Slags and fluxes are important interchangeable dimensions of pyrometallurgical processes. They can increase the efficiency of the smelting, converting and refining processes and improve the quality of the final products. A good slag should have appropriate physicochemical properties such as low liquidus temperature, optimal viscosity, maximum ability to attract undesirable elements, minimum potential of attracting valuable elements, etc. A good flux, on the other hand, when properly used, can considerably improve the physicochemical properties of the slag since by modifying its chemical composition it could decrease the liquidus temperature, improve viscosity, etc. Consequently, the choice of a good slag and the corresponding fluxing strategies has become indispensable in most of industrial processes. However, the properties of multicomponent slags as well as the effect of several fluxes are known only empirically and confusion exists in the literature and in the industrial practice. In today’s reality of frequent changes in the composition of raw materials and that of the fluxes themselves, in the existing or new developing technologies, the quantification of the thermophyiscochemical properties of multicomponent slags and the effect of fluxes becomes indispensable. This paper reviews some of the work carried out by the author’s group during the last ten years on the quantification of the thermophyiscochemical properties of multicomponent slags and on the effect of fluxes in several smelting and converting processes in close relation to their individual characteristics. Several examples have been given in order to demonstrate the fact that when taken outside the context some fluxes can become in fact anti-fluxes.

Introduction

Slags are an important dimension of pyrometallurgical processes. They directly affect their efficiency, production rates, the overall cost as well as the quality of the final products. A good slag must have appropriate thermophysical properties such as a relatively low liquidus temperature, optimal viscosity, maximum ability to attract undesirable elements, minimum potential of attracting valuable elements, etc. However the quality of the slag depends on the quality of the feed and raw materials. As a result of the frequent diversification of raw materials the resulting slags do not often have optimal properties. This is due to a change of the slag composition and to several new minor components that come from the feed. However these properties can be improved by adding additional components which are normally called fluxes. A good flux, when properly used, can considerably improve the thermophysical properties of the slag since it becomes its organic part, modifies its chemical composition and improves the slags properties such as the liquidus temperature, viscosity etc. In this view slags and fluxes become interchangeable dimensions of an important equation in pyrometallurgical processes. Consequently, the choice of a good slag and the corresponding fluxing strategy are indispensable for most industrial processes. However, the thermophysical properties of multicomponent slags as well as the effect of several fluxes and minor components on these
properties are known only empirically and a considerable confusion exists in the literature and in the industrial practice about this.

In the today's reality of frequent changes in the composition of the raw materials and that of the fluxes themselves, in the existing or new developing technologies, the quantification of the thermophysicochemical properties of multicomponent slags and the effect of fluxes have become indispensable. The author's group has been working on this subject for more than a decade1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17 and the work is still ongoing. It consists of an original combination of thermophysicochemical modeling and experimental measurements that verify and validate the model. This paper reviews some of the results of this work related to the quantification of the physicochemical properties of multicomponent slags and the effect of fluxes in several smelting and converting processes in close relation to individual characteristics of these processes. It will deal more specifically with the liquidus temperature and viscosity. The FLOGEN™ software package has been used throughout the work4,15.

**New Types of Multicomponent Diagrams**

The way of representation of multicomponent liquidus diagrams is of considerable importance if correct conclusions need to be drawn about the thermophysicochemical properties of the slags and the effect of fluxes and minor components. As it will be subsequently explained, an incorrect or ambiguous way can lead to serious incorrect conclusions about the effect of fluxes and minor components. For this purpose, new types of multicomponent diagrams have been invented6,15 which not only waive the need for a multidimensional representation of multicomponent slags but also yields a series of practical two-dimensional diagrams which quantify in an unambiguous way the liquidus temperature as well as the effect of fluxes and minor components on the slag properties.

**Iron-silica slags**

A new type of diagrams has been developed to describe the liquidus surface and the liquid regions of multicomponent iron-silica slags. This is a two-dimensional diagram given as the content of any component versus Fe/SiO₂ ratio6. This is a very convenient way that represents unequivocally and unambiguously the slag liquidus surface, liquid regions and especially the effect of any component on the slag properties. It can easily eliminate any confusion found in the literature and in the industrial practice.

Figure 1 shows a polythermal projection diagram representing the liquidus surface of FeO-Fe₂O₃-SiO₂-Al₂O₃-MgO slag at 4% Al₂O₃, 3% CaO and PO₂ of 1.4x10⁻¹¹ atm in the region of interest of non-ferrous smelting.

![Figure 1 - Liquidus surface of FeO-Fe₂O₃-SiO₂-Al₂O₃-MgO slag](image)
iron silica slag in the FeO-Fe₂O₃-SiO₂-CaO-Al₂O₃-MgO system at a constant oxygen partial pressure and CaO and Al₂O₃ content. It can be noticed that the diagram quantitatively describes the effect of MgO on the liquidus surface of this slag.

