

Thermodynamic modelling of the system $\text{PbO-ZnO-FeO-Fe}_2\text{O}_3\text{-CaO-SiO}_2$ for zinc/lead smelting.

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ABSTRACT

Thermodynamic modelling of the six-component system $\text{PbO-ZnO-FeO-Fe}_2\text{O}_3\text{-CaO-SiO}_2$ is part of a wider research program aimed at characterisation of phase equilibria and thermodynamic properties of zinc/lead smelting slags and sinters by interactive combination of experimental investigations and thermodynamic modelling.

The thermodynamic modelling of oxide systems was carried out using the computer system F*A*C*T. The F*A*C*T databases contain thermodynamic data on over 5000 compounds as well as evaluated databases for solutions (alloys, slags, salts, mattes, ceramics, etc.). The polynomial and sublattice models were used for the solid solutions in this study. The modified quasichemical model was used for the liquid phase.

Data available in the literature were initially evaluated using the computer system F*A*C*T. Where a significant discrepancy in existing experimental data was identified or where data were not available, experimental investigations of two- and three-component systems were undertaken. The new experimental data were used for further optimisations. All binary and ternary sub-systems were optimised to obtain a self-consistent set of model parameters.

The computer model parameters were adjusted to describe an extensive set of new experimental data obtained in air and at metallic iron saturation in the multi-component areas of particular importance for

industrial applications. This resulted in a significant improvement in the predictive ability of the computer model in the regions of interest for lead and zinc metallurgical production.

1. INTRODUCTION

In addition to lead and zinc oxides, the major components of a wide range of slag and sinter compositions which are used in zinc and lead production include lime, silica and oxides of iron 2+ and 3+. For the most part, phase relations in these complex slag systems were not well established even in slags which are used in commercial processes. The aim of the current study is to characterise phase equilibria and thermodynamic properties in the six-component system $\text{PbO-ZnO-SiO}_2\text{-CaO-FeO-Fe}_2\text{O}_3$ by combination of experimental investigations and computer-aided thermodynamic modelling.

In the thermodynamic "optimisation" of a system, all available thermodynamic and phase equilibrium data for the system are evaluated simultaneously in order to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, all of the thermodynamic properties and the phase diagrams can be back-calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram, and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can be identified. These discrepancies can then be resolved through new experimental studies. Experimental investigation is also undertaken in areas essential for further thermodynamic optimisations.

The self-consistent thermodynamic database developed in this way is used within the computer system F*A*C*T for interpolations and extrapolations in a thermodynamically correct manner.

2. RESULTS OF THERMODYNAMIC OPTIMISATIONS

For the molten slag phase a modified quasi-chemical model has been used. A description of the model and its application to various systems was reported previously¹⁻¹⁵. Parameters for the computer model of the slag system are obtained from existing thermodynamic information on binary and ternary systems. The optimisations for the binary systems are performed using least-squares optimisation programs which are part of the F*A*C*T computer database system. The polynomial and sublattice models were used for the solid solutions in this study.

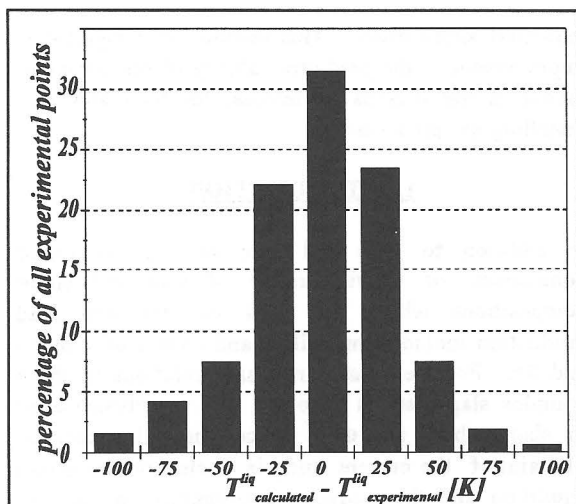


Figure 1. Comparison between calculations and experiments for multi-component composition regions.

The six-component system PbO-ZnO-SiO₂-CaO-FeO-Fe₂O₃ contains fifteen binary and twenty ternary sub-systems. All these sub-systems were optimised initially in the course of this study. The agreement with an extensive set of new experimental data obtained in equilibrium with air and with metallic iron in the multi-component areas of particular importance for industrial applications (over one thousand experimental points) was then tested, and a number of binary and ternary systems were re-optimised to achieve agreement with experimental data in binary, ternary and multi-component systems. This iterative procedure was repeated a number of times until extensive experimental data sets in equilibrium with air and with metallic iron were well reproduced by computer calculations.

