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# MOLTEN SLAG PROPERTIES AND THEIR USE IN STEELMAKING PROCESS CONTROI

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**Synopsis:** This text discusses models which have been recently developed to represent physical (viscosity) and thermodynamic (phase diagrams, component activities) properties of multicomponent iron- and steelmaking slags. For industrial applications, the development of such models is the necessary complement of basic experimental work on binary and ternary systems. Beyond equilibrium properties of homogeneous systems, comments are made on some of the aspects of slag behavior that are only poorly documented, e.g. the rheology of liquid + solid slags.

Applications of this information for the control of steelmaking operations are presented. The selected examples concern the protection of refractory linings by slag coating of reactors walls, and the monitoring of actual steelmaking reactions in ladle metallurgy, and in inclusions control.

**Key words:** viscosity, activities, phase diagrams, slag models, slag coating, inclusion control.

## 1. Introduction

Each progress in the knowledge of slag properties provides new possibilities of more accurate control of the iron- and steelmaking processes. Examples can be taken along the whole line of production

- in the sintering process, control of liquid phase formation, from the fine fraction of sinter mix components,
- in the blast furnace, numerous applications concerning, the beginning of melting temperature, the formation of solid accretions on the walls, and the overall slag composition selection,
- in hot metal pretreatments and refining processes, an essential role upon liquid metal composition control,
- in the control of solid steel properties, through the influence of inclusions initial shape, of their rheology during steel solid state shaping, of their relative expansion coefficient, and their ability to influence ferrite crystallization (i.e. in oxides metallurgy).

We will first present and comment some frequently used properties ; as examples, we have selected viscosity and thermodynamic properties: phase diagrams and components activities. Beyond equilibrium properties of homogeneous systems, comments will be made on some of the aspects of slag behavior that are only poorly documented, e.g. the behavior of liquid+solid slags.

Among the above quoted applications of slag properties, most will not be detailed here since they are developed in several following communications in this Conference. Selected examples concern the protection of refractory linings by slag coating of reactors walls, and the description or the prediction of actual steelmaking reactions in ladle metallurgy, and in inclusions control.

## 2. Slag properties and behavior

In recent years, control of high temperature metal-slag reactions and metal-oxide inclusions has significantly progressed through the use of models describing physical and thermodynamic properties of multicomponent slags; development of such models is the necessary complement of basic work on binary and ternary systems.

In order to represent industrial processes, these models should be able to describe multicomponent systems, as the steel quality is very often conditioned by minor components of the slag. They are also required to be reasonably time efficient as, in kinetic reaction models, the values of slag properties have to be reactualized many times during the course of treatment to take into account slag evolution.

The amount of work, needed for experimental determination in large portions of systems containing more than three components, is such that one cannot hope to get such data in a foreseeable future. This explains the increasing interest for mathematical descriptions of slag properties. Preference is of course granted to models whose parameters depend mostly upon data obtained in simple binary or ternary systems.

Far from removing interest for fundamental approaches of slag properties, the development of these models for industrial applications has strongly increased the incentive for experimental determinations and theoretical studies. Development of the models help to focus attention on the most decisive missing data, and to grade the determinations that should be undertaken.

## 2.1 Viscosity estimations

Viscosity measurements [1] over a large range of temperature have shown that the best fit of experimental data, as a function of temperature, is obtained with Frenkel relation :

$$\eta = A.T.\exp(B/T)$$

where A and B are viscosity parameters, T the temperature in Kelvin.

G. Urbain [1] has also shown that such an equation can be justified by theoretical considerations, and should be preferred to the more widely used Arrhenius relation,

$$\eta = \eta_0.\exp(E/RT),$$

although the latter is sufficient to describe viscosity variations over a limited range of temperature. Furthermore, the same author has also shown that the values of the two parameters,"A" and "B", are linked by a relation :

$$-\ln A = m \cdot B + n$$

where m and n are two constant parameters, determined experimentally, characteristic of a large number of liquids. Literature data have been used to estimate the values of m and n for several of these categories of liquids [1]:

- liquid silicates, alumino-silicates and ionic liquid oxides,
- network liquid oxides, $GeO_2$, $SiO_2$ ,
- molten salts, (Cl, Br, I, $NO_3$, $CO_3$) (Li, Na, K),
- liquid metals, In, Zn, Pb, Cu, Ag, Au, Fe, Co, Ni,
- H-bonded liquids, such as water, ethanol, methanol, mineral oils, glycerol, glucose.