Figure 2 gives an isothermal diagram representing the liquid regions of the same slag at constant temperature, oxygen potential and lime content for various combinations of MgO and Al₂O₃. It can be noted that the diagram describes unambiguously the slag liquid regions for certain combinations of magnesia and alumina. Both diagrams are very easy to be read and directly applicable in the industrial practice.

Lime-ferrite slag

The liquidus surface and the liquid regions of lime ferrite slags have also been quantitatively described by another innovative way as the content of any component versus Fe/CaO ratio. This is also a new and very convenient way to unambiguously describe the liquidus surface, the liquid regions and especially the effect of any component on the slag properties. This type of diagrams can easily eliminate any confusion found in the literature and in the industrial practice on the effect of several fluxes.

Figure 3 shows an example of the liquidus projection diagram of the lime-ferrite slag at constant oxygen potential. It can be seen that the diagram unequivocally describes the effect of SiO₂ on the liquidus surface of lime-ferrite slag.
Oxygen Potential

The effect of oxygen potential on the liquidus temperature has been ignored for a long time by metallurgists who have continuously used the liquidus surface of iron-silica systems at iron saturation or in air, in reductive and oxidative processes, respectively. However, most of the industrial processes are carried out at intermediate oxygen partial pressures far away from the limiting conditions of iron saturation or in air. We have recently found that ignoring the effect of oxygen potential can be troublesome for the industrial processes. Through the use of the aforementioned new type of diagrams it is proven that a change of the oxygen potential has a considerable effect on the slag liquidus surface and on the effect of minor components.

Figure 4 describes the effect of oxygen potential on the liquid regions of an iron silica slag at constant temperature. It can be seen that the oxygen potential considerably affects the slag liquidus surface. In this particular case an increase of the oxygen potential decreases the liquid region and increases the risk of solid precipitation.

Figure 5 describes the liquid regions of lime-ferrite slag at 1300°C at two different oxygen potentials. Again, it can be noted that the effect of the oxygen potential is considerable but it is not uniform and can be different at different saturation areas. In this particular set of conditions an increase of the oxygen potential decreases the liquid region in the magnetite and $\text{Ca}_2\text{Fe}_2\text{O}_5$ areas and increases it in the $\text{Ca}_2\text{SiO}_4$ area.
Dynamic Changes of Oxygen Potential

There are some particular processes where oxygen potential changes dynamically mainly as a result of the continuous cooling of the slag and/or the use of coke in the process. An example of these processes is the settling phase of matte smelting in which temperature drops continuously from around 1300°C to 1150°C and sometimes coke breeze is used in the last stage. In these processes, as well as in some others, contradictions are often found between the microscopic results of the laboratory quenching measurements and slowly cooled solidified smelting slags from the industrial practice. Contradictory assertions are also given about the effect of minor components in these processes. This confusion has been clarified by the introduction of a new way of representing the liquidus surface at constant \( \text{CO}_2/\text{CO} \) ratio since it was found that during slow equilibrium cooling while oxygen potential changes continuously the \( \text{CO}_2/\text{CO} \) ratio remains almost constant. Figure 6 quantitatively describes the liquidus surface of an iron silica slag at constant \( \text{CO}_2/\text{CO} \) ratio. This diagram can be conveniently used to describe the mechanism of the solidification of a slow cooling slag and clarify the above-mentioned confusion. It can be seen that the primary precipitate phase of a slow cooling slag "X" is olivine while if oxygen potential would have been kept constant at \( 10^8 \) atm, the primary phase of a quenched slag equilibrated below the liquidus temperature would have been magnetite.

Effect of Some Fluxes

Effect of CaO

Lime has always been considered and is still being considered a universal good flux for several industrial processes. However, we have recently proven that this is an incorrect assertion and can lead to many wrong conclusions in the literature and in the industrial practice. In several sets of conditions lime not only does not improve the slag liquidus but it can play a harmful role by increasing the risk of solid precipitation.

Two examples that illustrate the entirely opposite effects of lime on the liquidus surface of "iron silica" slags are given in Figures 7 and 8.

Figure 7 describes the effect of CaO on the liquidus surface of an iron-silica slag with various minor components at an oxygen potential of \( 10^8 \) atm. It can be seen that at a Fe/SiO\(_2\) ratio of 1.5 (as an example) lime is a good flux since it decreases the liquidus temperature of the slag until a certain point and consequently decreases the risk of solid phase precipitation.
However, as Figure 8 indicates, the effect of lime for another iron silica slag at a different oxygen potential and content of minor components is undesirable since it increases the liquidus temperature and increases the risk of magnetite precipitation. In this case lime should not be used as a flux.