Figure 1 illustrates the agreement achieved between calculations and experiments in multi-component systems. The difference between calculated and experimentally determined liquidus temperatures is plotted along the x-axis in Figure 1, and the percentage of the total number of data points (over 1000) lying in a given difference range is plotted along the y-axis. Approximately 80 % of all experimental points in the multi-component composition regions are reproduced to within ± 25 K (45°F) and about 95 % of all experimental points are reproduced to within ± 50 K (90°F). Those points having larger disagreement in terms of liquidus temperature are in the composition regions where the liquidus surface is very steep, so that the maximum disagreement in term of composition is only 2-3 mol %.

The details of optimisations of the binary, ternary and multi-component systems performed during this study

will be published elsewhere.

3. THERMODYNAMIC MODELLING - EXAMPLES OF APPLICATION

A number of examples of the application of the developed thermodynamic model of the six-component system PbO-ZnO-SiO₂-CaO-FeO-Fe₂O₃ to the description of industrial slags are cited below.

3.1. Pseudo-ternary sections

Three pseudo-ternary sections:

- ZnO-"Fe₂O₃"-(PbO+CaO+SiO₂) at CaO/SiO₂ and PbO/(CaO+SiO₂) weight ratios of 0.35 and 5.0 respectively in equilibrium with air and
- ZnO-"FeO"-(CaO+SiO₂) at CaO/SiO₂ of 0.71 and 0.33 (weight) in equilibrium with metallic iron calculated by the computer system F*A*C*T are reported in this volume¹⁶. These three diagrams correspond to the experimentally investigated pseudo-ternary sections.

Lead oxidative smelting can be undertaken under a range of temperatures and oxygen pressures. All of the lead can be incorporated into the slag phase at high oxygen pressures. At lower oxygen pressures metallic lead can be formed in equilibrium with the slag. In these later cases the oxygen partial pressures in the smelting bath lie between those determined experimentally, ie between air (0.21 atm.) and iron saturation. The optimised model can therefore be used to predict the phase equilibria at these intermediate conditions. The computer predictions by the system F*A*C*T, using the database which has been developed, has shown that, in the composition range of industrial lead smelting slags in equilibrium with metallic lead, at liquidus temperatures the oxygen partial pressures are between 10⁻⁷ and 10⁻⁹ atm. Therefore the pseudo-ternary section of the form ZnO-"Fe₂O₃"-(PbO+CaO+SiO₂) at CaO/SiO₂ and PbO/(CaO+SiO₂) weight ratios of 0.35 and 5.0 respectively was calculated at an oxygen partial pressure of 10⁻⁸ atm. Figure 2 presents a projection of the liquidus surface on this section. In Figure 2, all Fe²⁺ is converted to Fe³⁺. That is, the "weight of Fe₂O₃" is actually ($m_{\text{Fe}_2\text{O}_3} + 1.111m_{\text{FeO}}$), where $m_{\text{Fe}_2\text{O}_3}$ and m_{FeO} are the weights of the components in a phase, and 1.111 is the ratio of the molecular weights of Fe₂O₃ and 2FeO.

The difference between this section at P_{O₂}=10⁻⁸ atm and the one calculated at P_{O₂}=0.21 atm (air) (see Figure 3¹⁶) is distinctive. The liquidus temperatures in the zincite primary field increase with a decrease of P_{O₂}. At the lower oxygen potential the range of compositions covered by the zincite primary field is greater than at high P_{O₂}. The wustite primary

