

Phase equilibria determination in complex slag systems

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Despite the wealth of information available on phase equilibria of oxide systems there remain many gaps and inconsistencies in our knowledge base. From an industry perspective there is an ongoing need to adequately describe the phase chemistry of slag systems in order to optimize process performance and improve productivity. Since this chemical behaviour cannot be predicted from first principles it follows there is also an ongoing need for accurate experimental data.

The advances made in recent years in the capabilities of sophisticated analytical and measurement equipment have made it possible to develop new experimental techniques for the direct determination of phase equilibria in low order and complex multi-component slag systems. In addition the development of powerful computer modelling tools makes it possible to provide more comprehensive descriptions of the phase chemistry, to present the information in a range of perspectives, and to critically analyse the various types of related thermodynamic and structural information available.

This review provides an overview of the types of information that can be used to determine phase equilibria in slags systems, analyses the influence of uncertainty and the relative importance of these types of data, and describes the advantages and limitations of the various experimental techniques that can be employed to obtain this information.

Examples of recent studies are provided that demonstrate how an integrated approach to the determination of phase equilibria in complex systems, involving the use of targeted experimental studies and systematic thermodynamic model development, can lead to a better utilization of our current research capabilities and resources and more accurate descriptions of these systems.

Keywords: slags, phase equilibria, experimental techniques

Introduction

Much of the early experimental work on the determination of phase equilibria in oxide systems was carried out on geological systems in order to understand rock formation from igneous melts. These early studies used principally petrographic microscopy for phase identification; later X-ray diffraction techniques were developed and used for crystal structure determination¹⁻². These experimental techniques were progressively extended to synthetic oxide systems, and to the study of metallurgical slag systems³⁻⁷. The focus of much of this early metallurgical work was on the liquidus temperatures in order to determine optimum melt compositions, flux additions and operating temperatures. From an improved understanding of phase equilibria and melt chemistry in these systems also came dramatic improvements in the performance of refractories⁸⁻⁹ and technical ceramic materials¹⁰. Today an understanding of phase equilibria is part of the tools of trade in materials science and metallurgical engineering. This is highlighted by the fact that compilations such as Phase Diagrams for Ceramists¹¹ and Slag Atlas¹² are widely used in process design and development. Much of the experimental work undertaken on slag phase equilibria in the past several decades has also been focussed on the determination of chemical activities of components in liquid phases and on the partitioning of minor elements between slag, metal and matte phases with the aim of improving smelting and metal refining technologies¹³⁻¹⁶.

In parallel with the expansion in experimental data

available on slag and metal alloy systems there have been significant advances in chemical thermodynamic theory and, with the advent of computing power, in the ability to describe the phase equilibria using mathematical models¹⁷⁻²⁰. These thermodynamic models combine all of the thermodynamic and phase equilibrium information on solid, liquid and gas phases so that they provide self-consistent and accurate descriptions of the systems. Using these powerful new computational tools it is now possible to assess the considerable volume of work that has been undertaken and collected over the span of a century, and to identify the new experimental data required to complete these models. Thermodynamic modelling has now become not only a powerful technological approach, but also an important research tool.

This past decade has seen major advances in experimental technologies through improvements in analytical capabilities and instrumentation. These advances now make it possible to provide new, more accurate, experimental data on lower order (binary and ternary) systems to resolve discrepancies and to provide new information important for thermodynamic modelling. These advances also make it possible to provide new experimental data on complex multi-component systems in composition ranges that

- are directly relevant to industrial needs
- cannot be described by current thermodynamic models or are required for model verification, and
- have not or could not previously be experimentally characterized.

Selection of experimental techniques

In general, making accurate phase equilibrium measurements at high temperature is difficult experimentally, and the compositions of the phases present cannot be directly measured. Selection of the appropriate properties and phenomena to be measured and the experimental technique to be used requires careful analysis of the many physical and chemical characteristics of these systems.

Properties and phenomena

Table I summarizes some of the properties and phenomena that can be measured and observed, and that have been used to, directly or indirectly, assist in the characterization of phase equilibria in oxide systems. These properties include chemical thermodynamic and physical properties in single phase and multi-phase systems. A change in any of these properties, marking the conditions for appearance or disappearance of a phase, directly provides information that can be used to construct phase diagrams. Chemical thermodynamic information in the form of state functions can also be used to predict the conditions for phase change as a function of composition, temperature and pressure.

Clearly, in designing an experimental program careful consideration should be given to a number of questions including, which of these properties/phenomena best provide the information required, how this information is to be used and how it is going to be obtained.

Experimental techniques for phase equilibrium determination

Many different experimental techniques have been used to measure the thermodynamic properties and phase relations in high temperature metallurgical slag systems; the principal experimental methods are summarized in Table II. References are also given in Table II to some examples of applications of these techniques. The list is not meant to be exhaustive but provides a starting point for consideration of these various approaches.

The experimental techniques used in phase equilibria studies can be divided into two main groups: dynamic and static methods.

Dynamic techniques are based on the measurement of property change that occurs as the system is undergoing a phase transformation. The most widely used dynamic techniques are thermal analysis (TA), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetric (TGA) analysis. The common disadvantage of any dynamic type of technique is that the system is, by definition, in a non-equilibrium condition. Kinetic and metastability effects are common sources of inaccuracies especially in systems with sluggish phase transformations. For these reasons dynamic methods are not appropriate for the liquidus determination in silica-containing slag systems in which nucleation and growth reactions are known to be slow, and for most reconstructive solid-state phase transformations that involve solid state diffusional processes. Dynamic techniques can be useful for highly fluid systems and some displacive transformations (e.g.) reactions that do not occur through diffusion mechanisms.

Dynamic methods used for the determination of liquidus and solidus are best suited to those systems that approach equilibrium during cooling or heating. During the

Table I
Properties and phenomena used in phase equilibria determination

Principal thermodynamic properties
Heat capacities
Enthalpies
Entropies
Activities
Gibbs free energies of reactions
Partitioning of elements
Principal properties used to detect phase transition phenomena and phase assemblages
Optical
Magnetic
Electrical
Crystal structure
Phase compositions
Chemical activities and other thermodynamic properties

Table II
Summary of the principal experimental methods used in phase equilibrium determination in oxide systems

Methods	Suitability for oxide systems	References ^{21–24}
STATIC METHODS		
Electrochemical	Thermodynamic props. (e.g. a_i , ΔG , ΔS)	[25–27]
Vapour pressure	Knudsen - low metal vapour pressure, non-aggressive slags	[28–30]
	Reactive gas equilibration – low metal vapour pressure - PO_2 control	[31]
	Isopeistic equilibria - high metal vapour pressure	[32]
X-Ray powder Diffraction (XRD)	Phase detection/identification; Extensive solid solutions - lattice parameters at temperatures	[23, 33–34]
Hot stage microscopy	Liquidus of low vapour pressure systems, transparent liquids	[35–36]
Calorimetry	Enthalpies, ΔH - of formation - of solution - of phase transition	[37–39]
Equilibration/quench/analysis techniques	Liquidus of high viscosity liquids (e.g. high silica slags); solid state phase equilibria	[23, 40–44]
DYNAMIC METHODS		
Thermogravimetric analysis (TGA)	Gas/solid; Gas/liquid reactions	[31]
Differential Thermal Analysis (DTA)	Rapid phase transitions (m.p. of congruently melting compounds)	
	Liquidus/solidus of low viscosity liquids	[23, 45–47]

solidification of a melt under equilibrium cooling conditions the solid phase composition remains uniform and in equilibrium with the melt, and progressively changes with the system temperature. In contrast under very fast cooling conditions there is no time for mass transport within the precipitated solid phase. In this scenario the centre of the precipitated crystalline phase approaches the composition of the first solid formed and the outside of the precipitate consists of solid in equilibrium with the last liquid to solidify. Thus, the mean composition of the solid is not the same as the equilibrium composition, and the apparent solidus temperature is not the equilibrium value for a given bulk composition. This non-equilibrium cooling or ‘coring effect’ is most pronounced for systems in which the primary phase exhibits extensive solid solution and increases with increasing cooling rate of the system (Figure 1).

During solidification the maximum rate enthalpy release is to be expected to occur at eutectic or invariant points where all of the liquid phase is transformed to solid at one temperature. For melt compositions in which there is a large difference between liquidus and solidus the solidification will occur over a wide range of temperatures, reducing the proportion of solids solidifying at any one temperature and increasing the uncertainty as to the start and finish temperatures of the transformation. The rates of phase transformation involving solid or liquid phases are also influenced by nucleation and growth phenomena. For these reasons when using dynamic methods these measurements are carried out at a range of heating and cooling rates and, if necessary, the corrections applied to take these kinetic effects into account⁴⁵.

Static methods are based on the ‘*in situ*’ measurement of a property or observation of a sample at the equilibrium state, for example, high temperature X-ray diffraction, hot stage microscopy and EMF measurements. The measurements using these techniques are usually carried out at constant temperature and pressure, or in a series of staged constant temperature/pressure experiments. This approach enables accurate control over temperature and oxygen partial pressure. However, there are limitations especially for complex slag systems. In some systems changes in composition during high temperature measurement are unavoidable due to the loss of

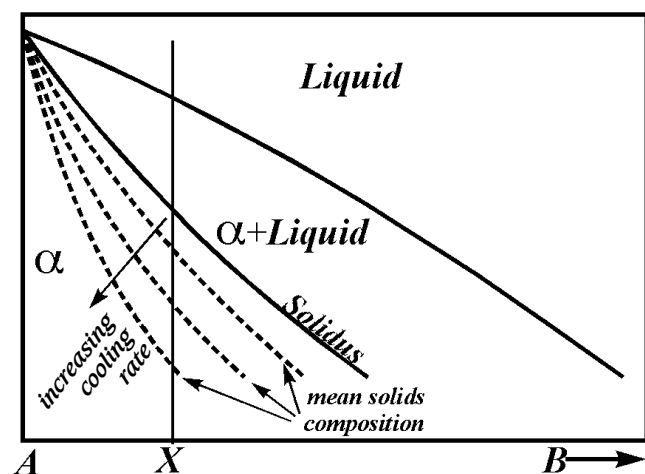


Figure 1. Illustration of non-equilibrium solidification in systems involving the formation of solid solutions

components through vapour phase reactions, or reactions with containment materials.

The *quenching technique* can be considered as a variation of the static method of high temperature investigations of phase equilibria. The quenching method involves the equilibration of the material at controlled conditions (usually fixed temperature and pressure) followed by rapid cooling. For systems in which the phase assemblage and phase compositions present at temperature can be preserved by cooling to room temperature, the quenching technique is superior for phase equilibrium studies. Solid solutions, solid-state phase relations and solid-liquid phase equilibria where liquid can be quenched to glass can be investigated using these quenching techniques. The measurement of properties at room temperature has the added advantages of improved accuracy and convenience.

