Experimental determination of phase equilibria in lead/zinc smelting slags and sinters.

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ABSTRACT

The system $PbO-ZnO-FeO-Fe_2O_3-CaO-SiO_2$ represents the major components of industrial zinc and lead smelting slags and sinters. The combination of experimental investigations and computer modelling has been used to characterise phase equilibrium and thermodynamic properties of this multi-component system.

The high vapour pressures of lead and zinc in this system make it difficult to obtain thermodynamic properties using conventional research techniques. However, an experimental methodology has been developed which enables phase equilibria in this system to be characterised. The experimental technique involves high temperature equilibration in controlled atmospheres, quenching, and electron probe X-ray microanalysis (EPMA).

Using this methodology solidus and liquidus measurements have been made on binary, ternary and multi-component systems. The systems were selected so as to obtain data essential for thermodynamic modelling, and to provide working diagrams which could be used directly by industry.

Two sets of experimentally determined pseudo-ternary diagrams

i) ZnO-"Fe_2O_3"-($PbO+CaO+SiO_2$) at six $PbO/CaO/SiO_2$ ratios in air, and
ii) ZnO-"FeO"-($CaO+SiO_2$) at four CaO/SiO_2 ratios at metallic iron saturation are of particular importance for the industrial lead and zinc sintering, smelting and reduction applications.

1. INTRODUCTION

The knowledge of the liquidus and solidus temperatures of slags and sinters is crucial to the efficient control and to the optimisation of pyrometallurgical processing operations. The lack of accurate liquidus data on these complex multi-component slags remains one of the outstanding obstacles to the better control of bath fluxing and operating temperatures, to the further reduction of operating costs and to the development of novel pyrometallurgical extraction processes.

The conventional research techniques used for phase diagram determination in this area is both time consuming and expensive. The present research program demonstrates the optimum use of the latest technologies to reduce time and costs whilst improving the accuracy of the determinations. The approach combines experimental investigations with computer-aided thermodynamic modelling to characterise phase relations and thermodynamic properties in the six component system $PbO-ZnO-SiO_2-CaO-FeO-Fe_2O_3$ over a wide range of compositions, temperatures and atmospheric conditions.

Using the existing thermodynamic data on binary and ternary systems computer thermodynamic models can be used to predict the behaviour of complex slags. Accurate models can only be constructed from accurate data and model predictions should also be experimentally verified in the range of conditions of interest.

To date there has been no systematic experimental study reported in the literature on the liquidus temperatures and primary phases formed in lead and zinc oxide-containing smelting and reduction slags. The principal reasons for this appear to be experimental difficulties associated with the high temperature equilibration of these melts, particularly PbO and ZnO losses through vaporisation.

The recent developments in research instrumentation in particular i) availability of, ii) easy access to and iii) low user costs of the electron probe X-ray microanalyser have enabled us to overcome these experimental difficulties and to develop experimental methodology for comprehensive characterisation of complex metallurgical slag systems.
New phase diagrams describing phase equilibria in binary, ternary and multi-component systems for complex lead/zinc smelting slags under oxidising and reducing conditions have been produced. These diagrams have provided significant insight into the operation of both sintering and reduction processes. These new experimental data have been used for thermodynamic optimisations using the computer system F*A*C*T.

2. EXPERIMENTAL METHOD

2.1. Quenching technique with electron probe.

The new experimental method developed for the determination of the liquidus temperatures is demonstrated with reference to Figure 1. The artificial slag of composition X (Figure 1) is equilibrated at the temperature T in a controlled gas atmosphere and quenched. The silica-containing liquid phase readily converts to glass so that the phase assemblage which existed at high temperature is frozen in. The compositions of the phases are then measured by electron probe X-ray microanalysis and plotted on the diagram (points e and f on Figure 1 are liquidus and solidus points respectively). The same approach is applied to systems with three or more components.