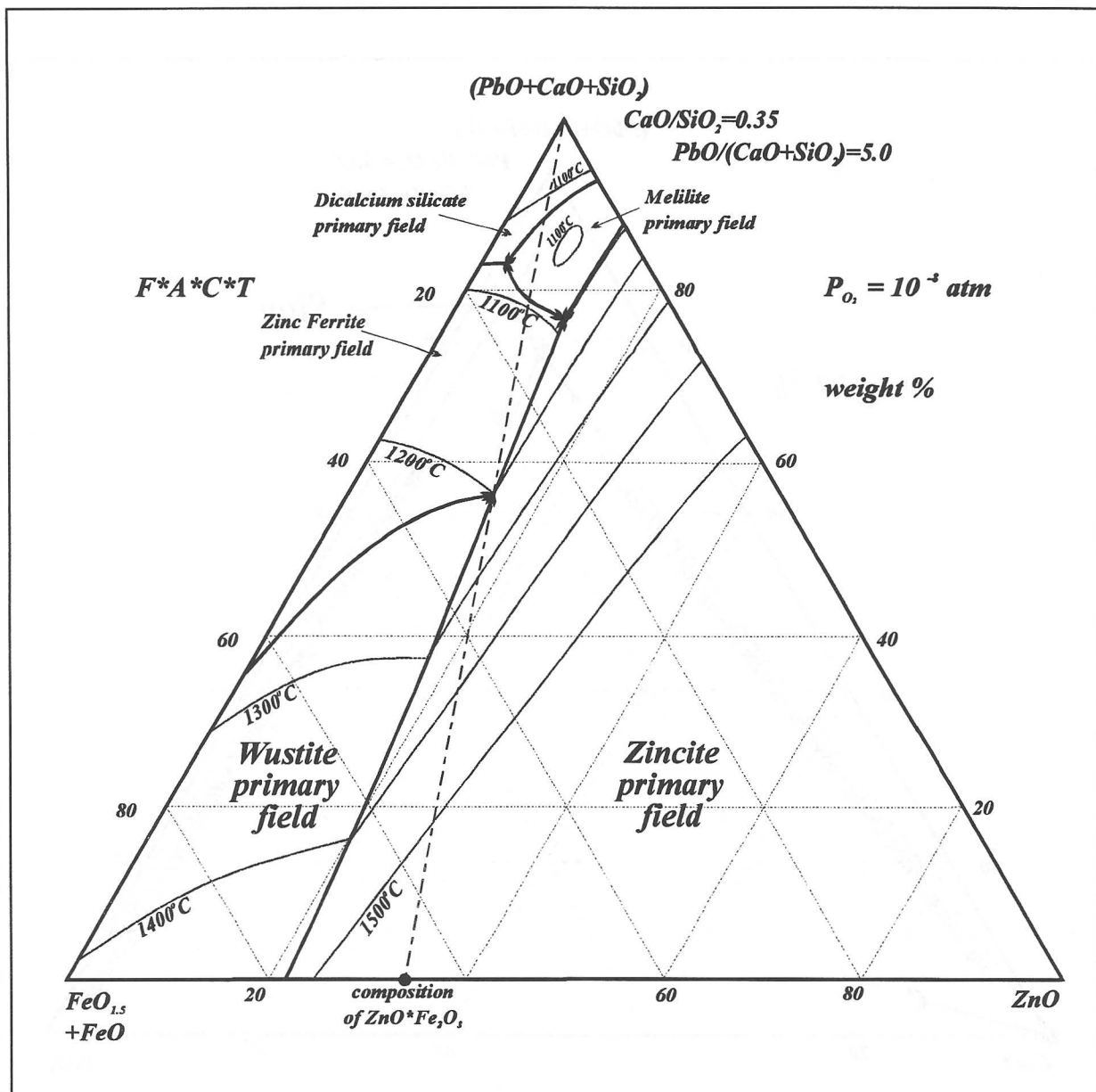


Figure 2. Liquidus in the section $ZnO-Fe_2O_3-(PbO+CaO+SiO_2)$, $CaO/SiO_2=0.35$ and $PbO/(CaO+SiO_2)=5.0$ at $P_{O_2}=10^{-8}$ atm.

phase field appears at $P_{O_2}=10^{-8}$ atm. There are no hematite and magnetoplumbite primary phase fields at $P_{O_2}=10^{-8}$ atm. The liquidus temperatures in the zinc ferrite and in the melilite primary phase fields are lower at $P_{O_2}=10^{-8}$ atm compared to those in equilibrium with air.