An example of experimental fit of this relation is presented on Figure 1 for some of the liquids belonging to the silicates and oxides family (in this case m = 0.298 and n = 11.15).

This leads to the remarkable result that viscosity as a function of temperature can then be described with only one parameter, B, that should be determined experimentally.

High temperature slag viscosity measurement are always difficult and our sets of data, are restricted to a number of binary and ternary systems such as $CaO-Al_2O_3-SiO_2$, and to discrete data on more complex systems. For viscosity estimations, it has been shown, with a large number of experimental confirmations, that one can rely on approximations of parameter B using linear interpolation of molar compositions between simpler systems, (e.g. $SiO_2-Al_2O_3-X$), (where X refers to various basic oxides). This provides a fair prediction of the order of magnitude of viscosity for most of the oxide slags ; it allows to compare accurately slags of the same composition family. This type of

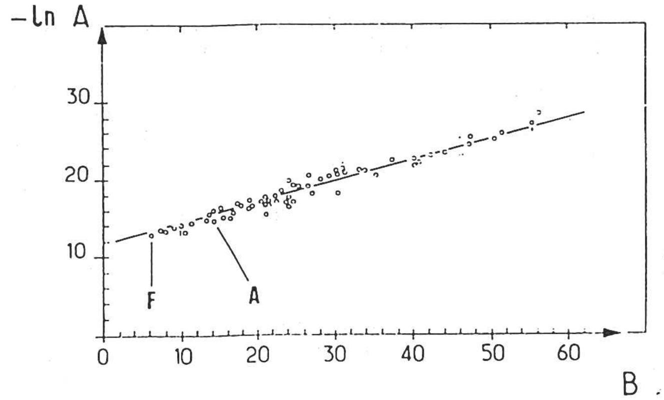



**Figure 1:** Correlation between A and B viscosity parameters for oxide, silicate, and alumino-silicate melts.
F stands for liquid FeO, A for liquid alumina.

information is often sufficient for most of the process analyses. Thus viscosity measurements should rather be devoted to precise determinations of the single parameter B for systems with a small number components, rather than to measurements for discrete compositions in industrial systems with a very large number of components. In the latter case the most important information, concerning slag rheological behavior, is the actual constitution of the slag, i.e. the presence of solids in suspension.

## 2.2 Modelling thermodynamic properties

These last few years have seen a large amount of experimental studies on various slag systems, in particular from Japaneese teams of S. Ban-Ya and N. Sano. An exhaustive review will be published in the near future in the revised edition of the Slag Atlas [2]. In addition, a quite vivid development of slag models has taken place, going from simple correlations in terms of composition variables or basicity indexes (for instance optical basicity [3]) to more sophisticated statistical thermodynamics models [4-5].

Although the simple correlations can be of practical interest when properly applied within the composition domains in which they have been fitted, their use outside of these domains can lead to considerable errors (for instance, errors of several orders of magnitude can be made when the slag metal sulphur partition coefficient is evaluated from published optical basicity correlations, for typical converter slag compositions).

This difficulty is largely reduced when applying the more complex statistical thermodynamics models. Thus, the model developed at IRSID [6] allows a very accurate description of the properties (phase diagrams and component activities) in the entire composition domain of the system

$$SiO_2 - Al_2O_3 - Cr_2O_3 - Fe_2O_3 - CaO - CrO - FeO - MgO - MnO - S,$$

and work is in progess for systems containing, in addition, $CaF_2$, $Na_2O$, $P_2O_5$ and Ti oxides. As an illustration, Figure 2 shows the very good agreement between model calculations and experimental determinations of the phase diagram and sulphide capacity in the $SiO_2$ - MgO - MnO system.

This slag model has been inserted in user friendly computer programs for the evaluation of the equilibrium between slag and metal or inclusions and metal. These programs are used on a routine basis in several French plants.

