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PHASE EQUILIBRIA IN THE SYSTEM FeO - Fe$_2$O$_3$ - Al$_2$O$_3$ - CaO - SiO$_2$, WITH APPLICATIONS TO NON-FERROUS SMELTING SLAGS.

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ABSTRACT

Using recently determined experimental data, a new chemical thermodynamic database for the system FeO - Fe$_2$O$_3$ - Al$_2$O$_3$- CaO - SiO$_2$ has been developed. Used in conjunction with the FACT computer package, phase equilibria and thermodynamic properties can be predicted for the wide range of process conditions relevant to non-ferrous metal processing.

In this paper information on a) the liquidus temperatures, and b) the fraction of solids present at equilibrium, is presented as a function of slag composition and oxygen partial pressure, for silicate smelting slags. These data can be used to determine the conditions for magnetite formation, the effects of silica and lime additions on the liquidus, and the sensitivity of the proportion of solids in the slags to changes in operating temperature and oxygen partial pressure.

INTRODUCTION

The system FeO-Fe$_2$O$_3$-CaO-SiO$_2$ forms the basis for smelting and refining slags in most non-ferrous smelting processes. The phase equilibrium studies that have been carried out on various aspects of this system have been widely reported in the literature (1-3).

The necessity to obtain more detailed information on the phase chemistry of these systems is driven by the need to take practical steps to optimise metallurgical outcomes, and to reduce operating costs. In particular the issues of use and selection of flux additions, refractory wear, control of solid phase formation are of general concern from a pyrometallurgical viewpoint.

The chemical and physico-chemical properties of the slag are intimately linked to the phases present and their compositions. Properties such as, the liquidus and proportion of solids, important to many aspects of the process, are controlled by variables, such as, bulk composition, temperature, and oxygen partial pressure.

To date prediction of the effects of these process variables has largely been carried out with the aid of ternary or pseudo-ternary phase diagrams, determined under particular experimental conditions. Whilst these diagrams are very useful as a guide to the general behaviour of the slags,

they are limited in the range of conditions which can be accurately described. These difficulties, largely stemming from the number of compositional and process variables which have to be considered, can be overcome by constructing chemical thermodynamic models of the slag.

THERMODYNAMIC MODELLING

The new optimised thermodynamic database has been constructed using a combination of experimental (4) and modelling techniques. (5) The methodology used for the database development involves a series of related steps. In the initial step, the phase equilibria and other thermodynamic information available on the individual components in this quinary system, and their combinations in the various binary, ternary, quaternary systems, are analysed for their consistency and accuracy. This process is then used to identify compositional areas where further experimental data are required, to resolve discrepancies or to provide new information on key aspects of the phase chemistry. The experimental program is then targeted at obtaining information in these areas. It has been particularly important to provide new data in higher order systems in composition ranges of interest to metallurgical operations. The final optimised model parameters are then obtained by simultaneously considering behaviour in low and high order systems, not merely by the extrapolation of parameters obtained from the binaries and the ternaries.

The FACT model has been developed through a collaborative project with researchers at the Centre for Research in Computational Thermochemistry (CRCT), University of Montreal, developers of the FACT program. Details of the model parameters in the various sub-systems will be provided in subsequent publications.

It is now possible, using the FACT computer program in conjunction with a new optimised thermodynamic database for the system $FeO-Fe_2O_3-CaO-Al_2O_3-SiO_2$, to predict the chemical behaviour of this complex system. The new model can be used to examine the chemistry of the system from a number of viewpoints not previously possible, and to present the predictions in a number of different ways.

PREDICTED PHASE RELATIONS

The examples given in the present paper illustrate the ways in which this new database can be used to systematically analyse and predict the effects of process variables on the phases present, their proportions and their compositions.

The selected examples refer primarily to the conditions encountered generally in copper smelting and converting technologies (3), but the use of the new FACT model can be extended to applications in any set of composition, temperature and oxygen partial pressure conditions in the system.

Liquidus

Of principal concern to smelting operations is the liquidus of the slag. In flash smelting the slag is exposed to a range of oxygen pressures, highly oxidising conditions are present in the smelting shaft and these oxygen pressures are lowered by contact with the matte phase (3,6). The liquidus at $1250^{o}C$ for the system FeO-Fe_2O_3-CaO-SiO_2 at oxygen partial pressures 10^{-6}, 10^{-8}, 10^{-10}atm, as predicted using the FACT model, is given in Figure 1. It can be seen that the liquidus does not vary significantly with oxygen pressure in the silica, wollastonite, and dicalcium silicate primary phase fields. The liquidus of iron rich slags is, however, very sensitive to oxygen partial pressure. At low oxygen pressures, e.g. $PO_2 = 10^{-10}$ atm, the bounding primary phase field of iron rich slags is wustite. At higher oxygen partial pressures the spinel (in this case magnetite) phase, becomes stable. The extent of the spinel field increases with increasing oxygen partial pressure, and the range of compositions at which the slags are completely liquid becomes smaller.