3.2. Slag fluxing by lime and silica

Lime and silica are used for the fluxing of lead smelting slags. Figure 3 illustrates possible means of pseudo-ternary section construction which can be used for the prediction of liquidus temperatures of a given

slag as a function of CaO and SiO₂ content. The calcium and silicon oxides are placed in two corners of the section and the sum of lead, zinc and iron oxides at the proportions corresponding to a given slag composition are placed in the third corner. Here and below the initial lead smelting slag composition is taken from¹⁷ and is indicated as a circle in Figure 3. In this method of construction of the pseudo-ternary section, the slag composition changes along the plane of the section with addition or removal of CaO and SiO₂. The arrows on Figure 3 indicate the slag composition changes associated with changes of either CaO or SiO₂. The amount of addition or

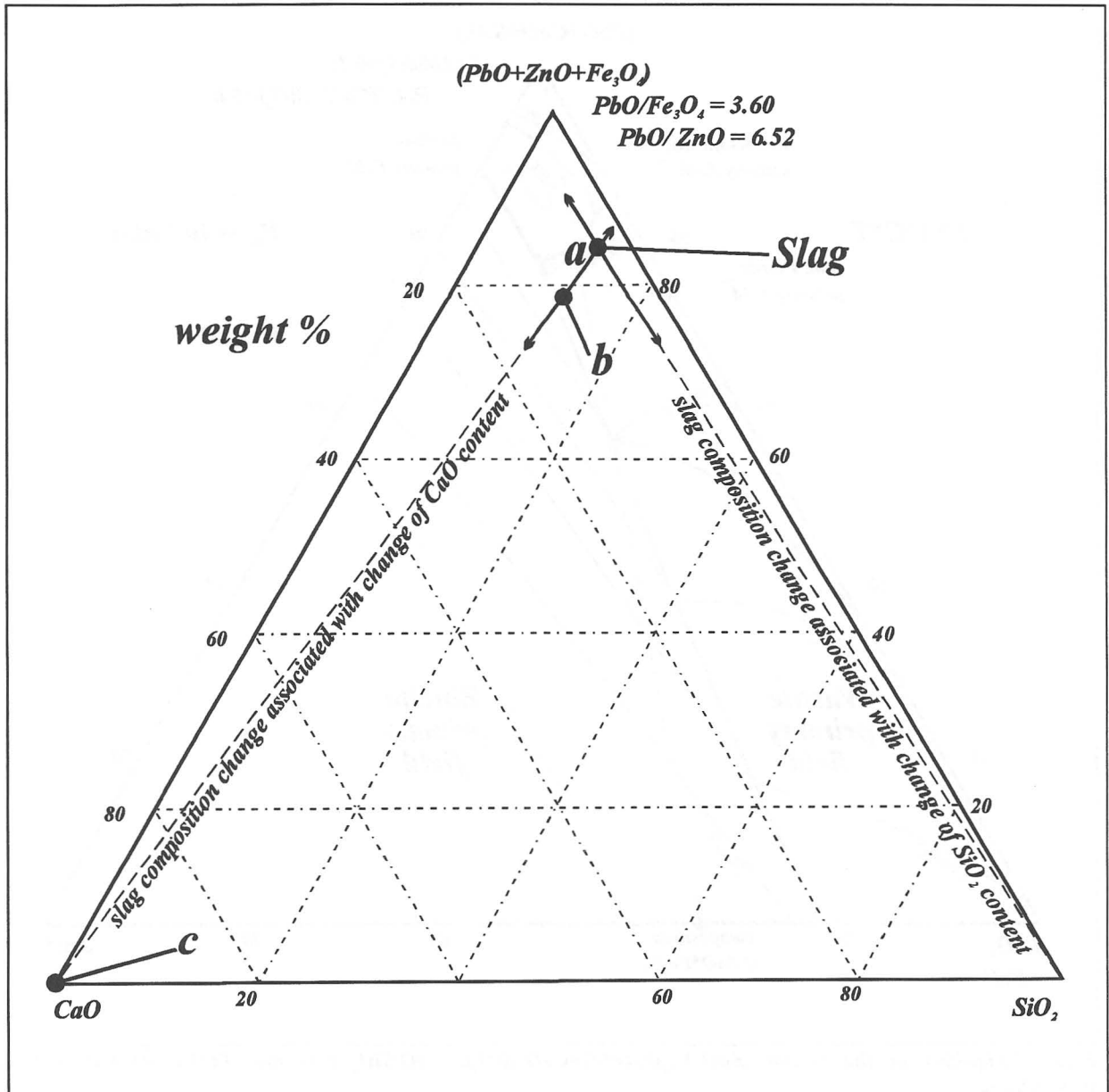


Figure 3. The section $\text{CaO-SiO}_2\text{-(PbO+ZnO+Fe}_3\text{O}_4)$ with $\text{PbO/Fe}_3\text{O}_4=3.60$ and $\text{PbO/ZnO}=6.52$.

removal of CaO or SiO_2 required to achieve a certain slag chemistry can be easily worked out from this diagram by means of the lever rule. For instance, to change the composition of the slag from an initial point a (see Figure 3) to point b by addition of CaO (point c), the amount of CaO should be $100 \cdot (ab)/(bc)$ gram per 100 gram of initial slag.