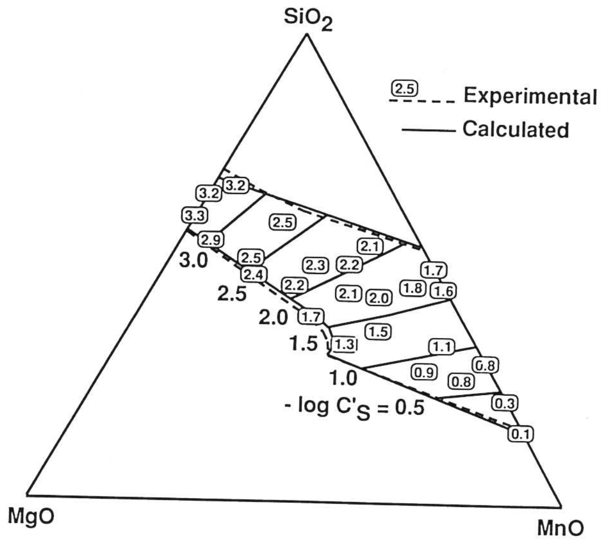



**Figure 2:** Comparison of experimental and computed phase diagram and sulphide capacity, using IRSID slag model, in the $SiO_2$-MgO-MnO system at 1650°C.

## 2.3 Needs of further research : rheological properties of liquid + solid slags

In a large proportion of industrial processes, slags are composed of a mixture of liquid and solids. This is due

- to the progressive reaction and melting of the initially solid slag components, or
- to equilibrium conditions such that the slag may be locally below its liquidus temperature.

This may be an undesirable situation, as it can hinder the slag capacity to play its part in the refining process, for example to extract impurities. On the contrary, it may also be a highly desirable situation in order to prevent excessive aggression of the refractories. The slag coating process in oxygen converters is now a major tool to extend lining life.

Despite its importance for process control and for refractories cost, the behavior of mixtures of liquid and solid oxides has not been extensively characterized. Most of the reasoning is based upon data obtained for metals. A few exploratory measurements have been performed using a high temperature Couette viscometer, similar to the one built by Joly and Mehrabian [7]. Experimental characterizations of slags rheology below their liquidus temperature, show that the apparent viscosity-temperature curve is very similar to the one obtained for metals [8]. Microscopic examination of iron- or steelmaking slags after quenching shows that their most frequent primary crystals, composed of lime, magnesia, or calcium silicates, precipitate with rounded shapes. Furthermore, their crystal size is not very dependant upon thermal and mechanical history. More detailed knowledge of their rheological behavior should not, therefore, be as complicated as in the case of metal slurries whose crystal shapes may vary from thinly branched dendrites to rounded particles, depending upon the thermomechanical history.

An example of "apparent viscosity"-temperature curve is shown on Figure 3. One of the important characteristics of the rheology of liquid-solid oxides mixtures is the decrease of apparent viscosity when stirring energy increases. Advantage is taken of this behavior in the control of converter coating, as explained below.

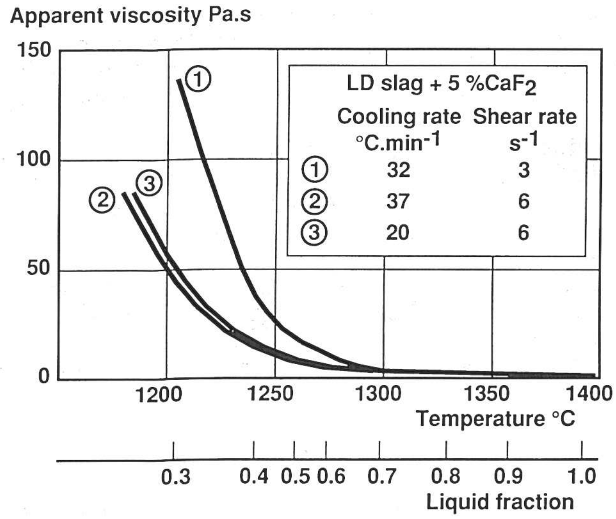



**Figure 3:** Example of "apparent viscosity" as a function of temperature, for an LD type slag for different experimental conditions.
Note the strong influence of shear rate, and the small influence of cooling rate, in the explored range, below liquidus temperature.

## 3. Examples of applications of slag properties in iron and steelmaking process control.

### 3.1. Refractories coating in steelmaking reactors

When emptying a reactor, the slag layer is brought into contact with wall portions previously covered with metal. This process has to be under control, since it can turn out to be either a quite favorable or detrimental for refractories life : it can deposit a protective layer or promote corrosion.

