Experimental investigation of liquidus temperatures of ISP slags

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The slags produced by the Imperial Smelting Process (ISP) are based on the system ZnO-'FeO'-Al_2O_3-CaO-SiO_2. The slag chemistry is important to the process since it determines the fluxing practice and the operating temperature of the furnace required to produce fluid slag.

The paper presents the results of the first systematic experimental investigation of these ZnO-containing slags in equilibrium with metallic iron, and provides information on the primary phase fields and liquidus temperatures in these slags over the range of compositions used in ISP practice. A feature of the slags is the presence of alumina, which has a major influence in stabilizing the spinel phase. This information presented in the form of pseudo-ternary sections ZnO-'FeO'-(Al_2O_3+CaO+SiO_2) enabling the data to be readily used by plant engineers.

Keywords: liquidus temperature, ISP, EPMA, ZnO-'FeO'-Al_2O_3-CaO-SiO_2, phase equilibria.

Introduction

The Imperial Smelting Process (ISP) is principally used to recover zinc and lead from complex sulphide concentrates, although increasing quantities of secondary materials are now being processed[1–2] In this pyrometallurgical process route the majority of the sulphur is removed in the sintering process by oxidation into the gas phase. Lead and zinc oxides in sinter are then reduced to metals in an Imperial Smelting Furnace (ISF). The resultant slag phase consists mostly of ZnO, 'FeO', SiO_2, CaO, Al_2O_3 and MgO, which are introduced into the ISF slag through concentrates, secondary feed materials, fluxes, coal ash and dissolved refractories.

Relatively few studies of the phase equilibria have been reported in the system ZnO-'FeO'-CaO-SiO_2 under reducing conditions. Dobrotsvetov *et al.*[3] used Differential Thermal Analysis (DTA), optical microscopy, chemical analysis and X-ray Powder Diffraction (XRD) to study the join $CaFeSiO_4$-Zn_2SiO_4 at or close to iron saturation.

Lenz and Lee[4] used DTA techniques to examine the liquidus temperatures of compositions close to those in the Brunswick lead blast furnace slags under an atmosphere of 90 pct N_2, 5.2 pct CO_2 and 4.8 pct CO. It was found that wustite [(Fe,Zn)O] and silicates are the primary phases in the composition range of 35–52 wt pct 'FeO', 5–20 wt pct ZnO and CaO/SiO_2 weight ratio between 0.4-1.2. No attempt was made to identify the silicate phases (olivine or melilite) in this study. The samples were not chemically analysed after the experiments.

Accurate determination of the liquidus and the phase relations in these high zinc systems, under reducing conditions has proved difficult because of the high zinc vapour pressures and the uncertainties in the oxygen partial pressures and the compositions of the bulk material and individual condensed phases.

These hurdles have been largely overcome with the development of new research methodologies and techniques[5–7], which have been applied to the system ZnO-'FeO'-CaO-SiO_2 in equilibrium with metallic iron. The results of these previous studies were presented in the form of pseudo-ternary sections ZnO-'FeO'-(CaO+SiO_2) with fixed CaO/SiO_2 weight ratios of 0.33, 0.71, 0.93 and 1.2. Wustite [(Fe,Zn)O], zincite [(Zn,Fe)O], olivine [(Fe,Ca)$_2$$SiO_4$], willemite [(Zn,Fe)$_2$$SiO_4$] and melilite [$Ca_2(Zn,Fe)_2$$Si_2O_7$] are the primary phases reported in the composition ranges relevant to lead and zinc blast furnace and zinc fuming slags.

Further studies[8–9] on zinc-free fayalite slags revealed that additions of Al_2O_3 and MgO can significantly affect the liquidus temperatures and the extent of the primary phase fields in these systems. The present studies have, therefore, been undertaken to characterize the effects of Al_2O_3 and MgO on the liquidus temperatures of ISF slags. This paper, presenting the experimental results in the system ZnO-'FeO'-Al_2O_3-MgO-CaO-SiO_2 with CaO/SiO_2 weight ratio of 0.71 in equilibrium with metallic iron, is the first in a series of studies examining the range of conditions encountered in ISF slags.

Experimental

Selection of pseudo-ternary sections

The selection of an appropriate pseudo-ternary section in a multi-component system is important for efficient research and for further use of the experimental information in industrial practice. In the system ZnO-'FeO'-Al_2O_3-CaO-SiO_2 with CaO/SiO_2 weight ratio of 0.71 the pseudo-ternary sections have been constructed as shown in Figure 1. The end members of the section were selected to be ZnO, 'FeO' and (Al_2O_3+CaO+SiO_2), with fixed CaO/SiO_2 and (CaO+SiO_2)/Al_2O_3 weight ratios for each section. In the system ZnO-'FeO'-Al_2O_3-MgO-CaO-SiO_2 the CaO/SiO_2 and (CaO+SiO_2)/Al_2O_3 weight ratios have been fixed and the pseudo-ternary sections have been constructed at constant MgO concentrations (as shown in Figure 2).