From a comparison of these two figures it can also be seen that the name of "fayalite slag" ("F") in many cases looses its meaning depending on the oxygen potential and the slag composition. The name "fayalite" has always been used for the slags consisting of iron oxide and silica of composition near \( \text{Fe}_2\text{SiO}_4 \) regardless of the oxygen potential to which they are exposed. In fact, this name is only meaningful at low oxygen potentials where the fayalite saturation surface exists. It can also be tolerated wherever the olivine area is present, as it is the case of Figure 7. However, in other situations, where only the spinel (magnetite) phase exists, as it is the case of Figure 8, this name is irrelevant and its use should be employed with caution because it can lead to incorrect conclusions like the ones explained below. A meaningful name for the so-called "fayalite" slag at
Effect of Al₂O₃

Alumina has been most of the times considered not a good flux for iron silica slags. This has been sometimes based on the rationale that alumina is a kind of refractory material with a high melting temperature. However, we have recently proven that this rationale is not correct. Alumina can be a good flux and this closely depends on the particular set of industrial conditions: slag components, oxygen potential etc.

Figure 9 describes the effect of alumina on the liquidus surface of an iron silica slag. It can be seen that in this particular set of conditions (slag components, PO₂ etc.) alumina is a good flux in term of the liquidus surface since it decreases it and thus decreases the risk of solids precipitation. For instance, at Fe/SiO₂ ratio of 1.5 alumina decreases continuously the liquidus temperature up to 8%.

However, at another set of conditions, such as those shown in Figure 10, alumina is not a good flux since it decreases the liquid regions, increases the liquidus temperature and increases the risk of magnetite precipitation. For instance, as illustrated in Figure 10 in contrast with the previous figure at the same Fe/SiO₂ of 1.5 alumina decreases continuously the magnetite solubility limit.
Effect of MgO

The effect of MgO on the liquidus temperature of iron silica slag is also a controversial subject in the literature. Some authors have written that magnesia increases the liquidus temperature while others state that it decreases it.

As shown in Figures 1 and 11 magnesia increases the liquid temperature of iron silica slag in both these sets of conditions and consequently increases the risk of solid precipitates. However this effect is not uniform and varies considerably from the specific set of conditions such as oxygen potential, slag composition etc. Only when the initial slag composition is in the silica saturation area magnesia decreases the liquidus temperature but, as will be subsequently explained, almost none of industrial slags have the original composition in this area.

Liquidus Temperature and Viscosity

Fluxes affect not only the liquidus temperature but also the viscosity of the slag. Historically but also presently both these effects are seen as going in the same direction. That is, if a flux is found good in terms of the viscosity it has been always presumed that it decreases the liquidus temperature. However, we have proven that this conclusion is not correct. The effect of a flux on the liquidus temperature and on the viscosity of a slag can go in opposite directions. In other words, if a flux is good in terms of the viscosity it might not be good in terms of the liquidus temperature.
As mentioned previously, the employed type of liquidus diagrams is of considerable importance if correct conclusions need to be drawn about the thermophysical chemical properties of the slags and the effect of fluxes and minor components. An incorrect or ambiguous diagram can lead to serious incorrect conclusions on the effect of several fluxes and minor components in the industrial processes. This is one of the reasons of the confusion and incorrect conclusions found in the literature and in the industrial practice. For instance, Fontana et al. have measured the effect of CaO and MgO on the liquidus temperatures of iron-silica slags at some oxygen potentials and have given the results in the form of liquidus temperatures versus Ca/Fe wt ratio at constant SiO₂ content as shown in Figure 14. Based on this type of diagrams they conclude that “CaO and MgO additions in iron silicate melts lower the liquidus temperature”. This seems to be a typical incorrect conclusion from an incorrect liquidus diagram. This type of diagram does not specifically give the effect of CaO and MgO on the liquidus temperature since at constant SiO₂ it does not simulate the real slag behavior during

Figures 12 and 13 give respectively the effect of Al₂O₃ on the liquidus surface and the viscosity of an iron silicate slag. It can be seen that an increase of the alumina is a good flux in terms of the liquidus surface since it decreases it but is not a good flux in term of the viscosity since it increases it.

Figure 13 - Effect of Al₂O₃ on the viscosity of a FeO-Fe₂O₃-SiO₂-CaO-Al₂O₃-MgO slag at Fe/SiO₂=1.1 (wt ratio), 3% CaO, 2% MgO and PO₂ of 10⁻¹¹ atm

Discussion
flux additions. The diagrams invented by us, as described above, eliminate these kinds of problems since they give unequivocally and unambiguously the effect of fluxes on the liquidus temperature. For instance at the same set of conditions as those of Fontana et al., our results show that lime and magnesia do not decrease the liquidus temperature but instead increase it.