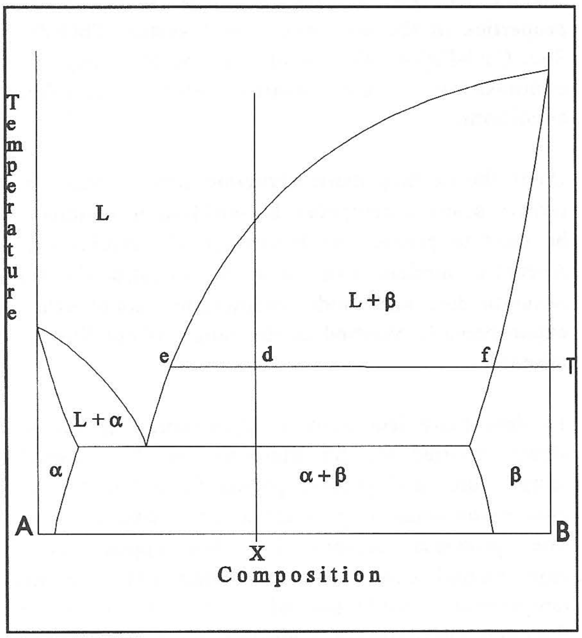

Figure 1. Hypothetical binary phase diagram.

This technique has a number of important advantages over the previously used techniques. More detailed information on the experimental technique, its advantages and its application to the investigation of binary, ternary and multi-component phase diagrams has already been reported[1-5].

One of the most important advantages of this experimental technique for lead and zinc containing systems at high temperatures is the elimination of the inaccuracies associated with the sample composition changes through lead and zinc oxide vaporisation at high temperatures. Bulk composition changes do not affect the final results since measurement is carried out after rather than before the experiment. In addition each experiment provides information on the liquidus composition and on the compositions of the solid phases formed. This greatly increases the productivity of the research and gives information on the extensive solid solutions found in these systems. This experimental technique have enabled for the first time the comprehensive characterisation of this complex multi- component system relevant to the zinc and lead smelting production to be performed.

2.2. Presentation of liquidus data.

In the research on the multi-component systems, pseudo-ternary sections are constructed. The appropriate choice of the end members in the pseudo-ternary sections enables the system to be represented in a simplified way. The results can then be presented in a form which is familiar, easy to use and interpret. This approach also reduces the number of experiments required to characterise the system. For example, in the primary fields of the components with compositions in the plane of the section these multi-component sections can be interpreted in the same way as ternary phase diagrams: eg: the lever rule can be applied to determine the proportions of liquid and solid phases and the crystallisation path can be traced.

The selection of the pseudo-ternary sections to be investigated is carried out so as to obtain information in the region of particular importance for industrial application. An example of this approach as applied to multi-component systems of particular interest for the lead Isasmelt production in Mount Isa Mines is reported[2,5]. This is the first time that systematic information in a useable form has been made available on this multi-component lead and zinc oxide-containing system for oxidising conditions.

2.3. Liquidus in zinc-containing slag under reducing conditions.

The system ZnO-"FeO"-CaO-SiO_2 at metallic iron saturation is characterised experimentally through construction of a number of pseudo-ternary sections of the form ZnO-"FeO"-(CaO+SiO_2) with selected CaO/SiO_2 ratios. An artificial slag containing ZnO, CaO and SiO_2 with selected CaO/SiO_2 ratio is mixed with excess of pure metallic iron powder, pelletised, placed into iron or platinum foil envelopes and equilibrated at given temperature. During equilibration the following reaction takes place:

$$ZnO_{(slag)}+Fe_{(metal)}\text{->}FeO_{(slag)}+Zn_{(gas)}.$$

ZnO is reduced to gaseous zinc metal. One mole of FeO transfers into the condensed slag system for each mole of zinc removed into the gas phase. This stoichiometric restriction together with measured zinc fuming rates are used to locate approximately the final bulk composition of the condensed system. After quenching the sample from the equilibration temperature the procedure is similar to that reported previously[1-5]. The sample is mounted, polished, examined using the optical microscope. The compositions of glass (liquid phase-liquidus) and crystalline phase (solidus) are measured with EPMA, and results are plotted on the pseudo-ternary section.

3. SUMMARY OF EXPERIMENTAL RESULTS ON BINARY, TERNARY AND QUINARY SYSTEMS

A number of binary, ternary and quinary sub-systems have been experimentally investigated in order to provide information essential for the thermodynamic optimisations. The systems were selected for the experimental investigation when no information was available previously or when significant discrepancies were found during a course of initial evaluations and optimisations using the computer system F*A*C*T.