There are a number of reasons for choosing ZnO, 'FeO' and (Al_2O_3+CaO+SiO_2) as the end members of the diagram.
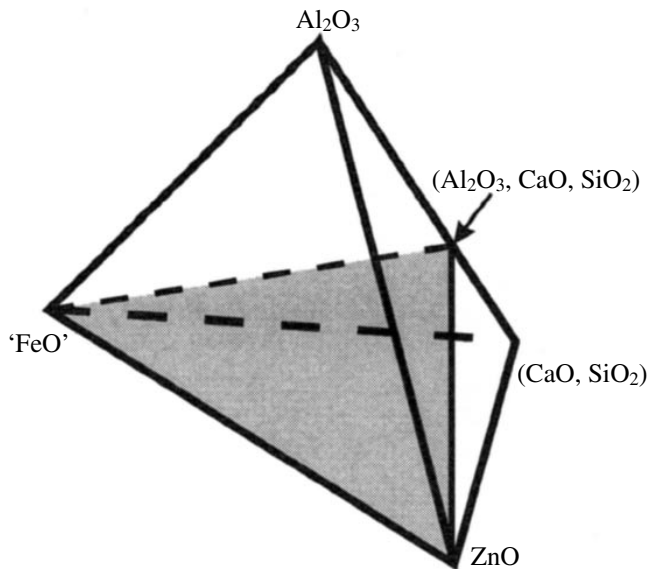
Figure 1. Pseudo-ternary section ZnO-'FeO'-(Al₂O₃+CaO+SiO₂) with fixed CaO/SiO₂ and (CaO+SiO₂)/Al₂O₃ ratios

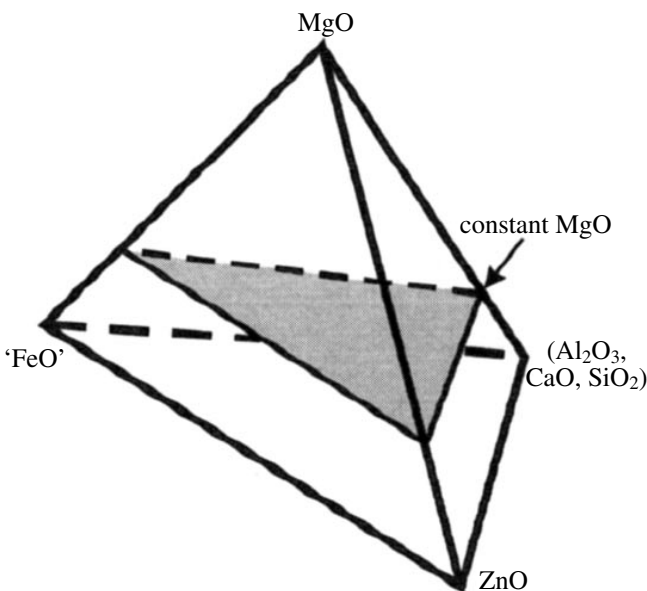(labels in figure: Al₂O₃, (Al₂O₃, CaO, SiO₂), (CaO, SiO₂), 'FeO', ZnO)

Figure 2. Pseudo-ternary section ZnO-'FeO'-(Al₂O₃+CaO+SiO₂) with fixed CaO/SiO₂ and (CaO+SiO₂)/Al₂O₃ ratios and MgO concentrations

(labels in figure: MgO, constant MgO, (Al₂O₃, CaO, SiO₂), 'FeO', ZnO)

- The zinc concentration of the slags changes as the reduction proceeds through the furnace. Zinc concentration is seen as an important process variable. When zinc vaporizes during processing or equilibration, the bulk CaO/SiO_2 and $(CaO+SiO_2)/Al_2O_3$ ratios in the sample do not change, therefore the bulk composition of the oxide system also remains in the original pseudo-ternary section.
- In the composition ranges relevant to industrial practice both zincite [(Zn,Fe)O] and wustite [(Fe,Zn)O] have been observed as primary phases.
- During experimental equilibration of the slags in the presence of metallic iron, the bulk composition of the slag changes as the results of the reaction

  Fe (metal) + ZnO (slag) -> FeO (slag) + Zn (gas)

Both iron oxide and zinc oxide concentrations of the

slag change during equilibration. The systematic changes in iron and zinc concentrations in the slag can be represented by choosing FeO and ZnO as apices of the section.