A projection of the liquidus surface on the section $\text{CaO-SiO}_2\text{-(PbO-ZnO-Fe}_3\text{O}_4)$ in the composition range near the industrial lead smelting slag composition¹⁷ is presented in Figure 4. This diagram is calculated at $P_{\text{O}_2}=10^{-8}$ atm using the $F \cdot A \cdot C \cdot T$

system with the optimised models.

In Figure 4 all iron is converted to Fe_3O_4 . That is, the "weight of Fe_3O_4 " is actually $(2m_{\text{Fe}_2\text{O}_3}/159.692 + m_{\text{FeO}}/71.847) \cdot 231.539/3$, where $m_{\text{Fe}_2\text{O}_3}$ and m_{FeO} are the weights of the components in a phase, and 159.692, 71.847 and 231.539 are the molecular weights of Fe_2O_3 , FeO and Fe_3O_4 respectively.

The liquidus temperature changes as a function of CaO and SiO_2 content in the slag can be easily read from this diagram.

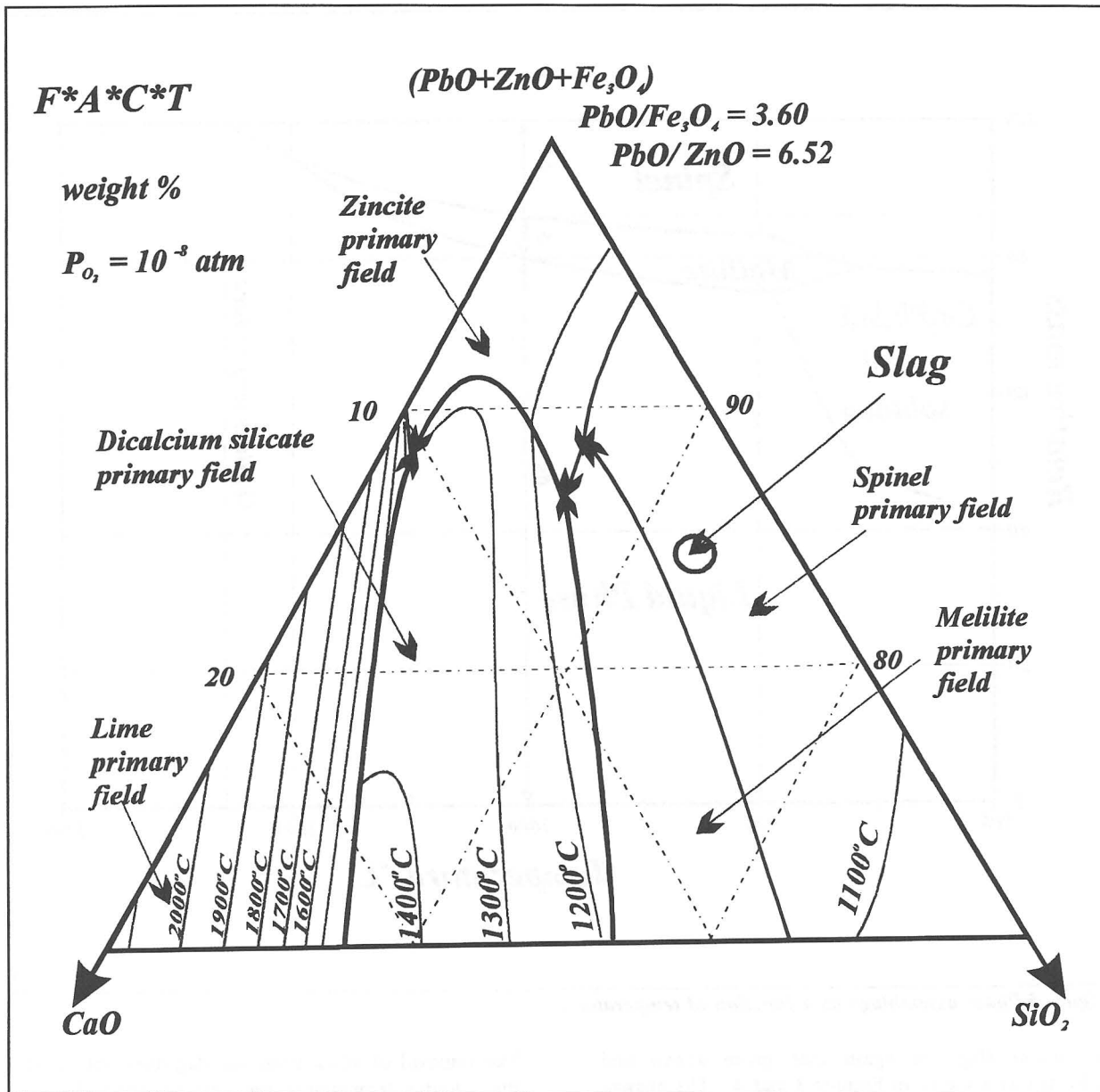


Figure 4. Liquidus in the section $CaO-SiO_2-(PbO+ZnO+Fe_3O_4)$ with $PbO/Fe_3O_4=3.60$ and $PbO/ZnO=6.52$ $P_{O_2}=10^{-8} \text{ atm}$.

3.3. Phase assemblage as a function of temperature

Figure 5 illustrates the use of the model to predict the proportions of liquid and solid phases as a function of temperature for a given slag composition. The overall slag composition¹⁷ is that considered above and is indicated as a circle in Figures 3 and 4. The oxygen partial pressure is 10^{-8} atm (see comments above).

As temperature is decreased below the liquidus, the proportion of spinel phase (zinc ferrite solid solution) grows, and the proportion of the liquid phase decreases. At a temperature of approximately 1100°C (2012 °F), the melilite phase starts to precipitate in

addition to the zinc ferrite phase. The proportion of liquid and solid phases can easily be read from Figure 5. For instance, at 1000°C (1832 °F), 100 g of the overall material consists of 80 g of liquid, 6 g of the melilite and 14 g of the zinc ferrite phase.

3.4. Liquidus temperatures as a function of CaO, SiO₂ and ZnO content

Figures 6 through 8 present liquidus temperatures of the slag at $P_{O_2}=10^{-8}$ atm as a function of CaO, SiO₂ and ZnO additions or removals (in grams per 100 g of initial slag along the x-axis). The composition of

