion is not the model for inclusion removal, but the data are used for the models. As mentioned in Section 2.2.2, it is impossible to determine the interfacial tension in a nonequilibrium system. On the other hand, the situation in the secondary steelmaking, e.g., ladle treatment, is rather complicated.

In the initial stage, the slag has not reached equilibrium with the liquid metal. This nonequilibrium condition is essential for steel refining. During this stage, the first term on the right-hand side of Equation (15), \( \Delta G_{\text{Reaction}} = \Delta G_{\text{Slag/metal}} \) (Slag/metal stands for the slag–metal reaction), is very profound. At the meantime, the use of the data \( \gamma_{\text{LS}} \) would be in great question, because the measurements of interfacial tension could only be done when the steel and slag are in equilibrium. In addition to the interfacial tension between steel and slag, the interfacial tension between the oxide inclusion and steel and the interfacial tension between inclusion and slag are also needed for the model application. In view that the inclusions are extremely small and have stayed in the metal for long time, at the inclusion–metal interface, the term \( \Delta G_{\text{Reaction}} = \Delta G_{\text{Inclusion/metal}} \) (Inclusion/metal stands for inclusion metal reaction) may be negligible. However, in the case of slag–inclusion interface, the first term \( \Delta G_{\text{Reaction}} = \Delta G_{\text{Slag/Inclusion}} \) (Slag/inclusion stands for inclusion and slag reaction) is expected to play essential role between slag and inclusion. This term is due to the dissolution of oxide inclusion into the slag, depending greatly on the composition of the slag and the composition of the inclusion.

In the later stage of ladle treatment, when slag and metal have almost reached equilibrium, the first term in Equation (15), \( \Delta G_{\text{Reaction}} = \Delta G_{\text{Slag/metal}} \), would be negligible. The value of \( \gamma_{\text{LS}} \) between slag and metal is, therefore, measurable. On the other hand, inclusion and slag are still not in equilibrium.

In a previous work carried out in the present laboratory, the mixing behavior between liquid silicon and slag was studied. The two liquids were stirred by an impeller. It was evidently observed that a huge number of tiny silicon droplets are formed initially in the slag on the start of stirring. At the same stirring intensity, the small droplets vanished when slag and silicon were reaching equilibrium (after about 300 s). The results revealed that the chemical driving force played dominating role in determining the interface, whereas the interfacial tension would only become important when the slag and metal were reaching equilibrium. It is an excellent example showing that the interfacial phenomena vary with the process due to the progress of chemical reaction.

Modeling of inclusion removal is a challenging task. The present discussion is meant to help in improving the modeling approach. It might be worthwhile to consider including the \( \Delta G_{\text{Reaction}} \) terms in the model, as the reaction is important in most of the period of the process. One can even consider neglecting the second term when the term \( \Delta G_{\text{Reaction}} \) is dominating, especially in the early stage of the process. In the later stages of the process, one should be able to measure the value of interfacial tensions between metal and slag as well as between the inclusion and the metal. Nevertheless, the model needs to consider the change of the interfacial data.

### 4. Final Remarks

In view that the present communication addresses several areas that show a gap between the academic research and the industrial
realistic and all the involved topics still require in-depth understanding, the authors prefer giving some remarks, instead of conclusions to summarize the discussion. It is hoped that these remarks would provoke new research activities that would lead to more reliable results and information for steelmaking practices.

1) The use of literature data must be done with caution. For example, the reported slag data, such as slag capacities involving multivalent oxide species, could only be applicable in the oxygen potential range wherein the laboratory experiments have been conducted. In a real industrial reactor, the oxygen potential varies with position and time. These variations would impose additional challenges for the development of the dynamic process model.

2) The viscosities of two-phase mixtures do not comply with simple lever rule. Even the more complicated models could only be applied in the region of relatively low fractions of the second phase. Above a certain fraction of the solid/liquid/gas phase, the two-phase mixture is no longer Newtonian. Beyond this limit, the reported apparent viscosities are system-dependent. The apparent viscosities depend not only on the fraction of the second phase, but also on the size of the particles and droplets as well as their shapes. Researchers should not just take any model or reported apparent viscosity in their modeling for processes.

3) One should be very careful in adopting interfacial tension data when the interface is not at equilibrium. In a nonequilibrium system, the chemical reaction driving force, viz., the Gibbs free energy would be more important than the interfacial energy term. The more away the system is from equilibrium, the more important is the chemical driving force. It is recommended that a model describing the interfacial phenomena, e.g., inclusion removal, should consider the chemical driving force.

4) Theoretically, it would be impossible to measure the interfacial tension in a nonequilibrium system at elevated temperature, where the reaction usually proceeds fast. The apparent interfacial tension obtained would depend greatly on the kinetic conditions in the experimental setup. Therefore, the application of these data to the process, which would have very different kinetic conditions, would need great caution.

5) The current knowledge of slag foaming is rather limited. Foam of slag in steelmaking has a very different structure in comparison with foam in cold model, e.g., silicon–gas mixture. The application of cold model results could only be done in a qualitative manner. Foams are non-Newtonian. The use of the CFD technique in the simulation of metallurgical foaming slag is questionable. This is particularly true in the case of BOF and EAF reactors, where slag foaming takes place dominantly.

6) The movement of solid particles and droplets in slag foam is profoundly slower than predicted using models for pure liquid. The slow movement of iron droplets in the foam would suggest new consideration of the process models for BOF and EAF.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
interfacial phenomena, slag, slag foaming, thermochemical properties, thermophysical properties

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