- The wustite and zincite crystals do not contain significant amounts of Al₂O₃, CaO or SiO₂ in solid solution. When these phases precipitate out of the liquid with given CaO/SiO_2 and $(CaO+SiO_2)/Al_2O_3$ ratios, these ratios in the liquid phase do not change. Therefore, the compositions of both these solid precipitates and the liquid phase remain in the plane of the selected section. The wustite and zincite primary phase fields, therefore, can be treated as if they were part of a true ternary phase diagram, and general phase diagram rules can then be applied within these primary phase fields.
- CaO/SiO₂ ratio is commonly used by process operators to control slag composition. The CaO/SiO_2 and $(CaO+SiO_2)/Al_2O_3$ ratios in ISF slags usually do not change significantly. The presentation of the experimental results in the form of this pseudo-ternary section means that the information can be readily used by industrial engineers.

The experimentally determined liquidus for six pseudo-ternary sections are presented in this paper. Three pseudo-ternary sections have been constructed to evaluate the effect of Al₂O₃ on the liquidus temperatures of the ISF slags. In each of the sections presented here the CaO/SiO₂ weight ratio is fixed at 0.71 and data for (CaO+SiO₂)/Al₂O₃ weight ratios of 7.0, 5.0 and 3.5 are presented. Three pseudo-ternary sections have also been constructed to evaluate the effect of MgO on the liquidus temperatures of the ISF slags. In each section the CaO/SiO₂ and (CaO+SiO₂)/Al₂O₃ weight ratios are fixed to be 0.71 and 5.0 respectively and data are presented for sections with 2.0, 4.0 and 6.0 wt% MgO in the liquid phase.

Experimental procedure

The experimental procedure used in this investigation is basically similar to that previously reported by the authors[5–10]. The detailed procedures have been adjusted so as to be suitable for the present study.

An iron-free, high-ZnO master slag was prepared first from the pure chemicals in the desired proportion. The pelletized slag was placed in a platinum crucible and heated in air at 1773 K for several hours. The slag was then quenched into water, dried at 393 K and reground in an agate mortar. The mixtures to be used in the equilibration experiments were obtained by mixing the high-ZnO master slag (approximately 0.2 g) with excess iron powder. The mixtures were then pelletized, and wrapped in an envelope of platinum or iron foil. During equilibration the zinc in the slag reacts with metallic iron forming iron oxide according to the reaction (1):

$$ZnO(solid) + Fe(solid) \rightarrow (solid, liquid) + Zn(gas) \qquad [1]$$
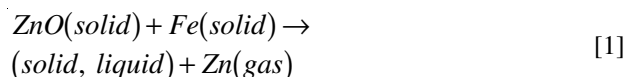
There are several advantages to this experimental technique. Most importantly the presence of dispersed solid iron after equilibration ensures that the slag is in local equilibrium with the iron metal. The intimate mixture of premelted slag and iron powder promotes rapid attainment of equilibrium, which not only makes it possible to study high zinc slags but also increases the productivity of the research. Samples with different zinc oxide concentrations were obtained by adjusting the period at temperature in the furnace for a given starting mixture.

The experiments were carried out in a vertical silicon carbide heated furnace. The furnace temperature was controlled within ± 1 K. To accurately measure the sample temperature a Pt-Pt/13%Rh thermocouple placed in an alumina sheath was located adjacent to the sample. The thermocouple was calibrated using a reference thermocouple supplied by National Measurement Laboratory (CSIRO, Melbourne, Australia), and periodically checked against the melting point of pure gold. The overall temperature accuracy was estimated to be within ± 5 K.

The envelope containing the sample was first attached to a platinum wire and placed in the cool zone of the furnace. The bottom end of the recrystallised alumina reaction tube was sealed using a plastic film. After ultra high purity nitrogen (total impurities ≤ 5 ppm, oxygen ≤ 1ppm) was passed through the reaction tube for 15–30 minutes to remove the air, the sample was raised into the hot zone to a position adjacent to the thermocouple. The experiment was usually carried out in two steps. The first step was to premelt the sample at a temperature higher than the liquidus to ensure the mixture is homogeneous. The sample was then equilibrated at the desired temperature for a time sufficient to achieve equilibrium. There was no attempt to control the oxygen partial pressure of the system in the gas phase since local equilibrium with iron metal is achieved in the sample. The oxygen partial pressure in these experiments, therefore, is controlled by the condensed system. After equilibration the sample was quenched directly into the cooling water.