The quenching technique has been successfully used to determine liquidus temperatures of silicate slag systems for many decades. The approach essentially involves the preparation of a range of materials of known starting compositions (e.g. composition X in Figure 2). A series of tests is then carried out involving the equilibration, quenching and subsequent examination of these samples (e.g. temperatures T_1 through T_4 in Figure 2). The phase diagrams of these systems are constructed by mapping the equilibration temperatures at which various phases appear or disappear from the quenched samples. The quenching technique is suited to the determination of phase equilibria in silicate slag systems due to the relatively high viscosities of silicate melts and ability to retain these as glass on fast cooling. This conventional use of the quenching technique relies heavily on a number of assumptions, i.e. that

- a sufficient number of experiments can be carried out to identify the liquidus accurately
- equilibrium at temperature has been achieved

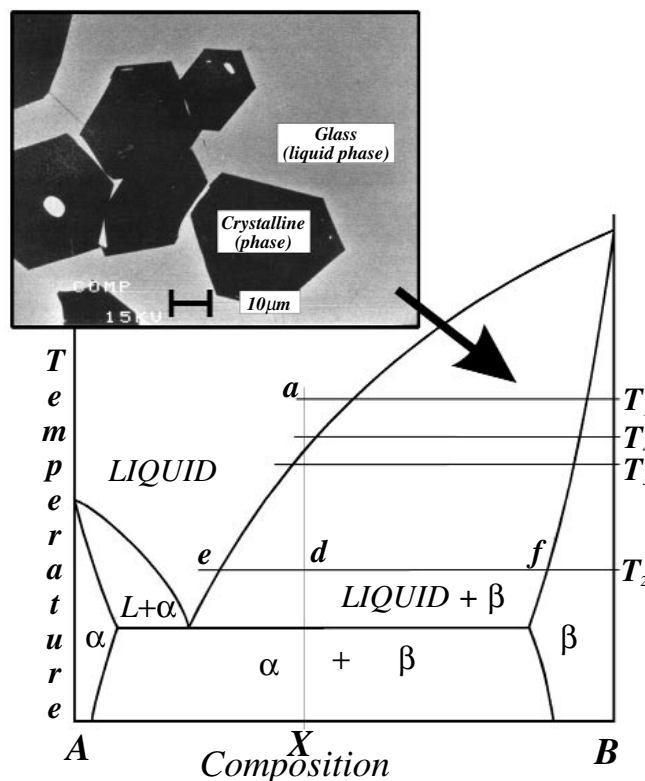


Figure 2. Experimental approaches to phase equilibrium determination using equilibration, quenching and EPMA

- iii) there is no change in sample bulk composition during equilibration through vaporization, reaction with the gas phase, containment materials or other mechanisms
- iv) either no crystallization occurs during quenching or that precipitates formed during quenching can be distinguished from those formed at the equilibration temperature, and
- v) very small quantities of the primary crystalline phase can be detected.

Bearing these points in mind it is clear that the liquidus and solidus data obtained using this technique need to be carefully assessed due to the inherent uncertainties.

*The segregation method*²³ involves deliberately equilibrating the sample at constant temperature below the liquidus, and allowing the physical segregation of the solid and liquid phases to occur through differences in relative density. The phases are subsequently physically or chemically separated or sampled, then chemical analysis of the individual phases is carried out. Clearly the temperature of the system can be accurately controlled and the uncertainty in the result derives principally from the accuracy of the separation, sampling and chemical analysis.

This segregation method is equivalent to the single or multiple phase saturation methods that have been employed to determine liquidus isotherms and phase boundaries in a number of multi-phase systems^{48–51}. This saturation approach is suitable for those systems in which all of the primary phases have been established, and is best suited for applications in which the primary phases consist of stoichiometric compounds whose compositions remain constant throughout the equilibration.

Types of multi-phase systems

There are many examples in the literature of multi-phase equilibrium measurements involving gas/liquid (Figure 3a), liquid/liquid (Figure 3b) and solid/liquid (Figure 3c) reactions. The compositions of the phases, or the activities of components in the phases, can variously be measured following or during high temperature equilibration using bulk chemical analysis or electrochemical techniques. In each of these cases the liquid slag can be contained in a material that:

- is inert, or dissolves very sparingly in the slag (e.g. Pt, Mo...), or
- reacts chemically with the system, controlling the activity(ies) of one or more components in the system (e.g. solid Fe metal, solid SiO₂, solid primary phase compound,...).

Open and closed systems

In analysing experimental data reported in the literature and in planning of future experiments consideration should be given whether the system is open or closed. An open system is one in which gas controls the compositions of the condensed phases. A closed system is one that has limited gas volume so that condensed phases control the composition of the gas phase.

Clearly, in selecting an experimental technique for phase equilibrium determination careful consideration is required of

- the property to be measured
- the degrees of freedom of the system and reaction conditions (activities, compositions, temperature, oxygen partial pressure P_{O₂}....) to be controlled
- the chemical and physicochemical properties of the system under study, and

- the reactivity of the system with potential containment/measurement materials.

Theoretically based tools

The fundamental relationships between phase equilibria in a system and chemical thermodynamic properties of its components are now well established^{52–54}. A range of theoretical tools can be used in the design and selection of process conditions and in the interpretation of phase equilibrium data. Some of the theory commonly used in phase equilibrium studies is outlined below.

The phase rule^{53–55} can be used to determine degrees of freedom, *F*, in any chemical system at equilibrium. The phase rule states that

$$F = C + P + 2 \quad [1]$$

where *C* is the number of independent chemical components, *P* is the number of phases present for a given temperature and total pressure.

In unary and binary systems the determination of the degrees of freedom is quite straightforward and may appear trivial. In systems containing many components, some of which can exist in more than one oxidation state, the ability to identify the number of coexisting phases at equilibrium for a given set of process conditions is extremely useful in confirming that the system conditions are uniquely defined and in the interpretation of phase equilibrium data.

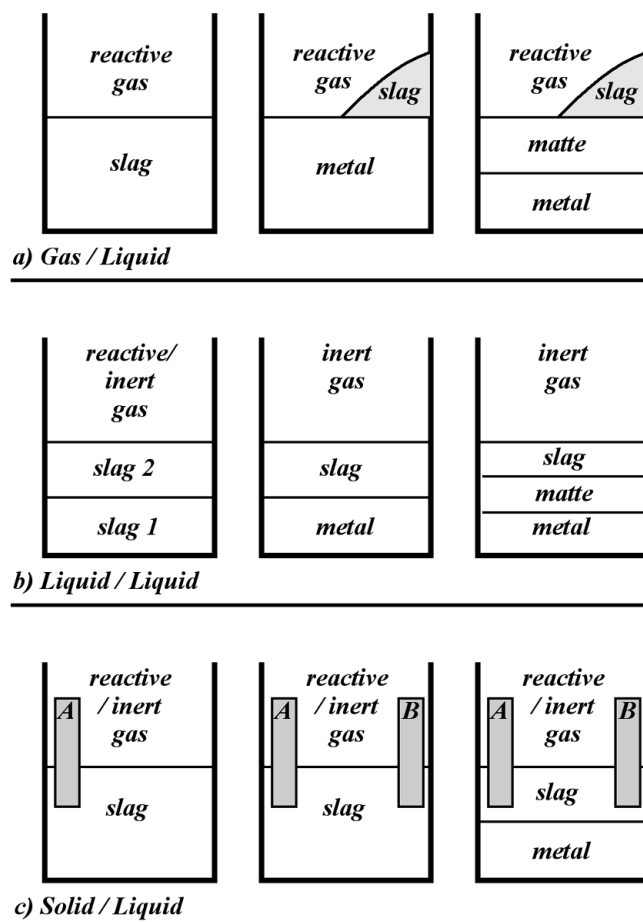


Figure 3 Multi-phase equilibrium systems involving a) gas/liquid, b) liquid/liquid and c) solid/liquid reactions

Scheinemakers' rule defines the shape of intersecting phase field boundaries and useful when constructing phase diagrams from a sparse data set. In applying this rule to ternary isothermal sections Scheinemakers found that⁵⁴ 'the extrapolations of the phase boundaries of the one phase field must either both fall inside the three phase fields or one inside each of the adjacent two phase fields'. It has been shown⁵⁶ that this rule can be extended and applied to higher order systems.

Van Alkemade's theorem states that 'the direction of falling temperature on the boundary curve of two intersecting primary phase fields is always away from the Alkemade line. The Alkemade line in a ternary phase diagram is a straight line connecting the composition points of two primary phases whose areas are adjacent and the intersection of which forms a boundary curve. If the Alkemade line intersects the boundary curve, the point of intersection represents a temperature maximum on the boundary curve. If the Alkemade line does not intersect the boundary curve, then the temperature maximum on the boundary curve is at that end which if prolonged would intersect the Alkemade line'¹¹.

Van Alkemade's lines construction can be used to identify the equilibrium products of crystallization of melts in systems or subsystems of compositional space; using the rule the complexity of behaviour of multi-component systems can be reduced to a level where it is readily understood. Examples of how this rule can be used in the interpretation of phase diagrams are given¹¹, which states that 'in a ternary phase diagram a network of straight lines can be constructed joining the composition points of primary phases whose areas are adjacent and the intersection of which forms a boundary curve. In a condensed ternary system composition triangles can be formed by the three joins connecting the composition points of the three primary phases whose liquidus surfaces meet at a point. If the three substances designating the vertices of any of these triangles are not miscible in the solid state, they represent the final equilibrium products of crystallization at the solidus temperature for compositions within the triangle.' By way of illustration the ternary system, CaO-Al₂O₃-SiO₂, (C-A-S) is described in terms of 14 ternary subsystems e.g. S-CS-CAS₂, CS-CAS₂-C₂AS, S-CAS₂-A₃S, ...etc.¹¹.

The lever rule is used to find the proportion of phases formed for a given bulk composition. The lever rule states¹¹ that 'when a particular bulk composition separates into only two phases, this bulk composition and compositions of these two new separated phases are co-linear; the amounts of these two separated phases are inversely proportional to their distances from the bulk composition'¹¹. The lever rule follows directly from a mass balance analysis of the components in the system, and in its general form can be applied to multi-component systems.

Chemical thermodynamic models incorporated into computer packages describe the chemical thermodynamic properties of elements and phases in mathematical terms. These models utilize information on heat capacities, enthalpy, entropy, activity data, and phase transitions and equilibria to describe the Gibbs' free energies of a phase as functions of composition, temperature and pressure. These descriptions are then incorporated into chemical thermodynamic databases. Using sophisticated computer packages, the minimum free energy of the system can be calculated and hence the phases, their proportions and compositions present at equilibrium are predicted. The

software capabilities that are currently available are such that phase relations can be displayed in a number of ways, and the calculation of binary, pseudo-binary and ternary sections in compositional space can now be undertaken routinely to assess and compare experimentally determined phase equilibrium and activity data with thermodynamic model predictions.⁵⁷⁻⁶¹

Phase equilibria, thermodynamics and experimental uncertainties

Most phase diagrams are constructed by using a combination of phase equilibrium and property data obtained by differing researchers using a variety of experimental methods. Invariably there are differences between the data obtained from the various studies. There are no fixed rules that can be used to decide which data are to be preferred. However, the uncertainties inherent in some techniques and their relative effects on the phase diagram can be quantified through the use of thermodynamic models of the systems; this form of sensitivity analysis is illustrated in the following examples.