Remarkable converter lining life improvement has been obtained through an accurate control of slag composition [9]: at the end of each heat, the layer of slag deposited on the walls has a consistency such that a protective coating is obtained. However, when too thick layers of slag are deposited on the walls of a ladle, its free volume available for steel may be undesirably decreased.

In the analysis of these coating processes, three successive steps can be distinguished :

- the streaming of slag on the converter walls during tilting, leaving a limit layer of adequate thickness,
- the adhesion of this layer, that prevents its sliding or its unsticking during further converter movement, governed mostly by surface forces,
- the complete solidification of the deposited layer, the "setting", so called by analogy with the phenomena occurring with glues or with cements.

We will comment only the first point: slag flow on the converter walls

When they are completely liquid, basic slags have a very low viscosity, around $5.10^{-2}$ Pa.s; only a thin film remains to coat the lining, and the remaining flows over its surface. When completely, or almost completely solid, the slag takes different shapes depending upon the type of conditions during solidification : as slab portions, or chunks with little agitation, or as granular material when strongly stirred. In neither case, can they be adequate for coating : they do not adhere to the walls.

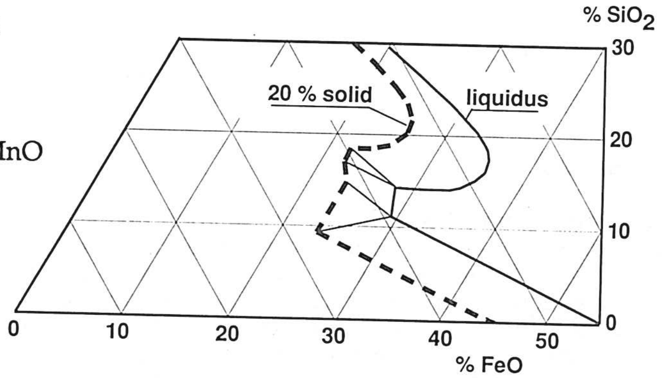
When the proportions of solid phases suspended in the liquid are in adequate proportions, the mixture behaves as a paste coating the walls with a thick layer. Therefore the whole process should be conducted in such a way that the liquid / solid proportions in the slag towards the end of the heat are correctly adjusted. Accurate knowledge of thermodynamic properties and of slag phase diagrams is required in order to define the optimum refining conditions in order to obtain the desired state : studies performed on industrial oxygen converters have shown that optimal coating conditions are satisfied when the proportions of solids are around 20 %. Due to the type of rheological behavior of these liquid-solid mixtures, these proportions are such that:

- mobility remains very high in the intense stirring conditions prevailing during blowing : refining reactions rates remain high,
- consistency corresponds to a mushy state in quiet conditions, during the slow movements of the metal slag interface.

Figure 4 shows schematically the method to select the operational conditions for the converter. On a pseudo-ternary diagram presenting the major slag components, the thermodynamic model provides data to draw the heavy dotted line corresponding to the aimed compositions of slags, containing 20 % solids at end-blow temperature. Selection of a definite operating point on this curve can then be made taking into account the other metallurgical requirements in terms of basicity or iron oxide activity.

Such a slag adjustment allows to maintain stable operation of porous elements in the LBE type converters, or to maintain long life of refractories around tuyeres, without excessive increase of bottom thickness layers, in all types of mixed blowing converters.

**Figure 4:** Part of the phase diagram showing the slag compositions corresponding to 20% solid in equilibrium with liquid, in the $SiO_2$-CaO-FeO-2% $P_2O_5$-4% MgO-4% MnO system at 1650°C.




## 3.2 Inclusion control during ladle treatments, casting and solidification

The steelmaker is more and more often led to make various treatments designed to control the composition of non-metallic inclusions, generally in order to decrease their harmfulness. At present, these treatments consist either in adding calcium, mainly for aluminum killed steels, or in adjusting the metal composition by reaction with an adequate slag during ladle treatment. The slag model is the center piece of procedures which have been developed to optimize these treatments.