Sample examination

The quenched samples were mounted and polished for analysis. Firstly optical microscopy was employed to identify the phases present in the sample. The rapid quenching of these silicate slags results in the retention of the liquid phase at temperature as a homogeneous glass phase. The crystalline solids present at temperature are also retained on cooling. The compositions of these phases were then measured using a JEOL 8800L Electron Probe X-Ray Microanalyser (EPMA) with Wavelength Dispersive Spectrometers (WDS). An accelerating voltage of 15 kV and a probe current of 15 nA were used. The Duncumb-Philibert ZAF correction procedure supplied with JEOL-8800L was applied. The standards used for analysis were from Charles M. Taylor Co. (Stanford, California): Al_2O_3 for Al, MgO for Mg, Fe_2O_3 for Fe, $CaSiO_3$ for Ca and Si, and from Micro-Analysis Consultants Ltd (Cambridge, UK): ZnO for Zn. The average accuracy of the EPMA measurements was estimated to be within 1 weight per cent.

Only metal cation concentrations were measured by EPMA; the oxygen concentration was calculated according to the assumed oxidation state of the metal cation. Since all of the slag samples were in equilibrium with metallic iron, all iron in the slag was assumed to be in the form of FeO for the purpose of the calculations.

Results and discussion

Liquidus surfaces

The liquidus surfaces of the pseudo-ternary sections constructed from experimental data are presented in Figures 6 to 8. Figures 3 to 5 show the liquidus surfaces of the pseudo-ternary sections ZnO-'FeO'-(Al$_2$O$_3$+CaO+SiO$_2$) with CaO/SiO$_2$ ratio of 0.71 and (CaO+SiO$_2$)/Al$_2$O$_3$ ratio of

7.0, 5.0 and 3.5 respectively. Figures 6 to 8 show the liquidus surfaces of the pseudo-ternary sections ZnO-'FeO'-(Al$_2$O$_3$+CaO+SiO$_2$) with CaO/SiO$_2$ ratio of 0.71, (CaO+SiO$_2$)/Al$_2$O$_3$ ratio of 5.0 and fixed MgO concentrations of 2.0, 4.0 and 6.0 wt% respectively.

It can be seen from Figure 3 that five primary phase fields are present in the region investigated: wustite (Fe,Zn)O, zincite (Zn,Fe)O, spinel (Fe,Zn)O(Al,Fe)$_2$O$_3$, fayalite (Fe,Zn,Ca)$_2$SiO$_4$ and melilite Ca$_2$(Fe,Zn)(Al,Si)$_2$O$_7$.

It has been reported by Jak *et al.*[5–6] that wustite, zincite, olivine and melilite are the major primary phases in the system ZnO-'FeO'-CaO-SiO$_2$ with CaO/SiO$_2$ weight ratio of 0.71 in equilibrium with metallic iron. It can be seen from Figures 3 to 5 that with the addition of alumina into the system CaO-'FeO'-ZnO-SiO$_2$ a new phase spinel appears in the composition range investigated. With
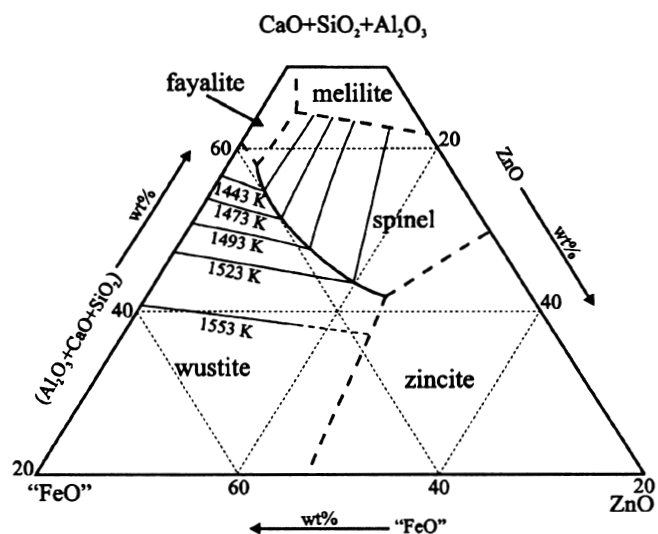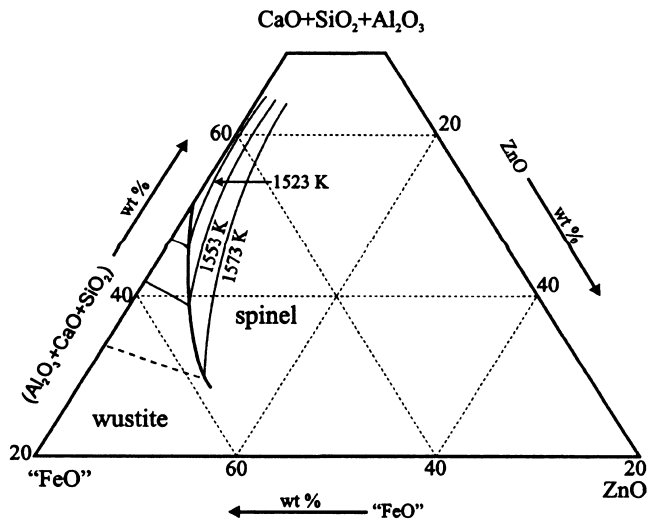