For instance, significant discrepancies had been identified between existing activity and phase equilibrium data on the systems PbO-ZnO-SiO_2 and

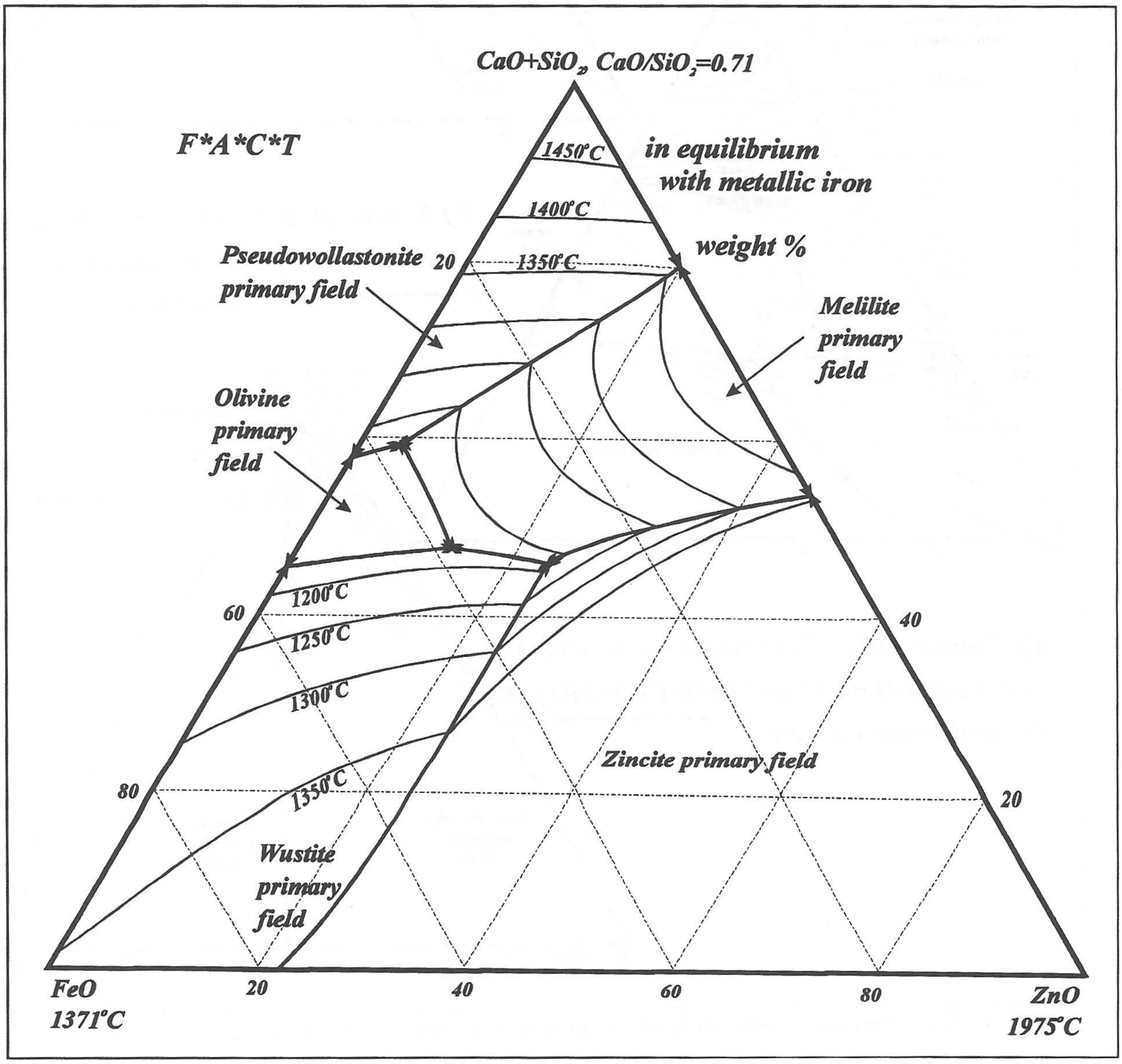

Figure 2. Experimentally determined liquidus in the section ZnO-"FeO"-(CaO+SiO_2) with CaO/SiO_2=0.71 at metallic Fe saturation.