In light of the increasing significance and growing application of thermodynamic modelling, consideration should also be given to the extent to which experimental uncertainties influence the accuracy not only of the final phase diagram, but also of the final thermodynamic model.

Figure 4 shows experimental data obtained for the liquidus in the system Al-Fe-O in equilibrium with metallic iron⁶²⁻⁶⁷. Clearly for each sample composition there is a range of uncertainty as to the actual position of the liquidus of the order of +/-25 K, in many systems this uncertainty is even higher. Historically many of the phase diagrams that are quoted and used routinely in the literature have been estimated using a best guess or best fit approach, and have not had the benefit of a thorough thermodynamic analysis to determine which of the data should be accepted. Figure 4 also includes the liquidus predicted following consideration of all the thermodynamic data available on the system and by integration of these data into a self-consistent thermodynamic model⁶⁸; the phase equilibria are calculated using FactSage program⁶¹.

In systems where each of the metal species exists in a single oxidation state the phase relations do not change with oxygen partial pressure of the system. However, transition metals, such as Fe, Mn, Ti, V can be present in more than one oxidation state, and in slag systems containing these elements the oxygen partial pressure of the system can have a significant effect on the liquidus temperatures and phase equilibria⁶⁹. Figure 5 shows the effect of oxygen partial pressure on the liquidus in the spinel primary phase field of a complex lead slag PbO-ZnO-FeO-Fe₂O₃-CaO-SiO₂. Experimental points in Figure 5 are taken from Jak *et al.*⁷⁰, and FactSage predictions have been performed with the recently developed database⁷¹⁻⁷³. In this case the liquidus changes as much as 250K in low lead slags for a change in oxygen partial pressure of six orders of magnitude; the sensitivity of the system to changes in oxygen pressure is clearly dependent on slag composition since this same change in PO₂ has relatively small effects on the liquidus temperatures of high lead slags. The sensitivity of liquidus to oxygen pressure is also dependent on the primary phase field as is illustrated in the case of fayalite smelting slags (see Figure 6)⁷⁴. The difficulties in obtaining accurate control of slag/gas equilibria plagued much of the early experimental work on iron-containing slag systems. These

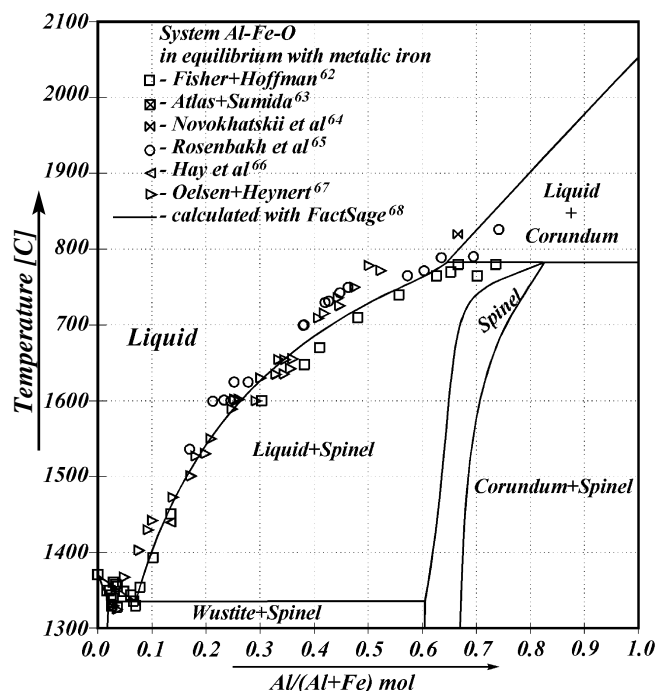


Figure 4. Comparison between best numerical fit and thermodynamic fit. Example of the use of thermodynamic modelling to assess/compare phase equilibrium data

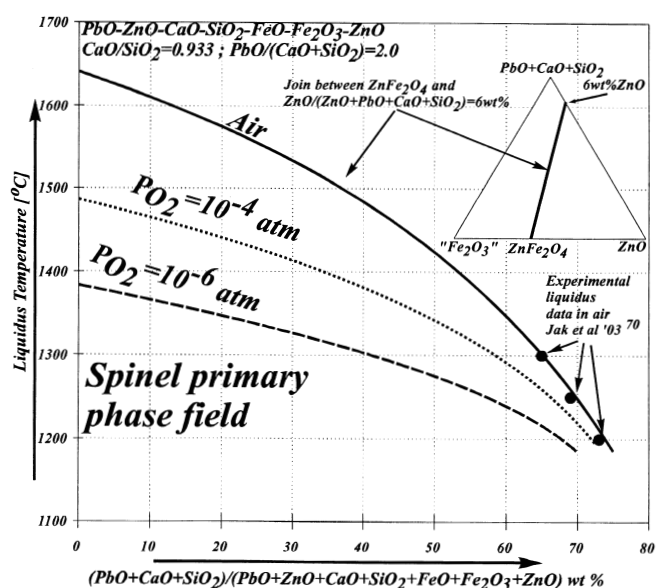


Figure 5. Example of the effect of oxygen partial pressure on liquidus temperatures (predicted using FactSage⁷¹⁻⁷³)

difficulties include thermal segregation of gas mixtures, extensive equilibration times and problems in the control of gas ratios in dilute gas mixtures. For these reasons metal saturation techniques are to be preferred over gas equilibration for accurate phase equilibrium determination in most cases.

Figure 7 demonstrates the interrelation between activity data in the liquid slag phase and the liquidus for the system $\text{Na}_2\text{O}-\text{SiO}_2$. In the example given in Figure 7 the measured Na_2O activities at a given composition⁷⁵⁻⁸¹ differ by as

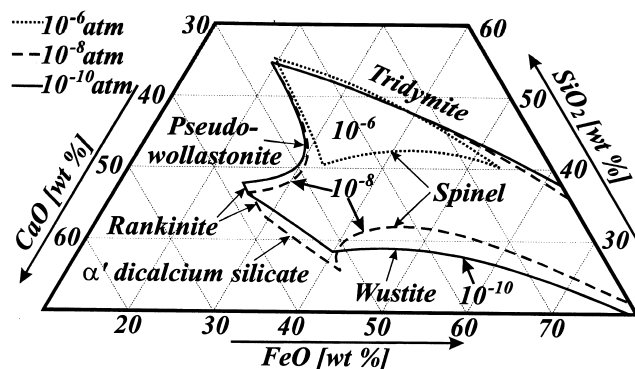


Figure 6. Liquidus isotherms at 1250°C in the $\text{FeO}-\text{Fe}_2\text{O}_3-\text{CaO}-\text{SiO}_2$ system at oxygen partial pressures of 10^{-10} (solid line), 10^{-8} (dashed) and 10^{-6} atm (dotted line) predicted by the FactSage model⁷⁴

much as an order of magnitude; an uncertainty of $\pm 25\%$ in the activity of a component is not uncommon in these types of measurements. Solid and dotted lines in Figure 7 represent two variants predicted by FactSage⁶¹ with the liquid Gibbs free energy expressions that give preference to different sets of the activity data but both describe the activity data within experimental uncertainty. The differences in the silica liquidus predicted by these two variants are significant, and are much higher than experimental uncertainties associated with direct methods of liquidus determination. The tridymite liquidus is more than 5mol% SiO_2 lower for variant 2 (dotted line) compared to that obtained using quenching techniques⁸²⁻⁸⁴ and that predicted using an optimized thermodynamic model⁶⁸ (variant 1, solid line) of the system. The example demonstrates that whilst activity data are useful for some applications, such as predictions of the partitioning of species between condensed phases, they cannot be relied on to provide the level of accuracy required for the prediction of phase boundaries and the development of thermodynamic databases for multi-phase systems.

Figure 8 represents Na_2SiO_3 liquidus experimental data obtained with quenching technique⁸³⁻⁸⁶ and liquidus predictions with FactSage⁶¹ using current thermodynamic database⁶⁸ (solid line) as well as liquidus predicted with the enthalpy of formation of Na_2SiO_3 changed by 1kJ (dotted line) in the $\text{Na}_2\text{O}-\text{SiO}_2$ system. Figure 8 demonstrates that an uncertainty of ± 1 kJ in the enthalpy of formation of Na_2SiO_3 leads to an uncertainty of approximately ± 10 K in the liquidus, in this case this is within the uncertainty in the liquidus reported in the literature.

Figure 9 demonstrates the relative sensitivities of the liquidus and solid solubility data in the system 'FeO'- $\text{CaO}-\text{SiO}_2$ in equilibrium with metallic iron along the join $\text{Ca}_2\text{SiO}_4-\text{Fe}_2\text{SiO}_4$. The solid lines in Figure 9 indicate phase field boundaries predicted by the FactSage package⁶¹ with the thermodynamic database⁶⁸ that, in addition to various other data^{49,87-88}, takes into account latest liquidus and solid solubility data measured by Zhao *et al.*⁸⁹ (open circles in Figure 9). The dotted lines represent the phase boundaries with the thermodynamic properties of the dicalcium silicate solid solutions changed to agree with data reported by Bowen *et al.*⁸⁸ and with the properties of the liquid phase kept unchanged for both variants. This example shows that solid solubility information is vital for accurate description of the thermodynamic properties of the liquid slag phase.