Figure 3. Experimentally determined liquidus surfaces of the pseudo-ternary section ZnO-'FeO'-(Al$_2$O$_3$+CaO+SiO$_2$) with CaO/SiO$_2$=0.71 and (CaO+SiO$_2$)/Al$_2$O$_3$=7.0 in equilibrium with metallic iron
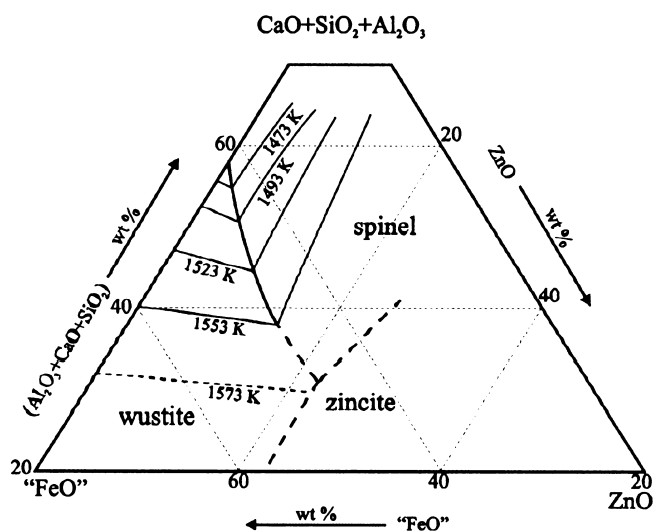
Figure 4. Experimentally determined liquidus surfaces of the pseudo-ternary section ZnO-'FeO'-(Al$_2$O$_3$+CaO+SiO$_2$) with CaO/SiO$_2$=0.71 and (CaO+SiO$_2$)/Al$_2$O$_3$=5.0 in equilibrium with metallic iron

Figure 5. Experimentally determined liquidus surfaces of the pseudo-ternary section ZnO-'FeO'-(Al₂O₃+CaO+SiO₂) with CaO/SiO₂=0.71 and (CaO+SiO₂)/Al₂O₃=3.5 in equilibrium with metallic iron

increasing alumina, i.e., decreasing (CaO+SiO₂)/Al₂O₃ weight ratio, the fayalite and wustite primary phase fields reduce in size, and the spinel primary phase field expands. For the sections with (CaO+SiO₂)/Al₂O₃ ratio of 5 and 3.5 the fayalite primary phase field is completely eliminated from the sections.

In this system liquidus temperatures above approximately 1573 K and at low-silica compositions could not be accurately experimentally determined because it was not possible to retain homogeneous glass from the liquid phase on quenching. In addition, the liquidus in regions of high ZnO compositions and high temperatures could not be investigated using the present techniques due to the very high ZnO reduction rates under these conditions.

It can be seen from Figures 3 to 5 that the spinel is one of the major primary phases in the composition range investigated. A feature to note is that the compositions of the spinel phase do not lie on any of the sections given in Figures 3 to 5. The precipitation of the spinel crystals from the melt will result in the selective removal of iron, zinc and aluminum oxides from the liquid phase. Thus, the (CaO+SiO₂)/Al₂O₃ ratio in the liquid phase changes so that the liquid composition no longer lies on the plane of a section. This phenomenon represents one of the major difficulties in the present experimental study. The adopted approach to overcome these difficulties was to i) select conditions with low fraction of spinel phase; ii) approach the spinel primary field indirectly, using a slag with high FeO/(Al₂O₃+CaO+SiO₂) ratio, removing most of the zinc at a higher premelt temperature, then equilibrating at a lower temperature. Although the experiments were carefully planned to overcome this problem to obtain the liquid composition with exact or near the selected ratio, this, in general, could not be achieved with the first experiment. It is usually necessary to repeat experiments in this phase field several times to adjust starting compositions before satisfactory results are obtained. Only those experiments with the CaO/SiO₂ and (CaO+SiO₂)/Al₂O₃ ratios in the liquid near the selected section were used for the construction of the pseudo-ternary sections. In the case of MgO-containing sections, none of the primary phase compositions lay on any of the sections given in Figures 6

to 8. Only those experiments with the CaO/SiO₂ and (CaO+SiO₂)/Al₂O₃ ratios and MgO concentration in the liquid near the selected section were used for the construction of the pseudo-ternary sections. However, the other data not having the required ratios and MgO concentrations are still useful for the optimization of subsequent thermodynamic models of the system.