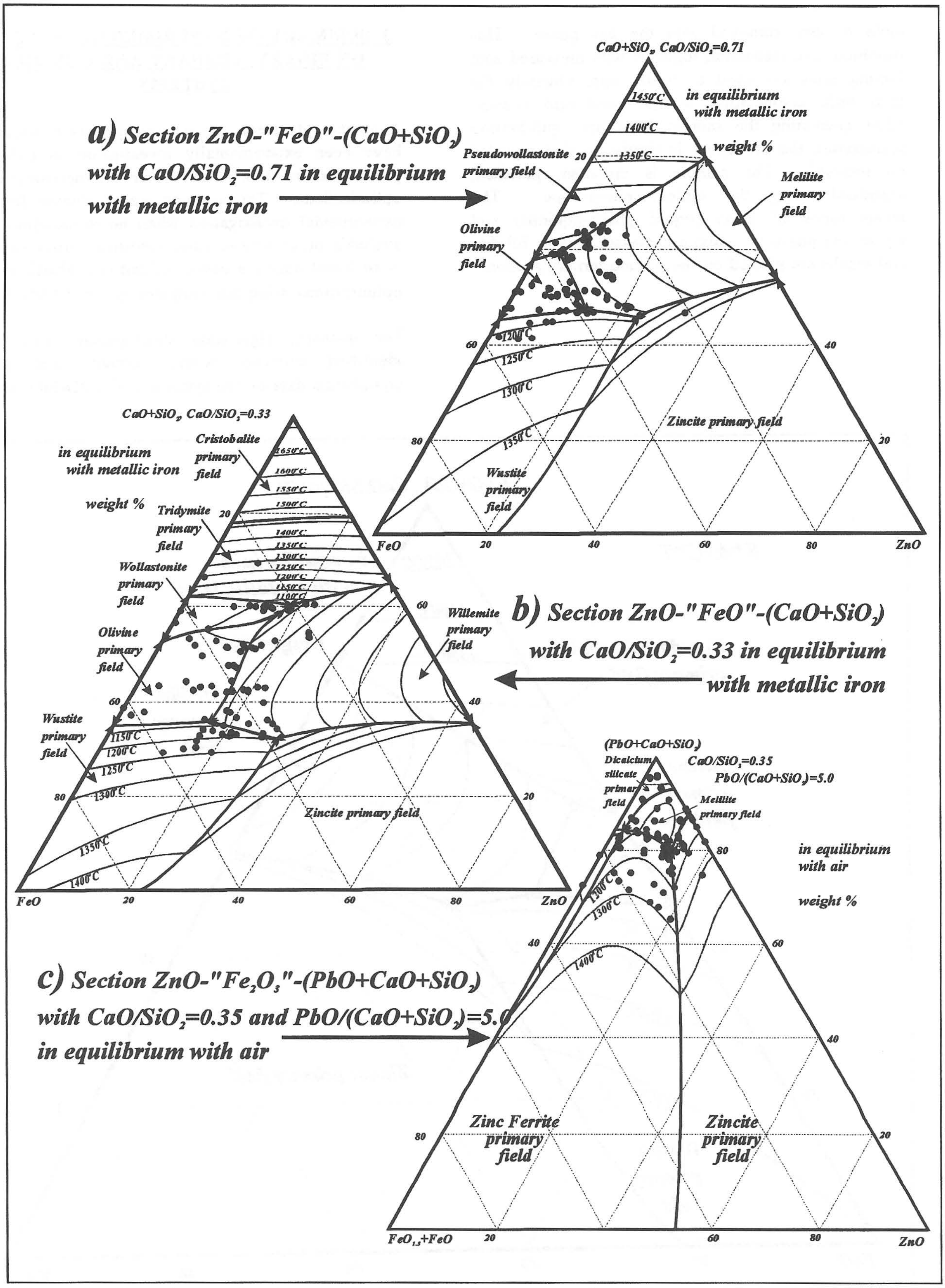

Figure 3. Experimental points in multi-component system from the present study.

$PbO-CaO-SiO_2$. These discrepancies were found during thermodynamic optimisations using the computer system F*A*C*T. Comprehensive experimental investigation was carried out which enabled these discrepancies to be resolved and these phase diagrams to be reconstructed and recalculated. The work on these systems has been previously reported[1,3,4].

No information on liquidus temperatures in the system $PbO-FeO-Fe_2O_3-SiO_2$ was previously available in the literature. Comprehensive experimental investigation has been undertaken on this system in equilibrium with air and results presented on the section PbO-"Fe_2O_3"-SiO_2. New experimental information have enabled us to optimise the system $PbO-Fe_2O_3-SiO_2$.

Recent experimental investigation[5] on the system $ZnO-FeO-Fe_2O_3$ not only resolved discrepancies among previously available experimental information on zinc ferrite activities, but also provided solid solubility data essential for the thermodynamic modelling.