The principle of the calculation of the equilibrium inclusion composition rests on an original procedure of multiphase equilibrium calculation that, from the global analysis of a steel sample, determines the composition of liquid metal and the compositions and amounts of oxides and sulphides that have possibly been precipitated at a given temperature.

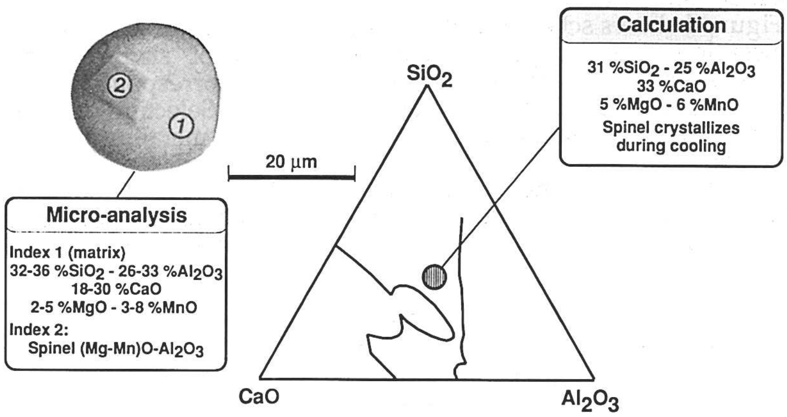
The model was first validated on Al-killed Ca-treated steels [10], and more recently applied to Si-Mn deoxidized steels [11].

The example presented concerns a high carbon steel (0.7% C - 1% Mn and 0.35% Si) containing trace amounts of Al, Ca and Mg, and shows that the inclusion population is strongly heterogeneous. A first family shown on Figure 5 consists of residual deoxidation inclusions, in which only 5 ppm oxygen out of the total 16 ppm are fixed. Their calculated composition is in very good agreement with the microprobe analysis of a large number of inclusions observed on as-cast metal samples (16 out of about 50). The calculations also show that the remaining 11 ppm of oxygen are fixed in manganese alumino-silicate inclusions formed during metal solidification or corresponding to reoxidations during casting. Again, the calculated compositions are in good agreement with analysed individual inclusions. As a general rule, the composition of these inclusions will be highly influenced by traces of easily oxidizable elements (Al, Ca, Mg) present in the liquid steel. Too high values in these elements can lead to the presence in the product of inclusions partially or totally crystallized (alumina, spinels, ...).

A procedure based on the slag model is used to define the appropriate ladle slag composition and treatment conditions that will lead to such small amounts of Al, Ca and Mg in liquid metal. It computes the complete metal composition resulting from slag-metal equilibrium in the ladle. To do so, it uses the value of oxygen potential calculated for relevant element/oxide couples (for instance Si and/or Mn in the case of weakly deoxidized steels), and from this information deduces the transfers occuring between slag and metal, especially for highly oxidizable trace elements: Al, Ca and Mg.

For this steel grade, in order not to exceed an Al content of about 5 ppm in liquid metal, and thus avoid the formation of inclusions containing alumina crystals at the beginning of metal solidification, it is necessary to aim for a slag composition corresponding to a $CaO/SiO_2$ ratio of about 1.1 with $Al_2O_3$ contents that do not exceed 10% and MgO contents around 5%. The slag alumina content has to be reduced further if the slag basicity increases due to an increase in CaO or MgO contents.

**Figure 5:** Prediction of primary deoxidation inclusions.
Steel composition:
C : 0.7 %
Mn : 1.0 %
Si : 0.35 %
Al : 8 ppm
Ca : 3 ppm
Mg : 0.4 ppm
O : 16 ppm




## 4. Conclusions

Two examples have been chosen to illustrate that slag properties models are an esential tool in the control of processes and of steel products characteristics:

- rheology of converter slag can be adapted for an optimum coating of reactor walls by prescribing adequate proportions of solids in the slag before tapping,
- inclusions composition control during ladle treatments, casting and solidification is performed in a more accurate way by using a slag thermodynamic model that takes into account the oxides of all the dissolved elements, even when present in trace concentration.

Further progress is, in many cases, hindered by the lack of experimental data: very much work is still needed in the experimental determination of physical and thermodynamic properties. Models allow to concentrate the experimental determinations on simpler systems, binary and ternary, instead of the multicomponent industrial compositions, while providing sufficient accuracy for practical use.

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