Effect of ZnO on liquidus temperatures

In the slag fuming process ZnO in the slag is reduced to zinc gas so as to be removed from the condensed system. In this process the ratios of other components, such as FeO/(CaO+SiO₂+Al₂O₃), CaO/SiO₂ and (CaO+SiO₂)/Al₂O₃, do not change. The liquidus temperatures of the slag, however, will change with changing the zinc concentration of the slag. The effects of ZnO on the
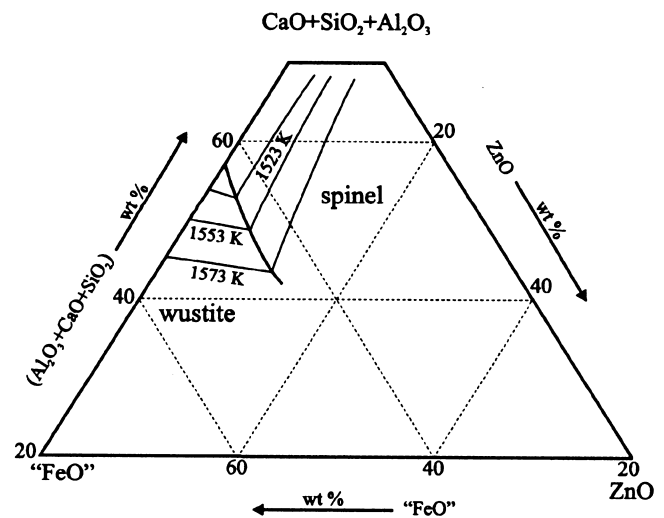

Figure 6. Experimentally determined liquidus surfaces of the pseudo-ternary section ZnO-'FeO'-(Al₂O₃+CaO+SiO₂) with CaO/SiO₂=0.71, (CaO+SiO₂)/Al₂O₃=7.0 and 2 wt% MgO in equilibrium with metallic iron
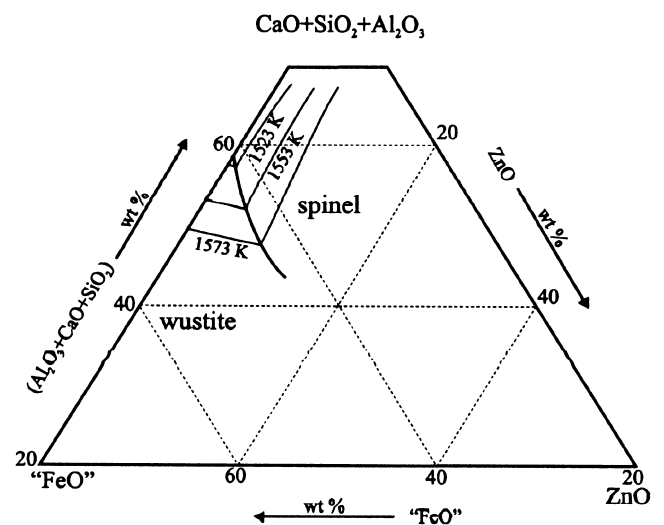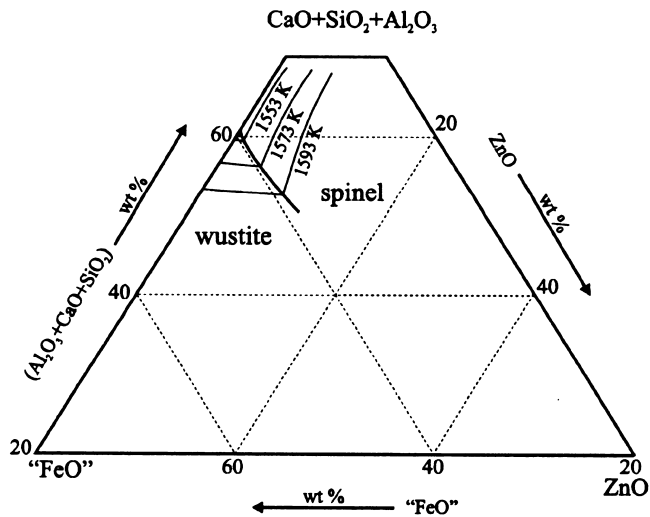

Figure 7. Experimentally determined liquidus surfaces of the pseudo-ternary section ZnO-'FeO'-(Al₂O₃+CaO+SiO₂) with CaO/SiO₂=0.71, (CaO+SiO₂)/Al₂O₃=7.0 and 4 wt% MgO in equilibrium with metallic iron

MOLTEN SLAGS FLUXES AND SALTS

Figure 8. Experimentally determined liquidus surfaces of the pseudo-ternary section ZnO-'FeO'-(Al$_2$O$_3$+CaO+SiO$_2$) with CaO/SiO$_2$=0.71, (CaO+SiO$_2$)/Al$_2$O$_3$=7.0 and 6 wt% MgO in equilibrium with metallic iron

liquidus temperatures are different in the wustite and spinel primary phase fields. It can be seen from Figures 3 to 5 that the liquidus temperatures in the wustite primary phase field only slightly increase with increasing ZnO concentration in the slag.