No accurate experimental information was available previously on liquidus temperatures in the four-component system $ZnO-FeO-Fe_2O_3-SiO_2$. Experimental work has been undertaken on this system in two extreme conditions in terms of oxygen partial pressures - in equilibrium with metallic iron and in equilibrium with air.

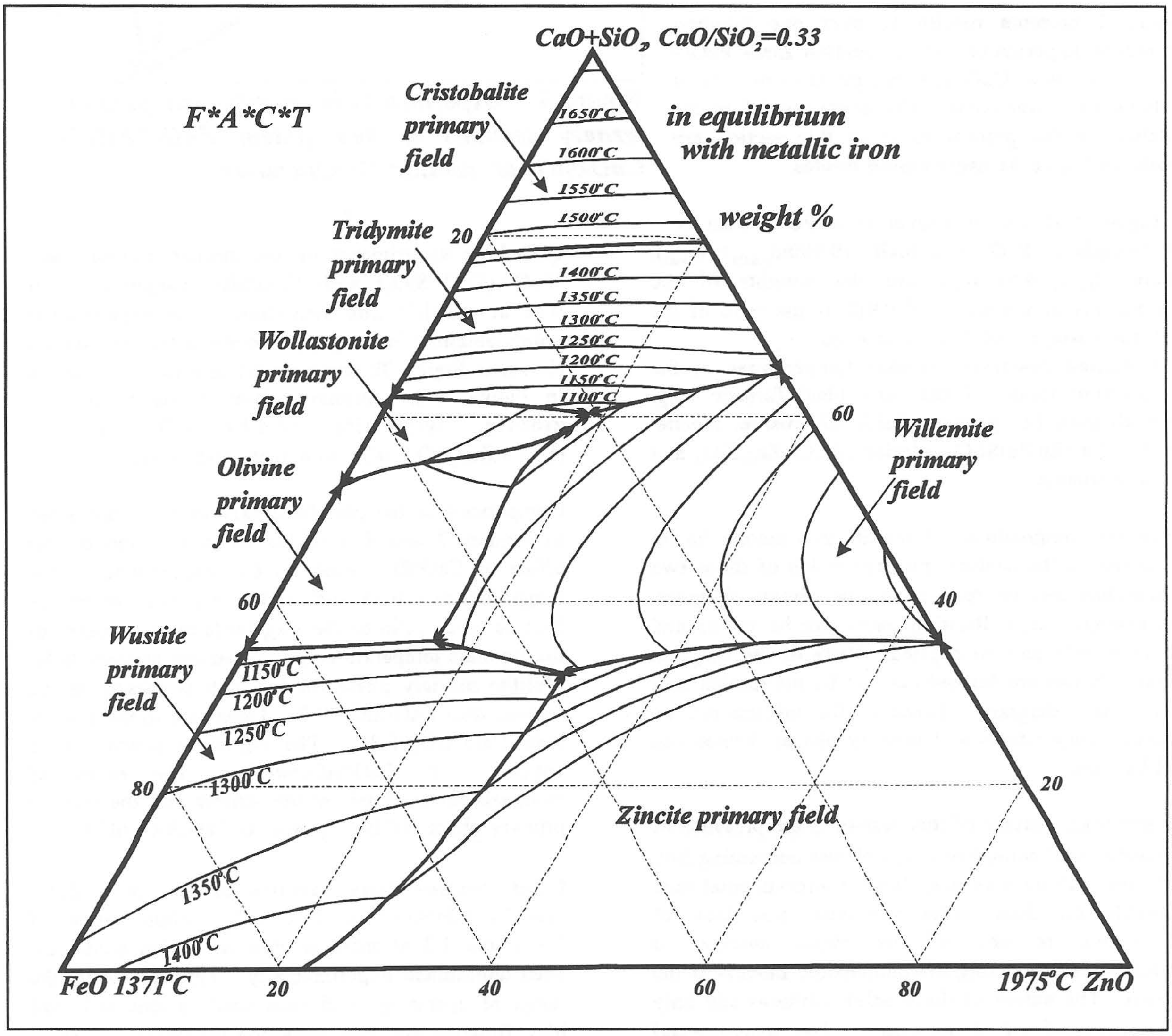

Figure 4. Experimentally determined liquidus in the section ZnO-"FeO"-(CaO+SiO$_2$) with CaO/SiO$_2$=0.33 at metallic Fe saturation.