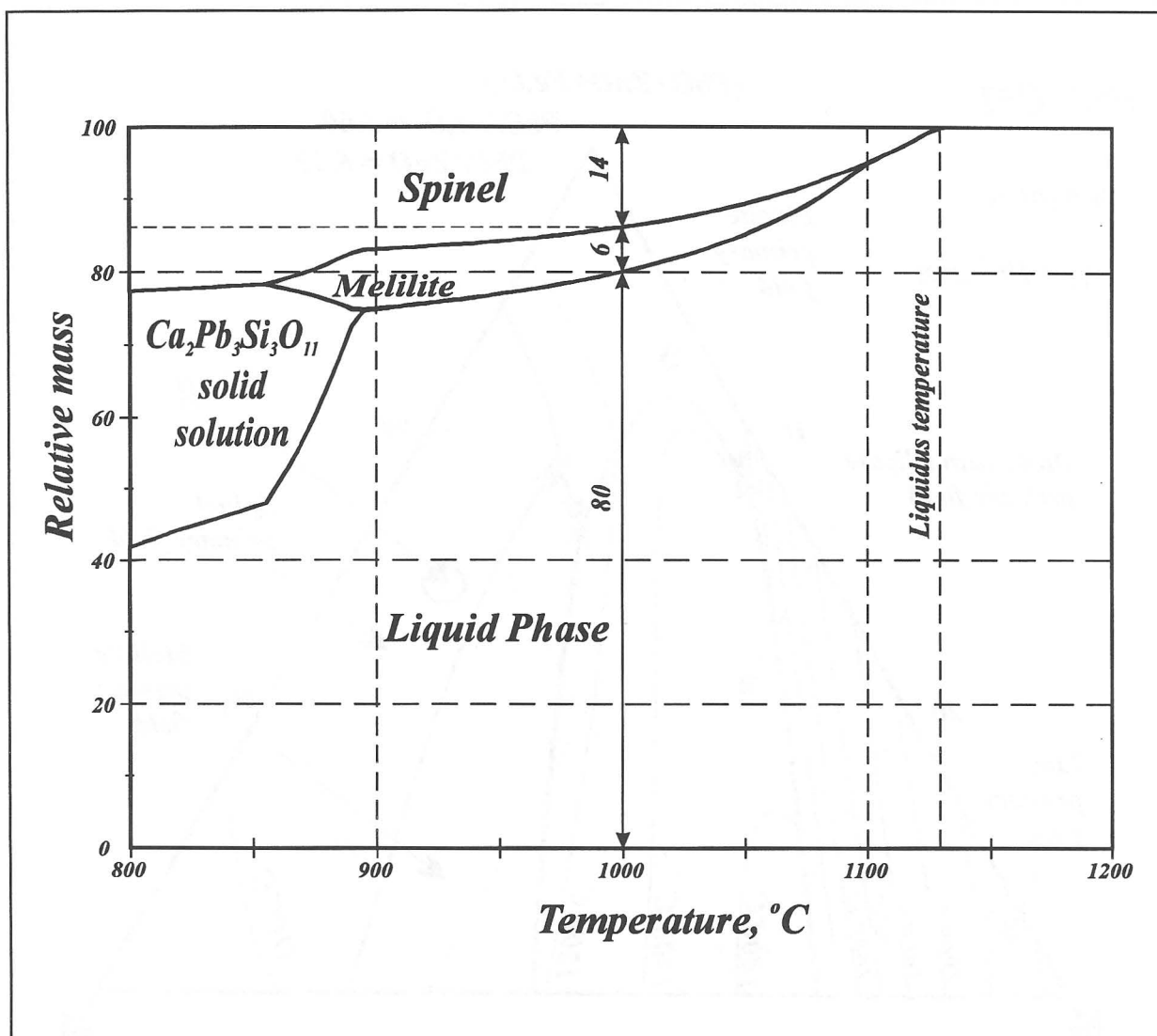


Figure 5. Phase assemblage as a function of temperature.

the initial slag¹⁷ is again that given above and indicated as a circle in Figures 3 and 4. The change of liquidus temperatures can easily be calculated and read from these figures as a function of an oxide addition or removal.

The liquidus temperature increases slightly as CaO is removed from the slag (see Figure 6). The liquidus temperature decreases slightly with addition of CaO to the initial slag before the slag composition reaches the melilite primary phase field at about 1 g of CaO added per 100 g of the initial slag. Further addition of CaO leads to an increase of the liquidus temperature in the melilite primary field and a sharp increase of the liquidus temperature when the slag composition enters the di-calcium silicate primary field.