However, the liquidus temperatures in the spinel primary phase field increase significantly with increasing ZnO concentration. The effect of ZnO on liquidus temperatures in the spinel primary phase field is presented in Figure 9. The points in Figure 9 were interpolated from Figures 3 to 5. To have as many as possible liquidus points in the curves the starting point (0 weight pct ZnO) for each of the pseudo-ternary sections were selected at different 'FeO'/(CaO+SiO$_2$+Al$_2$O$_3$) ratios. For example, the 'FeO'/(CaO+SiO$_2$+Al$_2$O$_3$) ratios for the slags with (CaO+SiO$_2$)/Al$_2$O$_3$=7.0, 5.0 and 3.5 were selected equal to 0.64, 0.73 and 0.92 respectively. It should be noted that for the section (CaO+SiO$_2$)/Al$_2$O$_3$=7.0 the liquidus points at low zinc concentrations are located in the melilite primary phase field, for this reason the corresponding liquidus curve for the section (CaO+SiO$_2$)/Al$_2$O$_3$=7.0 in Figure 9 does not start from zero zinc. It can be seen from Figure 9 that liquidus temperatures in spinel primary phase field increase dramatically with increasing ZnO content. For example, a typical ISP slag has the CaO/SiO$_2$=0.71 and (CaO+SiO$_2$)/Al$_2$O$_3$=5.0. It can be seen from Figure 9 that increase of the zinc concentration in the slag from 0 to 10 pct results in approximately 100 K increment of the liquidus temperature in the spinel primary phase field.
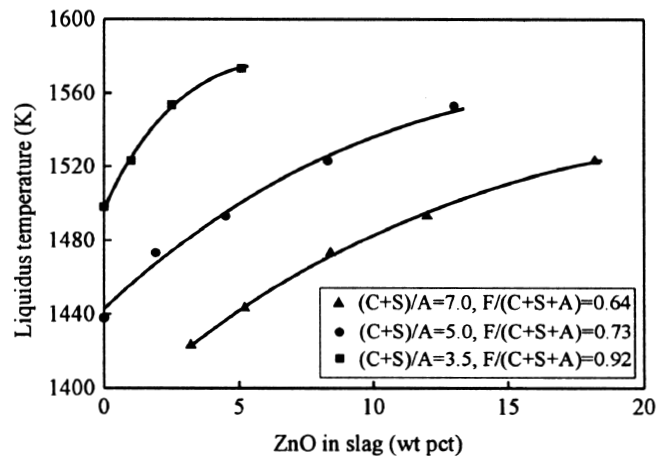
Effect of Al$_2$O$_3$ on liquidus temperatures

The way to consider the effect of Al$_2$O$_3$ addition on liquidus temperature is to add Al$_2$O$_3$ to a base slag containing ZnO, 'FeO', CaO and SiO$_2$.

Two slags are taken as examples to demonstrate the effect of Al$_2$O$_3$ addition on liquidus temperature. The first one is a zinc-free slag with initial composition of 55.0 pct 'FeO', 18.7 pct CaO and 26.3 pct SiO$_2$ by weight. Another slag was selected to contain 10 pct ZnO, 50.0 pct 'FeO', 16.6 pct CaO and 23.4 pct SiO$_2$ by weight. When Al$_2$O$_3$ is added

into the slags the ratios of these components remain constant. The relationship between liquidus temperatures and Al$_2$O$_3$ content in slag is plotted in Figure 10. It can be seen from Figure 10 that, for these two slags, the liquidus temperatures in wustite primary phase field always decrease with Al$_2$O$_3$. There is no spinel phase formed for the zinc-free slag with up to 11.4 pct Al$_2$O$_3$ addition. For the zinc-containing slag the spinel appears from 7.4 pct Al$_2$O$_3$ addition. In the spinel primary phase field the liquidus temperatures increase sharply with increasing Al$_2$O$_3$ concentration in the slag.