The formation of magnetite during smelting operations is widely recognised as a major problem in industrial practice(3). The formation of this solid phase impedes slag/matte separation, and ultimately reduces bath volume due to the build up of magnetite deposits on the reactor walls. To select operating conditions that avoid or minimise these undesirable effects further detail on the slag chemistry is required.

The influence of SiO_2/Fe weight ratio, CaO/SiO_2 weight ratio and oxygen partial pressure on the liquidus temperatures of the slags is illustrated in Figure 2.

The predicted slag liquidus as a function of SiO_2/Fe ratio for the CaO/SiO_2 weight ratios of 0, 0.1, 0.2, 0.3 at an oxygen partial pressure of 10^{-4}atm is given in Figure 2a. The predictions show that increasing SiO_2/Fe ratio leads to a decrease in slag liquidus in the spinel primary phase field. The liquidus increases with increasing SiO_2/Fe ratio in the tridymite (SiO_2) primary phase field. A feature of the equilibria at this relatively high oxygen partial pressure is that the liquidus temperatures are, in general, above $1300^{o}C$.

The general shape of the liquidus is retained on lowering the oxygen partial pressures progressively to 10^{-6}, 10^{-8}, and 10^{-10}atm (Figures 2b-d) The absolute and relative values of the liquidus temperatures change with changing oxygen pressure. In the iron oxide primary phase fields lowering the oxygen pressure is accompanied by the lowering of liquidus temperatures, whilst the liquidus temperatures for the silica and fayalite primary phase fields remain almost unaffected by PO_2. At 10^{-10}atm there is a significant range of compositions that are fully liquid at $1200^{o}C$. This is associated primarily with the appearance of the fayalite or olivine primary phase field.

By way of comparison the liquidus for the pseudo-ternary system FeO_x-CaO-SiO_2 at iron saturation, is given in Figure 2e.

The effect of the CaO/SiO_2 weight ratio in the slag on the liquidus (Figures 2a-e) is also dependent on the primary phase field. Note that increasing CaO/SiO_2 generally increases slightly the liquidus in the magnetite and wustite primary phase fields, but reduces the liquidus in the olivine or fayalite, and tridymite (SiO_2) primary phase fields.

The slag liquidus temperature as a function CaO/SiO_2 weight ratio is given in Figure 3 at an oxygen partial pressure of 10^{-8}atm for a range of SiO_2/Fe ratios. The diagram again shows that increasing the lime/silica ratio significantly reduces the liquidus temperatures for slags in the silica primary field. It also illustrates a point apparent from Figures 2a-e, that CaO additions increase the SiO_2/Fe ratios at which silica saturation is achieved. This effect is particularly important for matte smelting operations where the recovery of dissolved metal values into the matte increases as silica saturation is approached. (7)

Sub-Liquidus

Figures 4 and 5 show the weight proportion of liquid at 1250^oC as a function of oxygen partial pressure for SiO_2/Fe weight ratios of 0.6 and 1.0 respectively, at various CaO/SiO_2 ratios. The data at $SiO_2/Fe = 0.6$ shows that the slags with CaO/SiO_2 less than 0.3 are fully liquid for oxygen pressures below 10^{-8} atm. With no lime additions, solids formation does not occur until oxygen pressures exceed approximately 3×10^{-7}atm, once this critical oxygen pressure has been achieved, however, there is a dramatic reduction in the proportion of liquid present in the system. As lime is added to these slags the critical oxygen pressures for the appearance of solid spinel decreases. From the point of view of operating above the liquidus at high oxygen pressures, lime addition does not appear to be useful for this SiO_2/Fe ratio.

In contrast, the data at SiO_2/Fe weight ratio of 1.0 shows that the slags with no lime contain approximately 10 wt% solids for oxygen pressures in the range 10^{-12} to 10^{-7}atm. Small additions of lime lower the proportions of solids present over the same range of oxygen partial pressures, and extend the range of oxygen pressures under which the system can be operated without the catastrophic precipitation of the solid phase. In general low slag fluidity, high viscosity, is to be expected if the solids content of the slag exceeds 20 wt%.

The influence of Al_2O_3

The effects of minor elements on the phase relations in this system in areas of interest to non-ferrous smelting should not be overlooked. This has been illustrated in recent experimental work on the effect of Al_2O_3 on liquidus temperatures in fayalite slags, examples of which are given in Figure 6 (8). The effect of Al_2O_3 on the liquidus temperature at a particular bulk composition is relatively minor; the liquidus in the fayalite phase field is lowered by approximately 3^oC for every one wt % Al_2O_3 added. More importantly the presence of Al_2O_3 changes the compositions at which silica saturation occurs.

The presence of Al_2O_3 also significantly reduces the critical oxygen pressure for the formation of the spinel solid phase. As an example (Figure 7), at the oxygen partial pressure of 10^{-8} atm, with no Al_2O_3 the slag is completely liquid, with 6 wt% Al_2O_3 under the same conditions over 20wt% solids are present.