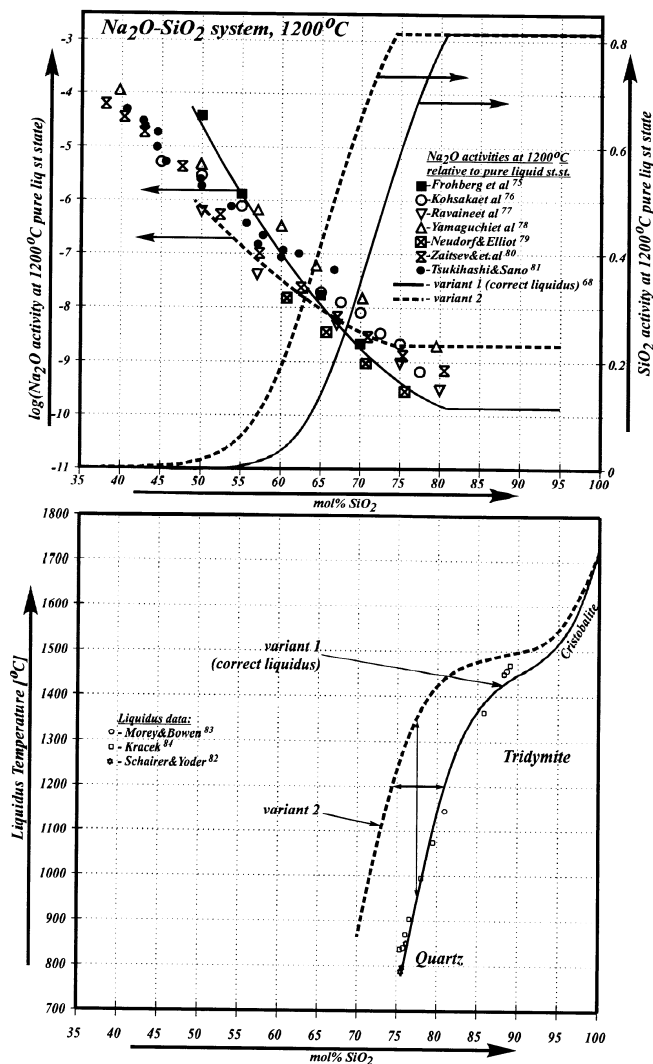


Figure 7. Example of the relation between activities and liquidus temperatures

The selected examples given clearly do not cover all possible scenarios. They do, however, serve to illustrate the need for careful analysis before experimental work is undertaken to ensure that the data obtained will contribute to more accurate phase equilibrium determination and will be focused on supporting thermodynamic database development.

Experimental approach and techniques for phase equilibria in complex slag systems

Despite the large number of experimental studies that have been carried out to determine phase equilibria in slag systems most of this work is limited to binary, ternary and selected quaternary systems whereas most industrial slags are composed of higher order systems containing many components. Information on lower and higher order systems is required for the development and verification of accurate thermodynamic models of slag systems.

The following section describes some of the recent advances made in the determination of phase equilibria in complex slag systems. These include

- the use of thermodynamic models to analyse and assess available data

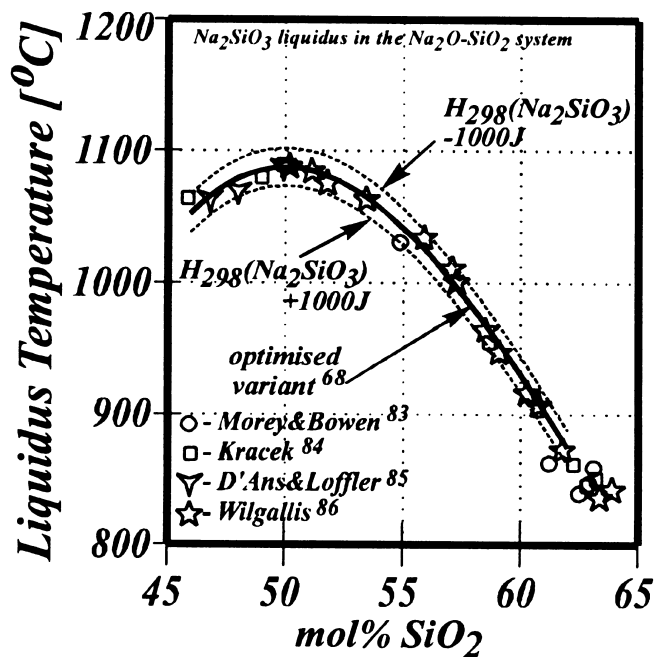


Figure 8. Example of the relation between enthalpy of formation of a compound and liquidus temperatures

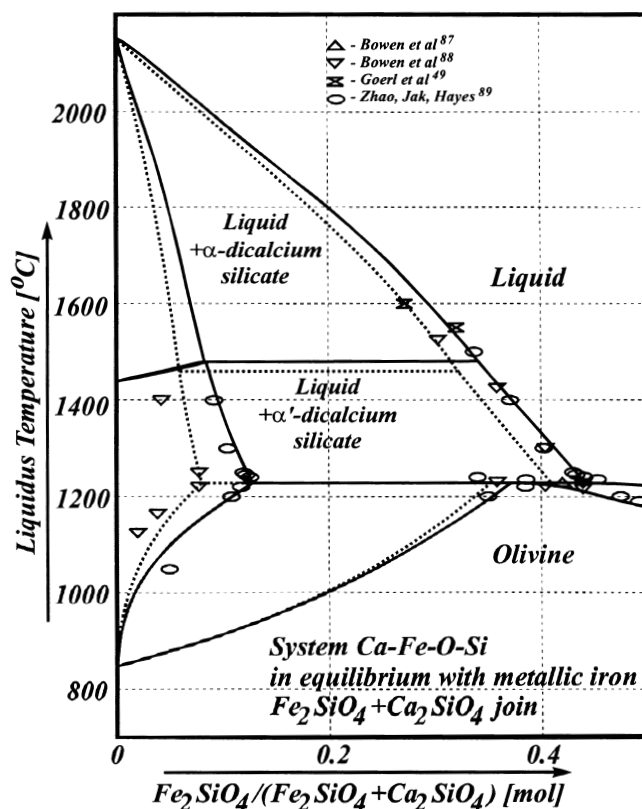


Figure 9. Example of the relation between solid solubility and liquidus temperatures

- the development and use of new isothermal equilibration/quenching/microanalysis techniques to directly determine phase equilibria in multi-phase systems, and
- systematic studies of complex slags used in industrial practice.

Assessment of data

As indicated a number of powerful thermodynamic models and computer packages are now available to assess existing phase equilibrium information on slags and to compare this with experimental thermodynamic data available on these systems. These assessments should take into account the inherent accuracies and uncertainties associated with the various experimental techniques, some examples of which have been discussed, the extent to which the compositional and process variables have been controlled during the experimental measurements, and the consistency of the data with that obtained from other experimental and theoretical techniques.

The comparison of previous experimentally determined phase equilibrium data is something routinely carried out and reported in the literature. However, the access to and use of computer tools and sophisticated slag models by experimentalists to assist in the assessment of data from different sources is something that has been a relatively recent development. Discrepancies in the available data can often be identified using these computer tools, and interpolations and extrapolations can be made in a thermodynamically correct manner.

An example of the value of thermodynamic assessment in the planning of the experimental program is illustrated with reference to the pseudo-binary join $\text{Fe}_2\text{SiO}_4\text{-Ca}_2\text{SiO}_4$ at metallic iron saturation. Figure 9 shows liquidus and solidus experimental data obtained by a number of previous workers^{49, 87-88}. Thermodynamic optimization of all the experimental data available on the system $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ revealed that the data are not thermodynamically consistent. To obtain an accurate description of the system further experimental measurements were necessary. The new experimental data obtained by Zhao *et al.*⁸⁹ using equilibration and quenching techniques followed by Electron Probe X-ray Microanalysis (EPMA) confirmed the liquidus determined by previous researchers^{49, 87-88} but found the solidus reported by Bowen⁸⁸ to be incorrect. The approach used by the authors⁸⁹ enables direct measurement of the α' -dicalcium silicate composition, the studies by Bowen⁸⁸ rely on the detection of the α' -dicalcium silicate and olivine phases at low concentrations using optical metallography leading to uncertainties in the positions of the phase boundaries. The new data on the α' -dicalcium silicate liquidus and solidus were described by a thermodynamically consistent model of the overall system (see solid lines in Figure 9).

It can be seen from this example that even systems that appear to be well established and are widely quoted in the literature need to be carefully assessed for accuracy and thermodynamic consistency. Experience by the authors in undertaking these forms of critical reviews has shown that a lot of additional experimental studies on the lower order binary and ternary systems are still required to provide additional information, for example, on solid solubilities, or to resolve discrepancies between various sets of data.

The focus of research in geological and metallurgical oxide systems has progressed over the years from solid phase characterization, liquidus determination, liquid immiscibility to the effects of gas phase on the partitioning of major and minor elements. In practice many pyrometallurgical smelting and refining processes operate at sub-liquidus conditions. This indicates a need to further strengthen the linkages between solid and liquid phase equilibria in order to be able to develop accurate thermodynamic models.

Isothermal equilibration/quenching/microanalysis approach

Taking into account the many factors discussed in the previous sections the following approach involving isothermal equilibration and quenching followed by Electron Probe X-ray Microanalysis (EPMA) has been further developed and refined by the authors, and has been shown to be useful in providing phase equilibrium information in studies of multi-component slag systems⁴¹. Whereas many of the earlier techniques for the determination of phase equilibria rely on control of the bulk sample composition, in practice this is frequently very difficult to achieve in high temperature experiments. This points to an alternative strategy of undertaking experiments at sub-liquidus conditions followed by measurements of the phases coexisting at equilibrium. This strategy is employed in the segregation method previously outlined²³ and also forms the basis of the approach used by the authors to construct a number of phase diagrams. The approach can be visualized by considering the hypothetical phase diagram shown in Figure 2. If the sample of bulk composition X is deliberately equilibrated at a sub-liquidus temperature, for example, at T_2 , solid and liquid phases coexist. On rapid quenching of silica-containing slag samples the phases present at temperature can be retained at room temperature without change in composition or crystal structure. Examination of the sample microstructure will show the presence of homogeneous glass and a crystalline phase β . At this point microanalytical techniques, i.e. electron probe X-ray microanalysis (EPMA) can be utilized and the compositions of the individual phases accurately determined without destroying the sample.

It can be seen that using this constant temperature technique has the advantages that it can:

- provide accurately determined liquidus isotherms, in contrast to the uncertainties of the iso-compositional approach used by most previous researchers
- be extended from binary systems to the determination of liquidus isotherms in multi-component systems with no loss of accuracy
- provide information on phase equilibria at single, double or multi-phase saturation with no loss of accuracy
- provide phase equilibrium information on systems having high vapour pressures, provided equilibrium between condensed phases is achieved
- be used to determine phase equilibria in systems containing extensive solid solutions.

Since chemical analysis of the phases is carried out after the experiments, changes to bulk composition of the sample do not affect the final result provided local equilibrium is achieved in the sample. This is a very important advantage of this technique, one that has enabled a number of further modifications to be made which are discussed below.

This approach greatly enhances the ability to provide accurate direct measurement of phase equilibria in complex multi-phase systems, and provides a wealth of important information on coexisting phases.

Materials selection and preparation.

In most laboratory-based phase equilibrium studies high purity starting materials in the form of fine powders are used to avoid the effects of sample contamination. To ensure rapid approach to chemical equilibrium a range of pre-processing steps may be necessary involving

precalcination, mixing, grinding, consolidation, pre-heat treatment, regrinding, master slag formation. Most of these pre-processing steps are used commonly in ceramic materials processing. For further details the reader is referred to standard texts on this topic⁹⁰.