Effect of MgO on liquidus temperatures

MgO is added to a base slag to evaluate the effect of MgO on liquidus temperature. Two slag compositions are selected from the wustite and hercynite primary phase fields respectively. The first one is a zinc-free slag with initial composition of 45.0 pct 'FeO', 19.0 pct CaO, 26.8 pct SiO$_2$ and 9.2 pct Al$_2$O$_3$ by weight. Another slag is selected to contain 10 pct ZnO, 40.0 pct 'FeO', 17.3 pct

Figure 9. Liquidus temperatures of ISF slags as a function of ZnO concentration in the spinel primary phase field in equilibrium with metallic iron. A=Al$_2$O$_3$; C=CaO; F='FeO'; S=SiO$_2$
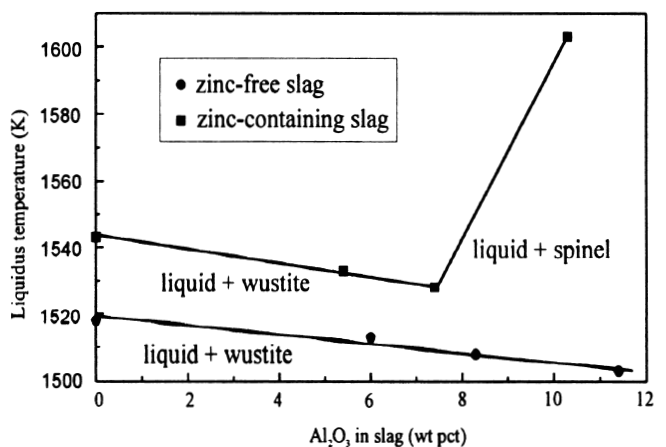
Figure 10. Liquidus temperatures of ISF slags as a function of Al$_2$O$_3$ concentration in equilibrium with metallic iron. Base slag compositions: zinc-free slag: 55.0 pct 'FeO', 18.7 pct CaO and 26.3 pct SiO$_2$; zinc-containing slag: 10 pct ZnO, 50.0 pct 'FeO', 16.6 pct CaO and 23.4 SiO$_2$

CaO, 24.4 pct SiO_2 and 8.3 pct Al_2O_3 by weight. The composition of the first slag is located in the wustite primary phase field and the composition of the second slag is located in the spinel primary phase field. The relationships between the liquidus temperature and MgO concentration for these slags are presented in Figure 11. It can be seen from Figure 11 that the addition of MgO increases the liquidus temperatures in both the wustite and spinel primary phase fields. The addition of 6 wt% MgO increases the liquidus temperature by approximately 90 degrees in the wustite primary phase field and by approximately 60 degrees in the spinel primary phase field for the given slag compositions.

Summary

Liquidus temperatures of the ISP slags with the average CaO/SiO_2 weight ratio of 0.71 have been experimentally determined in equilibrium with metallic iron. It was found that the presence of alumina in the slags results in the appearance of the spinel primary phase field. With increasing ZnO concentration in the slag the liquidus temperatures increase slightly in the wustite primary phase field and significantly in the spinel primary phase field. With increasing Al_2O_3 concentration in the slag the liquidus temperatures decrease in the wustite primary phase field but increase in the spinel primary phase field. Addition of MgO in the ISF slags significantly increases the liquidus temperatures in both wustite and spinel primary phase fields.
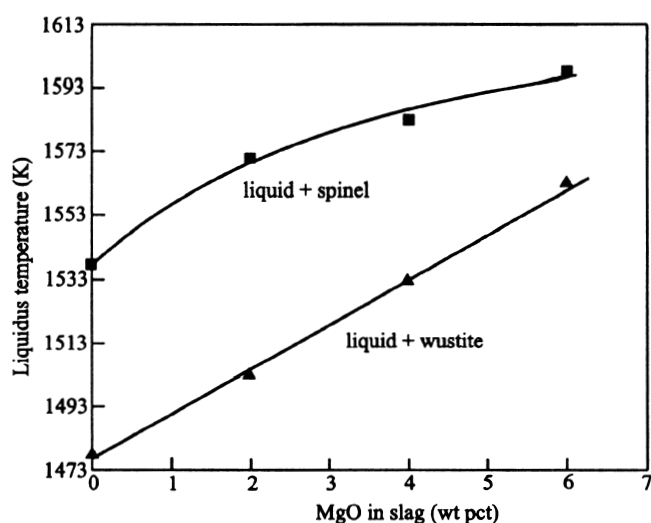
Acknowledgements

Figure 11. Liquidus temperatures of ISF slags as a function of MgO concentration in equilibrium with metallic iron. Base slag compositions: wustite slag: 45.0 pct 'FeO', 19.0 pct CaO 26.8 pct SiO_2 and 9.2 pct Al_2O_3; spinel slag: 10 pct ZnO, 40.0 pct 'FeO', 17.3 pct CaO, 24.4 pct SiO_2 and 8.3 pct Al_2O_3

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