This new experimental information and details of research on particular systems will be published elsewhere.

4. EXPERIMENTAL RESULTS ON THE SYSTEM ZnO-"FeO"-CaO-SiO_2 AT METALLIC IRON SATURATION

Research has been carried out to establish the liquidus temperatures in the five-component system ZnO-FeO-Fe_2O_3-CaO-SiO_2 in equilibrium with metallic iron in the composition ranges of lead reduction slags and lead and zinc blast furnace slags. The results are presented in the form of pseudo-ternary sections ZnO-"FeO"-(CaO+SiO_2) with fixed CaO/SiO_2 weight ratios.

Figure 2 presents results of over one hundred quenching experiments on the section ZnO-"FeO"-(CaO+SiO_2) with CaO/SiO_2 weight ratio of 0.71 at metallic iron saturation. The experimental points obtained in the present study in this section are shown in Figure 3a using closed circles.

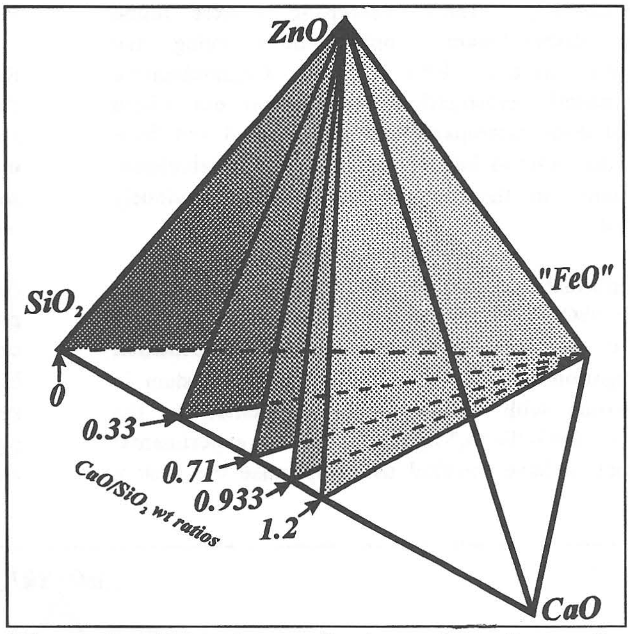

***Figure 5.** Experimentally investigated pseudo-ternary sections in the system ZnO-"FeO"-CaO-SiO_2 at metallic Fe saturation.*

In Figure 2 all Fe^{3+} is converted to Fe^{2+}. That is, the "weight of FeO" is actually ($0.900m_{Fe2O3}+ m_{FeO}$), where m_{Fe2O3} and m_{FeO} are the weights of the components in a phase, and 0.900 is the ratio of the molecular weights of 2FeO and Fe_2O_3.
This section describes liquidus temperatures in the composition range of the lead blast furnace slag. This diagram has primary fields of wustite, zincite, melilite $Ca_2(Zn,Fe)Si_2O_7$, olivine $(Fe,Ca,Zn)_2SiO_4$ and calcium silicate.

Since the compositions of wustite and zincite lie on the plane of the section, primary fields of these two compounds can be read as a true ternary diagram. For example, crystallisation paths can be traced and the lever rule can be applied. Parts of the diagram where silicates are formed can not be interpreted as a true ternary diagram. However the information on liquidus temperatures and primary phases formed can still be used.

An important feature of this system is the presence of extensive solid solubility in the phases containing iron and zinc. There was only limited experimental data available on these solid solutions; this lack of information is one of the major sources of inaccuracies of existing thermodynamic models of the system. The extent of these solid solutions can only be determined by experiment. The experimental method with EPMA enables direct measurements of solid solubility.

Figure 4 presents results of about one hundred quenching experiments on the similar section ZnO-"FeO"-(CaO+SiO_2) with CaO/SiO_2 weight ratio of 0.33 at metallic iron saturation. The experimental points obtained in the present study in this section are shown in Figure 3b using closed circles. The section in Figure 4 has primary phase fields of wustite, zincite, willemite $(Zn,Fe)_2SiO_4$, olivine $(Fe,Ca,Zn)_2SiO_4$, calcium silicate and silica.