In some systems the use of pure compounds having high vapour pressures in the starting mixtures, for example PbO, can lead to significant material loss during equilibration. The presence of high melting temperature oxides, for example SiO₂, can also make attainment of equilibrium difficult to achieve. In these cases pre-processing of selected material combinations can be carried out to incorporate the components into intermediate compounds, solid or liquid solutions and hence lower their respective activities and melting temperatures. The pre-preparation of glassy silicate materials can be carried out by completely dissolving the components in melts at low temperatures followed by rapid cooling. These intermediate glassy master slags can then be used to prepare the final mixture for high temperature equilibration. Since SiO₂ and other high-melting temperature materials are introduced into system in the form of glassy master slag, this also guarantees that crystalline silicate precipitates observed in the final microstructures after equilibration are not metastable, undissolved residual solid particles but stable equilibrium phases.

Crucible/support system design

The difficulties in containment of slags in high temperature systems constrains the range of experimental conditions that can be readily studied experimentally, this is true particularly for liquid equilibria involving, e.g. slag/metal and slag/matte systems. Containment materials such as Pt, Mo, Fe, C and selected refractory oxide material envelopes/crucibles, with and without lids, are commonly used to contain slags. Pt is suitable for oxidizing conditions; Mo, Fe can only be used in reducing or neutral gas atmospheres. The use of refractory ceramic materials is clearly restricted because of the solubility of these materials in the aggressive slags under study. The use of noble metals (such as Pt) is restricted because of the alloying by metals. This makes selection of suitable containment for slag/metal systems sometimes impossible. In addition, the containment material clearly affects the maximum cooling rates that can be achieved since it is the crucible material that first contacts the quenching medium.

A variety of support designs, therefore, have been developed for isothermal equilibration and quenching techniques using small sample masses; examples of these are illustrated in Figures 10a–d. Whereas the sample mass used in crucible experiments is typically in the range of 1–50 grams enabling wet chemical analysis to be undertaken, the slag mass used with envelopes and open support systems is of the order of one tenth of gram or less. Closed envelopes provide the easiest means of support and can readily be made from thin metal foil, (Figure 10b). The thickness of the foil should preferably be minimized to achieve faster cooling rates.

Open support systems (Figure 10c) use surface tension to hold the slag on the outside of the metal or compound substrate. The support can be made from inert material, or from primary phase material enabling isothermal single-phase and multi-phase saturation experiments to be undertaken in those systems in which a suitable crucible material is not available. Excess fine metallic powder is mixed together with the slag before placement on the

substrate for the systems where the activity of particular metal has to be controlled (for example, metallic Fe or Cu saturation). On quenching the slag comes into direct contact with the quenching medium resulting in rapid cooling. Open support systems, therefore, are particularly suitable for systems in which

- very high quenching rates are necessary to retain the liquid as a homogeneous glassy material, and
- some of the component are highly reactive and suitable crucible material cannot be found.

The levitation of metal droplets in an electromagnetic field can be used in systems where reaction with containment materials cannot be avoided⁹¹. In this case slag is attached to the metal through surface tension forces (Figure 10d). The principal difficulties with this technique are associated with coil design to obtain the levitation power, temperature ranges and stable temperature control. The temperature of the slag phase in this arrangement is determined indirectly through the metal droplet temperature measurement using a two colour optical pyrometer. This arrangement has the potential to be extended to gas/metal/slag systems through control of the surrounding gas mixture.

Both open support and levitation systems can have active chemical interaction between the substrate and the slag. Part of the substrate may be dissolved into the slag or some material from the slag system may be deposited on the substrate. These reactions may involve interactions with the gas phase, which is particularly important for the systems with metals that have several oxidation states. The final results, however, are not affected due to the use of EPMA to measure the final compositions of the phases in the quenched sample after the experiment; application of EPMA is the basis for applicability of these support systems.

An example of the application of the open support system (Figure 10c) and levitation technique (Figure 10d) is reported in recent research on the Cu-Fe-Ca-O system at metallic copper saturation⁹². Figure 11 presents a micrograph of the Cu-containing calcium-ferrite slag sample quenched after equilibration using the levitation technique. In case of the levitation technique the presence of metallic copper in contact with the slag is guaranteed. In case of the open support system with primary phase substrate an excess of fine metallic copper powder was added and dispersed in the calcium-ferrite slag to ensure the activity of Cu is maintained equal to unity relative to the pure liquid standard state. Improvements to the levitation technique, including methods of temperature control and calibration and its application to condensed phase metal/slag equilibration in the Cu-Fe-Ca-O system at metallic copper saturation, have recently been reported by the authors⁹².

Equilibration procedure

The time to achieve equilibrium and the thermal treatment program depends critically on the particular reaction system and conditions. Most experiments were undertaken using two-stage equilibration. The samples are first preheated to a temperature higher than the final equilibration temperature for 10–60 minutes, and then finally equilibrated at lower temperature. This enables samples to be first homogenized at higher temperature. This also ensures that the solids grow into shapes that clearly indicate equilibrium crystallization rather than irregular shapes of undissolved particles.

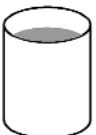
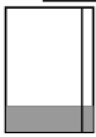

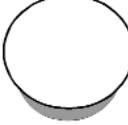
<i>Support type</i>	<i>Material</i>
 a) Crucible	- metal - ceramic
 b) Envelope	- metal - ceramic
 c) Open support	- metal - primary phase
 d) Levitated metal drop	- metal

Figure 10. Sample support types for slag phase equilibria determination (slag shaded)

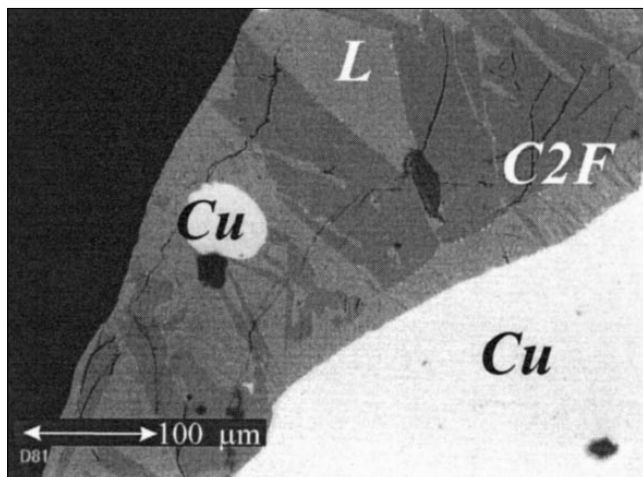


Figure 11. Example of the use of levitation and quenching techniques to investigate phase equilibria in calcium-ferrite slags in equilibrium with metallic copper (sample quenched from 1235°C, legend: C2F- dicalcium ferrite ($2\text{CaO}\cdot\text{Fe}_2\text{O}_3$), Cu - metallic copper, L - liquid slag, adopted from⁹²)

The heat treatment regime should always be selected individually to better take into account the particular system properties. Achievement of equilibria requires particular attention in all experiments. Some of the usual measures to ensure attainment of equilibria include repeated experiments at significantly increased equilibration times, approaching equilibria from various directions, and thorough microanalysis to ensure the homogeneity of all phases in the final sample. The actual pre-melt temperature and, most importantly, the time for final equilibration should always be selected after critical testing of the achievement of equilibrium has been carried out.

To obtain better control over the equilibration process it may be necessary to modify the heat treatment regime for particular systems. For example, a peritectic reaction on cooling involves the decomposition of the primary solid and the formation of the equilibrium phase below the peritectic temperature, since this takes place by diffusion through the solid, extensive times are required to obtain equilibrium. To avoid this slow diffusion step the component mixtures may be heated during premelting to temperatures where they are completely liquid and then quenched to glass thus ensuring no primary phase precipitated. On reheating the low temperature equilibrium phase assemblage then crystallizes directly from the metastable liquid. In contrast, for melts having high viscosities and slow rates of crystallization a premelting temperature below the liquidus can be selected so as to leave some primary phase seeding crystals as heterogeneous nuclei and reduce the time to achieve equilibrium. In the systems with high equilibrium vapour pressure components (for example, PbO) preliminary equilibration at relatively low temperatures, at which first liquid slag just appears, helps to homogenize sample and dilute high-vapour-pressure components before heating to the high temperatures thus significantly reducing losses through fuming. This low temperature homogenization step is similar to the preparation of the master slags previously described.

Quenching techniques

To obtain maximum cooling rates the samples should be directly quenched from the hot zone of the furnace. In the case of slag equilibria this is commonly achieved using water or brine as the quenching medium. Quenching into liquid nitrogen results in the formation of a protective nitrogen gas atmosphere, and heat transfer through this gas film is slow and cooling rates achievable are also relatively slow. Quenching into liquid nitrogen, therefore, was used only occasionally in cases when it was important to protect the outer layer of the sample from oxidation. If small slag samples (less than 0.1g) are used the effective cross-sections are small and hence cooling rate is extremely fast (10^3 – 10^6 K s⁻¹)⁹³. Direct contact between the slag sample and the cooling medium provides the fastest cooling. This direct contact is achievable using the open support and levitation techniques, where the slag sample is held on the support by surface tension forces (Figures 10c and d).

A number of other devices have been successfully used to achieve rapid solidification⁹⁴. Moving surface devices, such as spinning wheels, are suitable for low viscosity melts, such as metals, since these materials shear into thin (less than 100 μm) films and are rapidly cooled; high viscosity melts, on the other hand, do not readily shear and tend to be thrown from the cooling substrate surface and are not cooled rapidly. Piston and anvil devices provide rapid cooling for multi-phase materials; the sample is captured in the device and compressed into a thin film that ensures direct contact with cold copper plates.

Phase Characterization

After final quenching the samples are separated carefully from the container, mounted and polished for metallographic examination. This examination can be carried out using optical and scanning electron microscope techniques. If possible whole sections of melt from wall to wall, and from top to bottom, should be examined; this enables any segregation of the phases during equilibration to be detected.

The preferred technique for phase identification and measurement of the compositions of the glassy and crystalline phases is electron probe X-ray microprobe analysis (EPMA). XRD and other analytical methods can be used to compliment and confirm the phase identification. The application of modern EPMA techniques to the examination of the samples not only substantially increases the efficiency and accuracy of the analysis but also provides important additional information.

As discussed, in Figure 2 for a sample X, EPMA measurement of the glass and crystalline phase compositions in the sample from only a single quenching from, say, temperature T_2 , provides the liquidus (point e) and the solidus (point f) at that temperature. The same starting mixture can be used to obtain liquidus and solid solubility data sets by equilibration at several other temperatures. The accuracy of the liquidus determination by the EPMA technique is not dependent on a minimum detectable fraction of crystalline phase formed as it is with XRD and DTA. Changes to bulk composition of the sample do not affect the compositions of the individual phases present; only the relative proportions of the phases present may vary, provided the sample remains in the same phase field. Since the compositions and phase assemblages are measured after equilibration, any assumptions and therefore uncertainties as to the interpretation of the outcomes are avoided.