The removal of silica from the slag does not change the liquidus temperature appreciably while the slag composition is in the spinel primary phase field (see Figure 7). However, when more than 6 g of silica is removed from the slag, the slag composition reaches the zincite primary field and further removal of silica from slag leads to a sharp increase of the liquidus temperature. Addition of silica up to about 34 g per 100 g of the initial slag leads to a decrease of the liquidus temperature.

An increase of the ZnO content of the slag leads to a slight increase of the liquidus temperature while the slag composition is in the spinel primary field (see Figure 8). When the composition reaches the zincite primary field, the liquidus temperature grows sharply with further increase of the ZnO content.

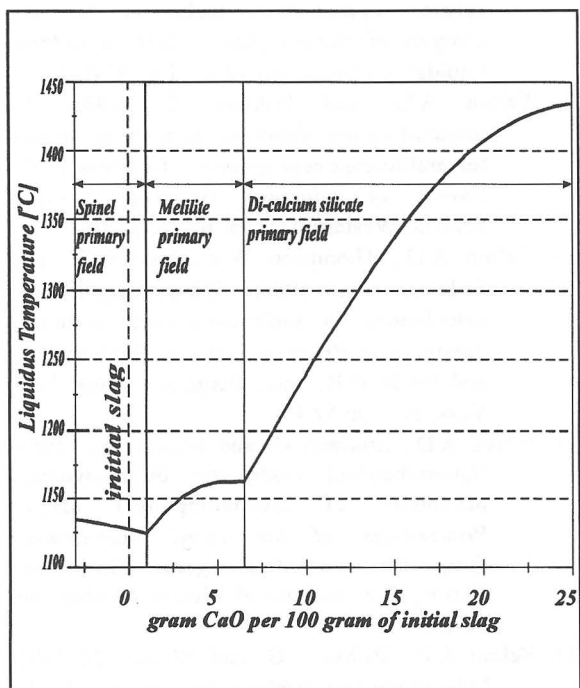


Figure 6. Liquidus temperatures of lead smelting slag as a function of the CaO content.