Comparison of the pseudo-ternary sections presented in Figures 2 and 4 provides an information on the effect of CaO/SiO_2 ratio on the slag system in the range between 0.33 and 0.71. An increase of the lime to silica ratio of the slag leads to an increase of the liquidus temperatures in the wustite primary field. Melilite primary phase field, which is present in the section with CaO/SiO_2=0.71, disappears in the section with CaO/SiO_2=0.33. The willemite primary field appears at CaO/SiO_2=0.33. The range of compositions covered by the zincite and the wustite primary phase fields is greater at CaO/SiO_2=0.71.

Other pseudo-ternary sections of the form ZnO-"FeO"-(CaO+SiO_2) at CaO/SiO_2 weight ratios of 0.933 and 1.2 at metallic iron saturation have also been determined experimentally. This set covers the range of operating conditions used in zinc and lead blast furnaces and lead reduction processes. Figure 5 illustrates the pseudo-ternary sections in the system ZnO-"FeO"-CaO-SiO_2 experimentally investigated in the present study. This is the first time the liquidus temperatures of zinc containing slags under reducing conditions have been experimentally determined.

5. EXPERIMENTAL RESULTS ON THE SYSTEM PbO-ZnO-FeO-Fe_2O_3-CaO-SiO_2 IN EQUILIBRIUM WITH AIR

Research has also been carried out to establish the liquidus temperatures in the six component system PbO-ZnO-FeO-Fe_2O_3-CaO-SiO_2 in air in the composition range of lead smelting slags and lead and zinc blast furnace sinters. The results are presented in the form of pseudo-ternary sections ZnO-"Fe_2O_3"-(PbO+CaO+SiO_2) with fixed CaO/SiO_2 and PbO/(CaO+SiO_2) weight ratios.

Figure 6 presents results on the section ZnO-"Fe_2O_3"-(PbO+CaO+SiO_2) in air with CaO/SiO_2 and PbO/(CaO+SiO_2) weight ratios of 0.35 and 5.0 respectively. The experimental points obtained in the present study in this section are shown in Figure 3c using closed circles.

In Figure 6 all Fe^{2+} is converted to Fe^{3+}. That is, the "weight of Fe_2O_3" is actually (m_{Fe2O3}+1.111m_{FeO}), where m_{Fe2O3} and m_{FeO} are the weights of the components in a phase, and 1.111 is the ratio of the molecular weights of Fe_2O_3 and 2FeO.

This section describes slag compositions close to those used in the lead oxidative smelting practices. The system in this composition range has primary phase fields of zincite (ZnO), zinc ferrite ($Zn_xFe_{3-x}O_4$), hematite (Fe_2O_3), magnetoplumbite (PbO*5-6Fe_2O_3), melilite ((Ca,Pb)$_2$(Zn,Fe^{2+},Fe^{3+})(Si,Fe^{3+})$_2O_7$) and dicalcium silicate ((Ca,Fe,Pb,Zn)$_2SiO_4$).