At local equilibrium the composition of the glass (or liquid phase) in the sample should be uniform. EPMA enables the glass composition to be measured as a function of position within the sample; the glass can therefore be shown to be homogeneous. Alternatively concentration profiles within the glass, for example, as a function of distance from precipitates makes it possible to detect incomplete equilibration as well as any precipitation that may occur during quenching. Incomplete dissolution of the pure high melting temperature component B (see Figure 2) due to the slow diffusion in the liquid phase will result in higher B concentration in the glass near undissolved B particles. Precipitation of β phase on quenching will result in lower B concentration in the glass near such β precipitates relative to the bulk glass. The coring within phases exhibiting solid solutions as a result of insufficient equilibration time is also detected. Accurate chemical analysis is obtainable on samples usually as small as a few microns, this take-off area depends on the matrix average atomic number in the phase and on the acceleration voltage.

Whilst the Energy Dispersive Spectrometry (EDS) approach makes it possible to rapidly identify the major components present in different phases, the information that can be derived from this is semi-quantitative at best-EDS is not suitable for accurate phase diagram determination. To obtain accurate chemical analysis of the phases Wavelength Dispersive Detectors (WDD) should be used.

The standards used to calibrate EPMA should be carefully selected. The standards preferably should be close in composition to the unknown phase under investigation to reduce uncertainties of the matrix correction procedures. The Duncumb-Philibert ZAF correction procedure inbuilt into the JEOL* 8800 EPMA was used by the authors. The potential uncertainties associated with the inappropriate selection of standards are illustrated in Figure 12 for the system ZnO-SiO_2 investigated by Hansson *et al.*⁹⁵. Open circles and squares, and dotted line represent the EPMA results obtained using quartz SiO_2 ** as the standard for silicon. Closed circles and squares, and solid lines represent the EPMA results obtained using willemite Zn_2SiO_4 *** as the standard for silicon.

* JEOL is a trademark of Japan Electron Optics Ltd., Tokyo, Japan.

** Charles M Taylor Co., Stanford, California, USA.

*** Micro-Analysis Consultants Ltd, Cambridge, UK.

Clearly, selection of willemite as a standard for Si provides correct composition measurements – for example, note that the composition of the willemite Zn_2SiO_4 in the samples was measured to have 0.667 mol fraction of ZnO and 0.333 mol fraction of SiO_2 . Standards should always be included into the analysis run as unknown samples to check the accuracy of the analysis.

Assuming the adequate selection of standards and accurate calibration and measurement procedures have been adhered to the average accuracy of the EPMA measurements better than + 1 wt % of the major components can be achieved, which is comparable to that in bulk wet chemical techniques in most systems. With careful preparation of homogeneous standards for the particular phases and elements of interest this level of accuracy can be improved.

EPMA essentially provides a chemical analysis of the metal cations present in a particular phase. In some cases knowing the stoichiometry of the phases it is possible to not only identify the phases present but also the relative proportions of the ions in particular oxidation states. For example, in the spinel phase $(\text{A}^{2+}, \text{B}^{2+})(\text{A}^{3+}, \text{C}^{3+})_2\text{O}_{4+y}$ with stoichiometric oxygen content ($y=0$) the proportions of A^{2+} and A^{3+} can be determined from EMPA analysis and mass balance of the metal ions present in the compound. Unfortunately this procedure cannot be performed for the complex solid solutions.

In some cases it is not possible to use the EPMA alone for phase identification, for instance, where a compound can be present in a number of polymorphs. In those cases EPMA can be complemented with other techniques, for example X-ray powder diffraction (XRD) to obtain unequivocal identification of the crystalline phase.

Examples of phase equilibria in multi-component systems

Whereas the representation of phase equilibria in one and two component systems as a function of temperature and pressure is relatively straightforward the situation becomes increasingly complex as the number of components is increased. Ternary systems can be readily represented using

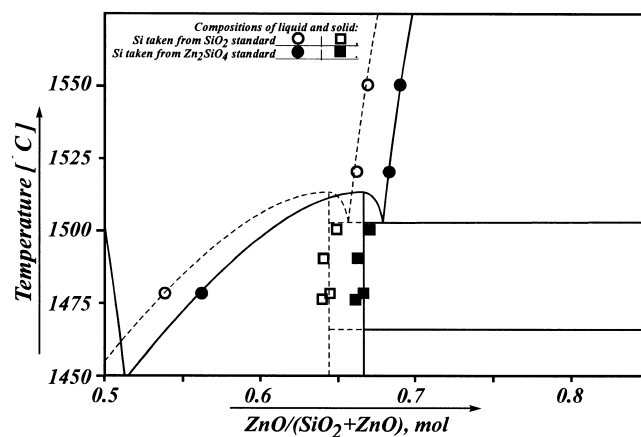


Figure 12. Possible uncertainties of the EPMA measurements with ZAF correction: importance of the standard selection (adopted from⁹⁵)

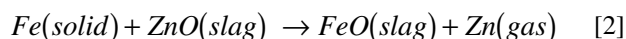
phase diagrams having triangular coordinates on a compositional plane and a temperature axis normal to this plane.

4-component compositional space can be represented in a tetrahedron. To simplify the visualization of phase relations in these systems, and to be able to present the effects of changing temperature, sections of the quaternary are commonly used including sections through the quaternary at fixed ratios of the components (Figure 13a), sections through the quaternary at fixed compositions of the fourth component (Figure 13b) and pseudo-ternary sub-systems defined by Alkemade compositional triangles (Figure 13c). For oxide systems containing transition metal species of variable oxidation state the phase equilibria can be described by considering each oxidation state as a separate chemical component, for example FeO-CaO-SiO₂ and Fe₂O₃-CaO-SiO₂ in Figure 13d. This is achieved by the projection of the composition from the oxygen apex on to a plane in compositional space. For example, in Figure 13d the slag of composition *a* may be represented as *a'* on the FeO-CaO-SiO₂ section. The various methods in which phase equilibria in complex chemical systems can be correctly presented are discussed further by Pelton⁹⁶ and Hillert⁵⁴.

Whilst these are convenient representations, in practice it is unusual for systems of metallurgical interest to lie exactly on these sections. Additional factors that affect the choice of section in compositional space include changes in composition of the slag during processing due to, for example, flux addition, reaction or crystallization. The

following examples illustrate some of the issues relating to the selection of sections in compositional space and the systematic analysis of multi-component systems. The phase equilibria in these complex systems have been determined experimentally using the approach described in the section 'Isothermal equilibration...'

An example illustrating a number of the points discussed can be found in the study of the system 'FeO'-ZnO-SiO₂ under reducing conditions⁹⁷. Previous attempts to obtain liquidus and phase equilibrium information on this system at controlled oxygen partial pressures using flowing gas mixtures have been unsuccessful because of the rapid vapourization of the zinc from the slag in reducing conditions. The experiments were therefore undertaken by equilibration with metallic iron, fixing the iron activity at unity relative to the pure solid iron. The ZnO and SiO₂ powders were mixed and premelted in air to produce a series of glassy silicate master slags. Each of these master slags were ground to fine powder then combined with metallic iron powder to produce the mixture for equilibration. The samples were placed in an iron metal envelope and heated to temperature in a neutral gas mixture, high purity nitrogen or argon gas. During equilibration the following reaction takes place,



Some of the zinc leaves the condensed phases and is removed as zinc gas, the oxygen remaining in the melt combines with iron to form iron oxide in the slag phase. The presence of excess iron metal ensures that the iron

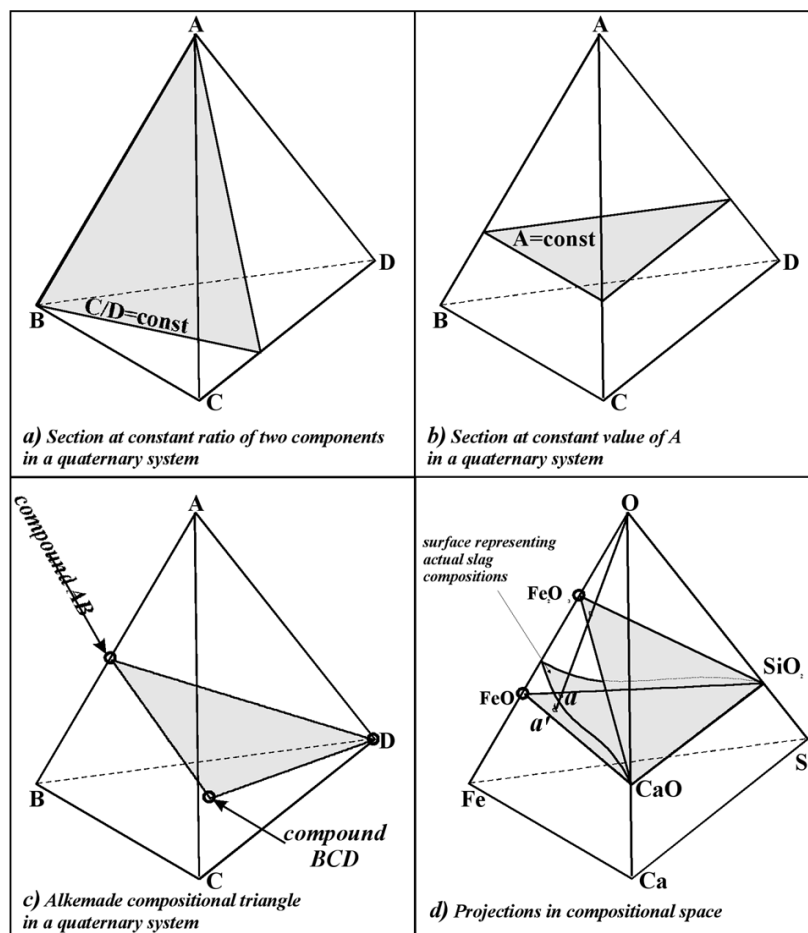


Figure 13. Projections and sections in compositional space

activity is maintained equal to 1. Analysis of the iron metal following equilibration indicates that there is no zinc dissolved in the iron and that the iron activity is, therefore, unity. During equilibration the FeO concentration of the slag progressively increases, one mole of FeO is produced for every mole of Zn lost to the gas phase according to the reaction stoichiometry (Equation [2]), provided no oxygen is introduced from the surrounding gas. These changes in bulk composition of the slag are illustrated schematically in Figure 14. The equilibration time is selected so as to achieve local equilibrium in the condensed phases, and the desired bulk ZnO concentration. Preparation of a series of master slags of various ZnO/SiO₂ ratios enables the phase diagram to be constructed for a wide range of compositions.