There are also other reasons that explain some of the confusion on the effect of fluxes in metallurgical processes. These include the use of non-sensitive techniques to measure the liquidus temperature that can lead to incorrect data. However an important reason is the interpretation of experimental results. For instance, in a publication related to copper continuous converting\textsuperscript{19} (PO\textsubscript{2} \textsuperscript{10.8-10.6 atm}) it is stated that "the presence of small amounts of CaO, MgO and Al\textsubscript{2}O\textsubscript{3} would lower the melting point of fayalite slags". This incorrect conclusion comes as a result of an apparent misinterpretation of the data of Kim and Sohn\textsuperscript{20} and Altman\textsuperscript{21} who have measured the ferric/ferrous ratio of silica saturated iron silicate slags at constant temperature but at the resulting variable silica contents. This procedure ignores the effect of silica and makes the results directly incomparable at constant Fe/SiO\textsubscript{2} ratios. Instead, as can be gauged from the above diagrams at some intermediate oxygen potentials, at a constant Fe/SiO\textsubscript{2} ratio, CaO, MgO and Al\textsubscript{2}O\textsubscript{3} increase the liquidus temperature of silica non-saturated "iron silicate" slags in the spinel surface and increase the risk of spinel (magnetite) precipitation. The origin of the confusion in the literature comes from the fact that the experiments have always been carried out at silica saturation. Under these conditions the addition of CaO, decreases the liquidus temperature of the slag only in the direction of silica saturation curve along with simultaneous and continuous decrease of Fe/SiO\textsubscript{2} ratio, which adjusts itself during the experiments. This is clearly shown in Figure 8, where the liquidus temperature is decreased only along the silica saturation curves. The same thing can be said for the effect of MgO and Al\textsubscript{2}O\textsubscript{3}. From figures presented in this work it can be stated that the solution of CaO, MgO and Al\textsubscript{2}O\textsubscript{3} suppresses the formation of solid silica and moves the silica boundary toward lower silica content. However this is associated with an increase of the liquidus temperature in the spinel surface and not with a decrease. Only when the original slag composition lies in the silica saturation area, additions of these minor components cause a decrease of the liquidus temperature as long as the composition lies in this area. Nevertheless, almost none of the slags in industrial processes at intermediate oxygen potentials have the original composition in the silica saturation area since, as explained above, the normal minor oxides that come from the feed materials suppress this area and place the original composition in the spinel surface. From this point on the additions of CaO, MgO and Al\textsubscript{2}O\textsubscript{3} would only increase the liquidus temperature of the slag at constant Fe/SiO\textsubscript{2} ratio. These effects can be gauged directly from the above-presented set of diagrams, which due to their simplicity and comprehensibility not only describe quantitatively and selectively the effect of minor components and oxygen potentials on the liquidus temperature of multicomponent slags but also easily defuse the confusion found in the literature.

Conclusions

This paper reviewed some of the work carried out by the author's group during the last ten years on the quantification of the thermophysicochemical properties of multicomponent slags and on the effect of fluxes in several smelting and converting processes in close relation to their individual characteristics.

Several new types of multicomponent phase diagrams were presented and the importance of the employed type of diagram in drawing correct conclusions about the thermophysicochemical properties of the slags and the effect of fluxes and minor components was discussed. It has been found that an incorrect or ambiguous diagram could lead to serious incorrect conclusions on the effect of fluxes and minor components and as a result to a considerable confusion in the
literature and in the industrial practice. It was also found that the use of non-sensitive techniques to measure the liquidus temperature and especially the incorrect interpretation of experimental results could lead to incorrect conclusions.

The effect of the oxygen potential on the slag liquidus temperature in a static or dynamic mode has been quantified for the first time through a series of new diagrams. Its importance on the phase relations and the effect of minor components was also emphasized.

The myths and the confusion in the literature and in the industrial practice on the effect of several fluxes have been clarified. It has been found that the effect of a flux is specific to a particular process and its set of conditions such as slag composition, oxygen potential, minor components, etc. It has also been found that if the effects of fluxes are globally asserted without taking into account the characteristics of individual processes and the particularities of certain employed laboratory procedures or are generalized from one process to another this could lead to serious errors and troubles. Several examples have also been given in order to demonstrate the fact that when taken outside the context some fluxes can become in fact anti-fluxes.

The relation between the liquidus temperature and the viscosity of the slag has been critically assessed and incorrect ideas have been clarified. It has been found that the effect of a flux on the liquidus temperature and on the viscosity of a slag could go in opposite directions. In other words, if a flux is good one in terms of the viscosity it might not be good in terms of the liquidus temperature. The effect of other fluxes and minor components as well as the slag properties in other processes are ongoing research.

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