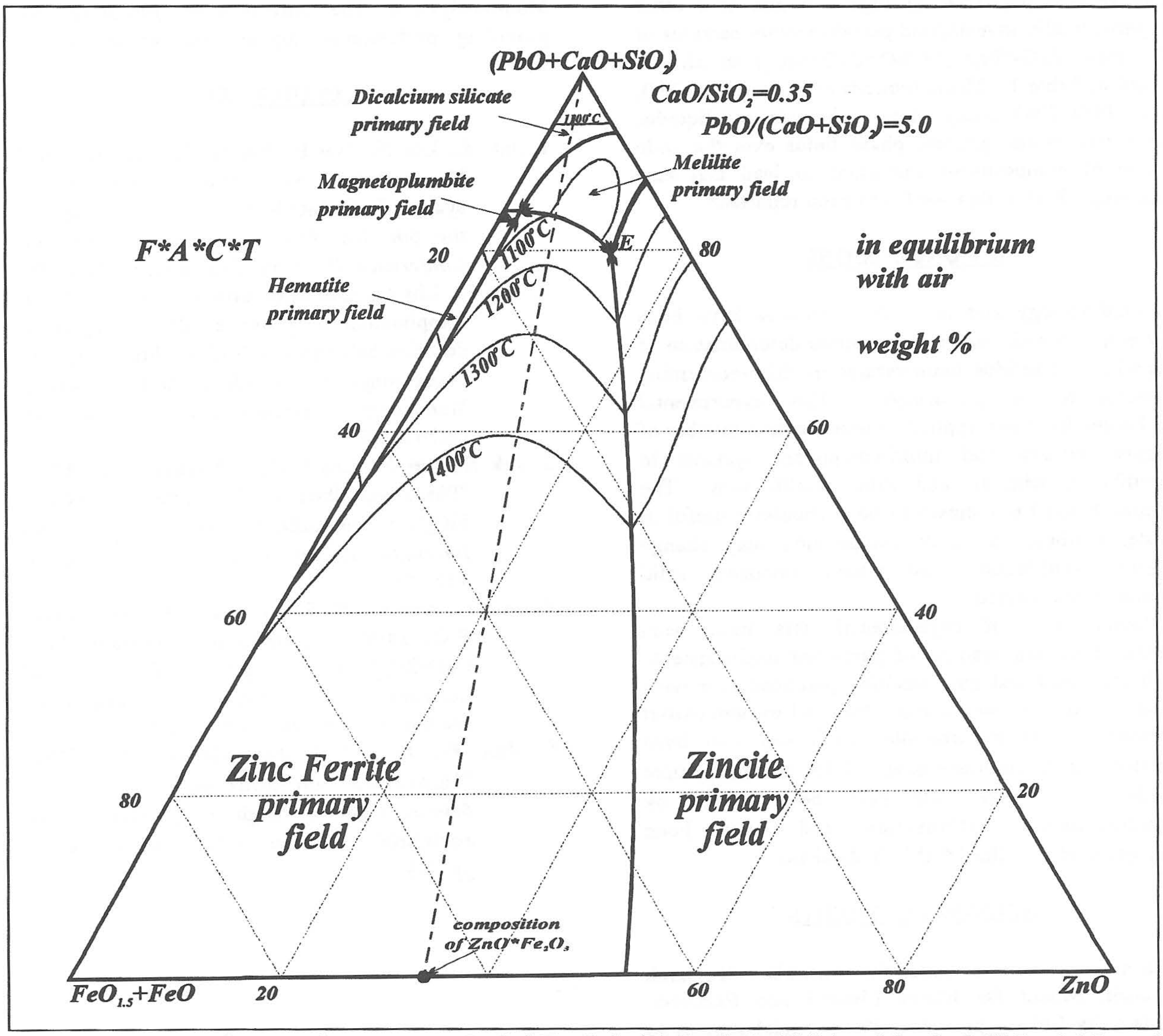

Figure 6. Liquidus in the section ZnO-"Fe_2O_3"-(PbO+CaO+SiO_2) with CaO/SiO_2=0.35 and PbO/(CaO+SiO_2)=5.0 in air.

Table 1. List of the pseudo-ternary sections in the system $PbO-ZnO-FeO-Fe_2O_3-CaO-SiO_2$ in air investigated during the course of this study.

CaO/SiO_2 on weight basis	$PbO/(CaO+SiO_2)$ on weight basis	Application
0.35	5	lead oxidative smelting slag
0.1	6.2	lead oxidative smelting slag
0.6	4.3	lead oxidative smelting slag
0.35	3.2	lead oxidative smelting slag
0.933	2	zinc ISF sinter
0.933	3.2	lead blast furnace sinter

This form of presentation allows the proportions of the phases present at temperature, and the solidification sequence, to be readily predicted in the primary fields of zincite and zinc ferrite.

The section presented in Figure 6 and five other experimentally investigated pseudo-ternary sections of the form ZnO-"Fe_2O_3"-$(PbO+CaO+SiO_2)$ in air are listed in Table 1. These sections at various CaO/SiO_2 and $PbO/(CaO+SiO_2)$ ratios characterise liquidus temperatures and primary phase fields over the wide range of compositions important to lead and zinc smelting. Part of this work has been reported[2,5].

6. CONCLUSIONS

A methodology and research techniques have been developed which enable the accurate determination of liquidus and solidus temperatures in silica-containing systems to be performed. This experimental technique has been applied to investigate a number of binary, ternary and multi-component systems in equilibrium with air and with metallic iron. The approach has been shown to be particularly useful in systems where the melt composition may change during equilibration and where extensive solid solutions are formed.
Extensive sets of experimental data have been obtained in slag systems of particular importance to industrial lead and zinc smelting practices over wide ranges of temperature, composition and oxygen partial pressure. The experimental work has also been carried out in the areas essential for thermodynamic modelling. These data have been treated by thermodynamic optimisation and have been incorporated into the F*A*C*T database.

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