The quinary system FeO-Fe₂O₃-ZnO-CaO-SiO₂ represents slags encountered in a range of lead and zinc smelting systems. At iron metal saturation the iron is present principally as FeO rather than Fe₂O₃, the system is then conveniently represented by the quaternary system 'FeO'-ZnO-CaO-SiO₂. The pseudo-ternary sections (Figure 15a adopted from⁹⁸) in this case indicate that the liquid phase compositions lie on these sections in compositional space. Liquidus isotherms from different sections can be superimposed on this same compositional grid. In the case of pseudo-ternary sections of the form 'FeO'-ZnO-(CaO+SiO₂) at fixed CaO/SiO₂ ratios the sections selected have the additional advantages that i) the effect of variable ZnO or FeO concentration is directly described for a given CaO/SiO₂ ratio (Figure 15b⁹⁹), ii) the ratio (CaO+SiO₂)/(FeO+ZnO) gives the proportion of flux added to the system for a given CaO/SiO₂ ratio (Figure 15b⁹⁹), and iii) the effect of changing CaO/SiO₂ ratio and flux addition on phase equilibria and liquidus is readily identified from comparison of a series of sections (Figure 15c⁹⁹).

This form of representation can be extended to higher order systems using the same principles as are outlined above. Under oxidizing conditions the system PbO-FeO-Fe₂O₃-ZnO-CaO-SiO₂ can be represented by pseudo-ternary sections of the form Fe₂O₃-ZnO-(PbO+CaO+SiO₂) (Figure 16a¹⁰⁰). At high oxygen pressure iron is principally

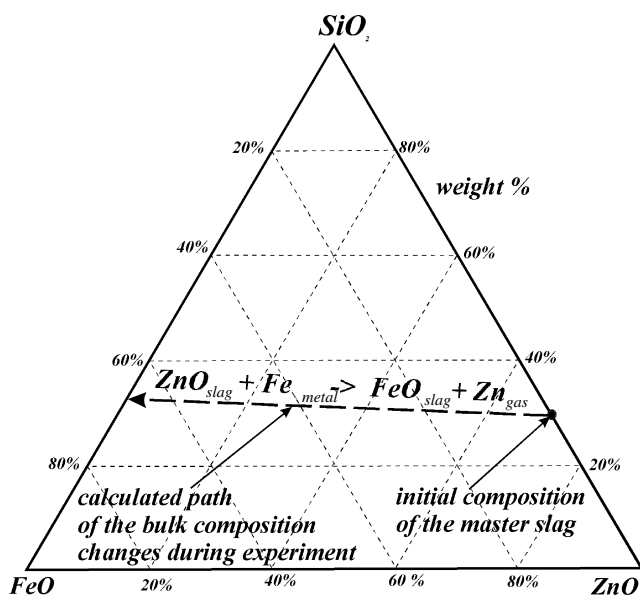


Figure 14. Bulk composition changes during the equilibration of the 'FeO'-ZnO-SiO₂ slags with metallic iron (adopted from⁹⁷)

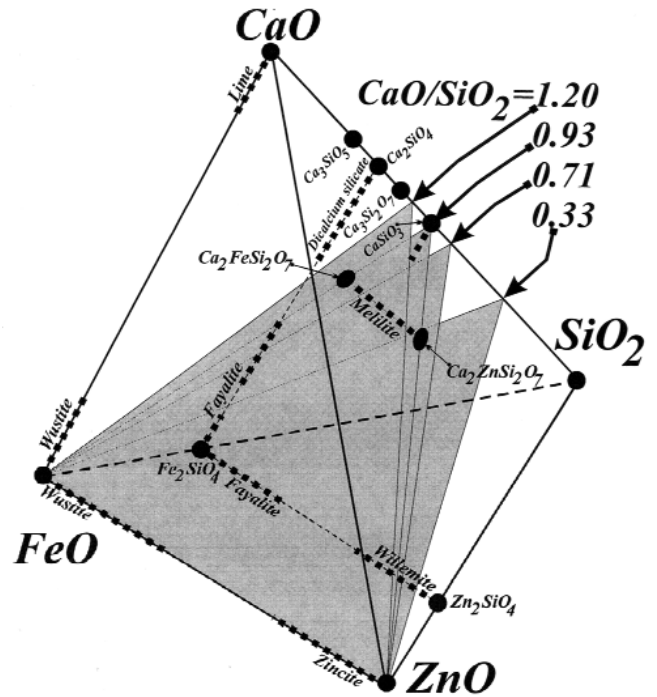


Figure 15a. Position of the pseudo-ternary sections with CaO/SiO₂=0.33, 0.71, 0.93 and 1.20 in the composition tetrahedron 'FeO'-ZnO-CaO+SiO₂ (adopted from⁹⁸)

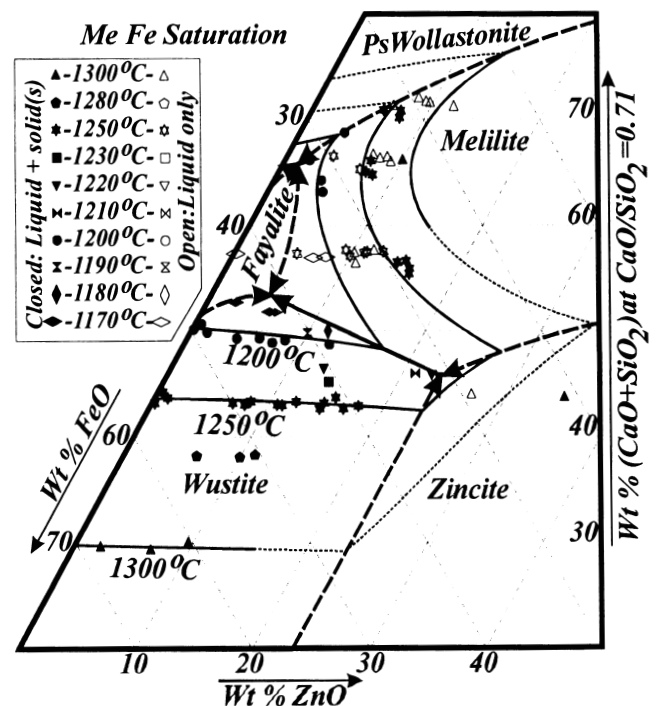


Figure 15b. Pseudo-ternary section 'FeO'-ZnO-(CaO+SiO₂) with weight ratio CaO/SiO₂=0.71 in equilibrium with metallic iron (adopted from⁹⁹)

in the form of Fe₂O₃, and there is no solid solubility of PbO, CaO or SiO₂ in hematite (Fe₂O₃), zinc ferrite (Zn_xFe_{3-x}O_{4+y}) or zincite ((Zn,Fe)O). The CaO/SiO₂ and the PbO/(CaO+SiO₂) ratios are fixed in this case and have been selected to appropriately describe a particular industrial slag system¹⁰⁰. The selection of the section of this form means that compositions of hematite, zinc ferrite and zincite solid

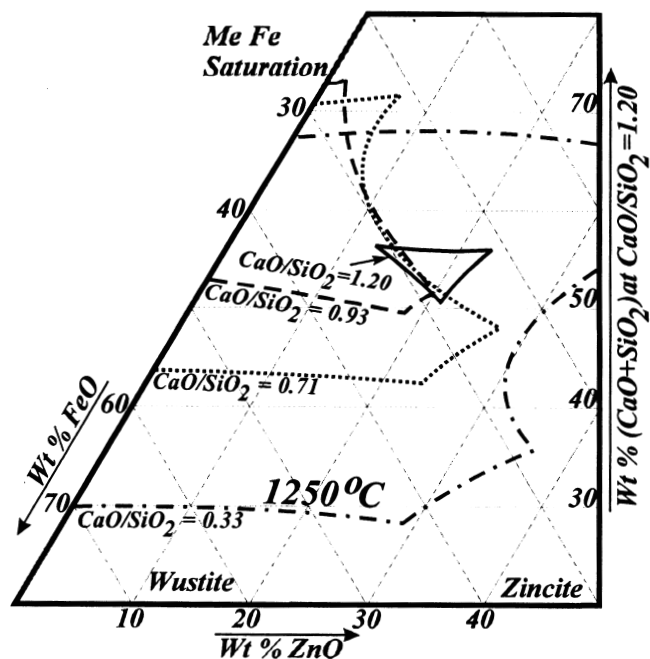


Figure 15c. Effect of the CaO/SiO₂ weight ratio on the 1250°C isotherm in the pseudo-ternary sections 'FeO'-ZnO-(CaO/SiO₂) in equilibrium with metallic iron (adopted from⁹⁸)

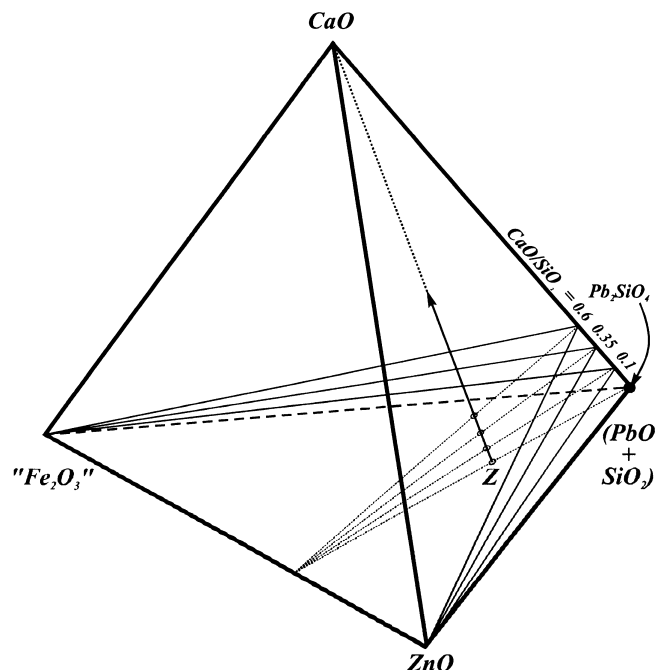


Figure 16b. Compositional tetrahedron CaO-ZnO-'Fe₂O₃'-(PbO + SiO₂) showing the pseudo-ternary sections for weight ratios CaO/SiO₂ = 0, 0.1, 0.35 and 0.6 at PbO/SiO₂ = 6.8 in air (adopted from¹⁰¹)

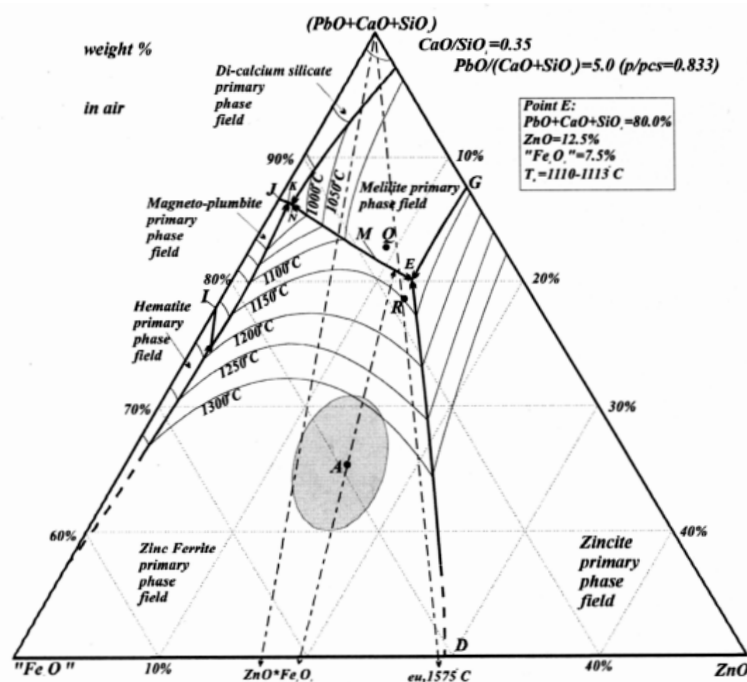


Figure 16a. Part of the experimentally determined liquidus surface on the pseudo-ternary section ZnO-'Fe₂O₃'-(PbO+CaO+SiO₂) with weight ratios CaO/SiO₂=0.35 and PbO/(CaO+SiO₂)=5.0 in air (adopted from¹⁰⁰)

phases also lie in the section. The crystallization of slags having bulk compositions in the hematite (Fe₂O₃), zinc ferrite (Zn_xFe_{3-x}O_{4+y}) or zincite ((Zn,Fe)O) primary phase fields can be interpreted as a true ternary, the crystallization sequence can be traced on this diagram, the lever rule can be applied to predict the proportions of solid and liquid phases formed, and the compositions of the remaining liquid phase at any temperature in these phase fields can be obtained. The effect of CaO flux addition on a base slag of

fixed PbO/SiO₂ can in this case be evaluated by construction of a series of sections at fixed CaO/SiO₂ ratios (Figure 16b¹⁰¹).