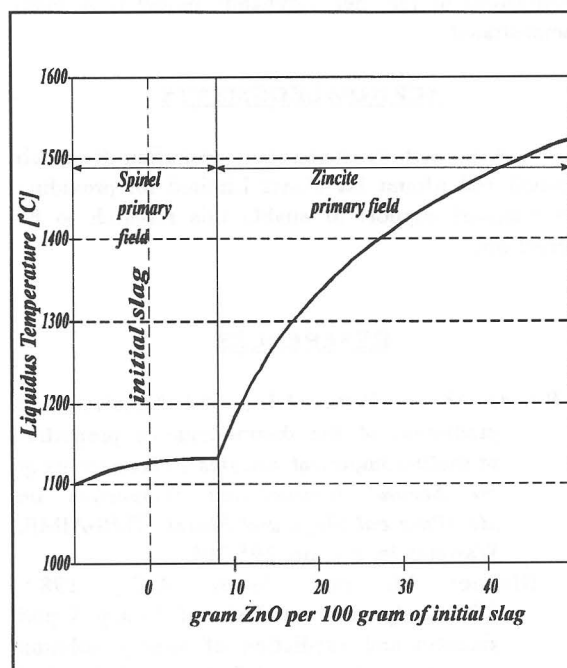


Figure 8. Liquidus temperatures of lead smelting slag as a function of the ZnO content.

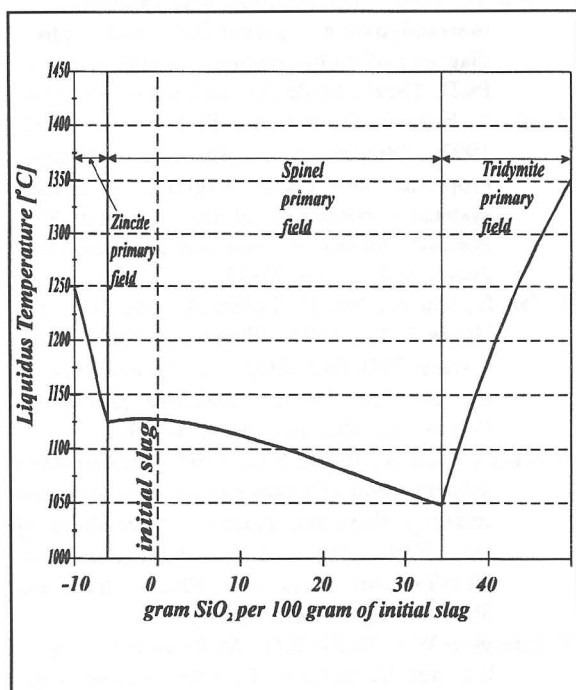


Figure 7. Liquidus temperatures of lead smelting slag as a function of the SiO₂ content.

4. CONCLUSIONS

An initial evaluation of the thermodynamic data and phase diagrams currently available for the PbO-ZnO-FeO-Fe₂O₃-CaO-SiO₂ system was conducted using the computer system F*A*C*T. The discrepancies in previously existing data were identified. To resolve these discrepancies, and to obtain experimental information essential for the thermodynamic optimisations, new experimental work has been carried out.

Using new experimental data, which has been determined over a wide ranges of composition, temperature and oxygen partial pressure in the present study, the thermodynamic properties in the binary, ternary and multi-component systems have been re-optimised, with the quasi-chemical model being used for the liquid phase, and with the polynomial and the sublattice models being used for the solid solutions.

A self-consistent thermodynamic database can now be used for the prediction of phase relations and various thermodynamic properties of the multi-component system PbO-ZnO-SiO₂-CaO-FeO-Fe₂O₃. The model provides a powerful tool to enable the thermodynamic properties and phase equilibria in these complex systems to be predicted accurately for a wide range of

slag compositions. A number of examples of applications of the thermodynamic model have been demonstrated.

ACKNOWLEDGMENTS

The authors wish to thank the Australian Research Council and Mount Isa Mines Limited for providing the financial support to enable this research to be carried out.

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