The effects of changing MnO concentration, fluxing with CaO and changing Al₂O₃/SiO₂ ratio on the liquidus of industrial manganese smelting slags can be readily followed by construction of pseudo-ternary sections of the form MnO-CaO-(Al₂O₃+SiO₂) (Figures 17a and b¹⁰² incorporate data from several sources^{43-44,102-104}). From a series of

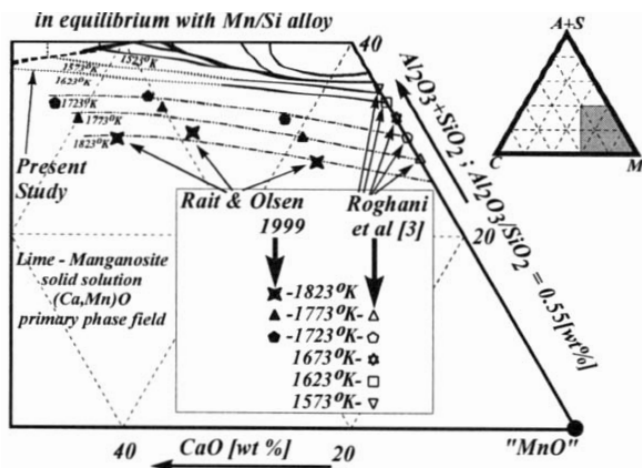


Figure 17a. Liquidus isotherms in the manganosite primary phase field for the 'MnO'-CaO-(Al₂O₃+SiO₂) system at Al₂O₃/SiO₂ weight ratio of 0.44–0.55 in equilibrium with Mn/Si alloy (data from Rait and Olsen^{43–44} and Roghani *et al.*^{103–104})

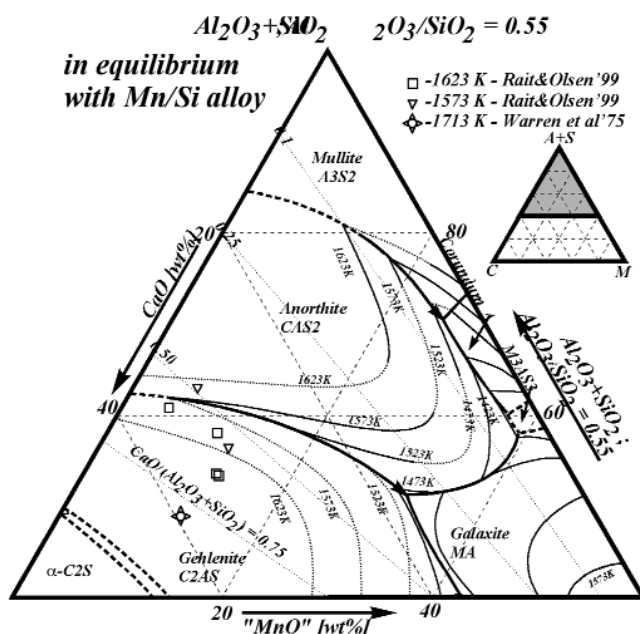


Figure 17 b. Liquidus in the 'MnO'-CaO-(Al₂O₃+SiO₂) system with Al₂O₃/SiO₂ weight ratio of 0.55 in equilibrium with Mn-Si alloy (Roghani *et al.*¹⁰³)

sections of this form the effect of MnO concentration and changing Al₂O₃/SiO₂ ratio on the liquidus temperatures and stability of primary phase fields can be systematically analysed (Figure 18).

By combining selected experimental studies with thermodynamic modelling it is also possible to predict the behaviour of systems that cannot be measured in laboratory studies using the current experimental techniques. An example of this approach given in Figures 19a¹⁰⁵ and 19b¹⁰⁶ for the systems 'FeO'-ZnO-SiO₂ and 'FeO'-ZnO respectively under reducing conditions and high temperature; the phase equilibria in the near liquidus region in the system 'FeO'-ZnO could not be measured directly because of the high vapour pressure of zinc. By incorporating experimental data on the solidus and liquidus of the system 'FeO'-ZnO-SiO₂¹⁰⁵ and sub-solidus 'FeO'-

ZnO^{105,107–110} into a thermodynamic model^{106,111} using the FactSage program⁶¹ the form of the 'FeO'-ZnO binary liquidus was predicted.

Summary

Experimental measurements of phase equilibria carried out over several decades have lead to the characterization of many oxide systems and provided the keys to our understanding of slag behaviour. In spite of these considerable efforts most of this information remains confined to binary, ternary and few selected higher order base systems.

Modern thermodynamic models make it possible to describe complex multi-phase slag systems and offer the potential to provide accurate predictive tools that can be used to optimize and improve process control of high temperature process systems. The development of these models still relies on the availability of improved experimental descriptions of slag chemistry. Experimental phase equilibrium research can provide

- critical data for thermodynamic model optimization and verification, and
- information on multi-component, multi-phase systems in composition ranges useful to industrial practice.

This review has provided some examples of how an integrated approach to the determination of phase equilibria in slag systems, involving the use of targeted experimental studies and systematic thermodynamic model development, can lead to the improved utilization of our current research capabilities and resources, and provide more accurate descriptions of complex slag systems.

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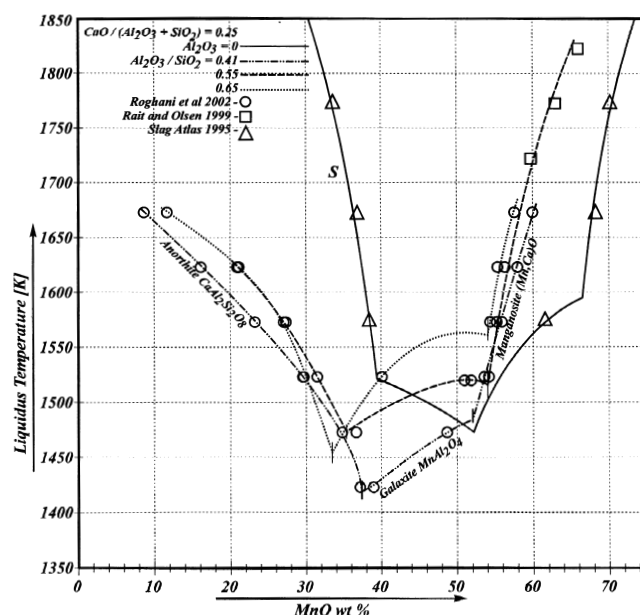


Figure 18. Pseudo-binary sections with CaO/(Al₂O₃+SiO₂)=0.25 in the MnO-CaO-(Al₂O₃+SiO₂) system with Al₂O₃/SiO₂ = 0, 0.41, 0.55 and 0.65 in equilibrium with a Mn-Si alloy

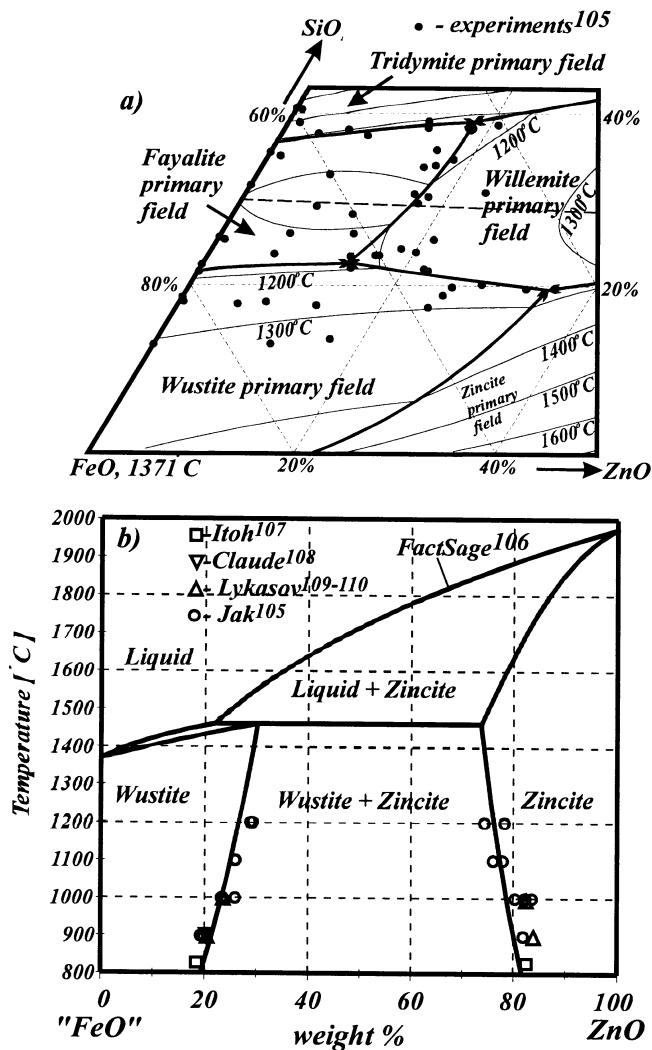


Figure 19. a) Liquidus in the 'FeO'-ZnO-SiO₂ system at metallic iron saturation measured with quenching/EPMA and calculated by FactSage after thermodynamic optimization (adopted from 105). b) Experimental solid solubility data and liquidus in the 'FeO'-ZnO system at metallic iron saturation calculated by FactSage after thermodynamic optimization (adopted from¹⁰⁶)

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