IMPLICATIONS FOR INDUSTRIAL PRACTICE

Most copper smelting processes operate with slags having SiO_2/Fe weight ratios in the range 0.6 to 1.0. The slag compositions and process conditions used in various copper smelting operations

are given in Table 1 (3), and marked on Figures 2 and 3. In general those smelters which operate with SiO_2/Fe weight ratio of approximately 0.6 use low CaO additions. Those smelters that operate with SiO_2/Fe weight ratios of approximately 1.0 and higher, have slags containing significant CaO concentrations. These compositions have been selected by operators following plant trials to suit the particular process technologies and operating practices in each case. It is, however, interesting to compare these practices to the predictions made using the slag model.

The calculated liquidus temperatures in the system FeO-Fe_2O_3-CaO-SiO_2 at iron saturation, shown in Figure 2e indicate that at SiO_2/Fe weight ratio of 0.6, CaO addition will result in a lowering of the liquidus. The system under these conditions is operating in the region described by the fayalite primary phase field. The equilibrium oxygen partial pressures in copper matte smelters are reported to be in the range 10^{-11} to 10^{-9} atm (5), however, local excursions above these values occur as the concentrates are contacted with oxidising gases (3). In direct smelting the oxygen partial pressures in equilibrium with copper metal are approximately 10^{-5} atm. Figures 2 a-d) show that, for SiO_2/Fe weight ratio of 0.6, as the oxygen partial pressure increases the extent of the iron oxide primary field expands, the slag moves into the region of influence of this new phase field and the liquidus temperatures increase dramatically. In addition, whilst CaO additions are beneficial in lowering the liquidus at SiO_2/Fe weight ratio of 0.6 for oxygen partial pressures below 10^{-9} atm, above this oxygen pressure the addition of CaO increases the liquidus temperatures making it more likely that solid spinel will form.

In contrast for those smelters operating at SiO_2/Fe weight ratios of approximately 1.0, in the silica primary phase field, the liquidus is largely unaffected by oxygen partial pressure, i.e. local over oxidation does not lead to a dramatic increases in the proportion of solids and magnetite is not the first solid formed. In this operating regime the addition of CaO is beneficial in reducing the liquidus temperatures and may lead to improved operability. The calculations, in fact, indicate that the liquidus temperatures for the SiO_2/Fe weight ratio of 1.0 and the CaO/SiO_2 weight ratio of 0.15 are the same as for SiO_2/Fe weight ratio of 0.6 with no lime additions.

SUMMARY

Using an optimised model of the system FeO - Fe_2O_3 - Al_2O_3- CaO - SiO_2, in conjunction with the FACT computer package, phase equilibria and thermodynamic properties can be predicted for the wide range of process conditions relevant to non-ferrous metal processing.

The new FACT model is both accurate in its predictions, and flexible in the form in which information can be provided. The model can be used to provide phase diagrams over a range of oxygen partial pressures, information on the effect of flux additions, and accurate predictions of the equilibrium concentrations, and activities, of all chemical species present in the system.

The model can be used to carry out trend and sensitivity analysis of the system, to explore the effects of changes in composition, temperature and oxygen pressure. The model therefore provides a powerful predictive tool that can be used in the selection of optimum process conditions in metallurgical smelting systems.

ACKNOWLEDGEMENTS

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Fig.1 Liquidus isotherms at $1250^{\circ}C$ in the system FeO - Fe_2O_3 - CaO - SiO_2 for oxygen partial pressures of 10^{-6} (solid line), 10^{-8}(dashed line), 10^{-10}atm. (dotted line) (Predicted by FACT model)

Fig.2 Slag liquidus as a function of SiO_2/Fe weight ratio for CaO/SiO_2 weight ratios of 0, 0.1, 0.2, 0.3 at oxygen partial pressures of a) 10^{-4}atm., b)10^{-6}atm., c)10^{-8}atm., d)10^{-10}atm. and e) at metallic iron saturation. (Predicted by FACT model)

Fig.3 Slag liquidus as a function CaO/SiO_2 weight ratio for SiO_2/Fe weight ratio of 0.6, 0.8, 1.0, 1.5 at an oxygen partial pressure of 10^{-8}atm. (Predicted by FACT model)

Fig.4 Weight % of liquid at $1250^{\circ}C$ as a function of oxygen partial pressure for SiO_2/Fe weight ratio of 0.6 and CaO/SiO_2 weight ratios of 0, 0.1, 0.2, 0.3. (Predicted by FACT model)

Fig.5 Weight % of liquid at $1250^{\circ}C$ as a function of oxygen partial pressure for SiO_2/Fe weight ratio of 1.0 and CaO/SiO_2 weight ratios of 0, 0.1, 0.2, 0.3. (Predicted by FACT model)

Fig.6 Experimentally determined liquidus in the Al_2O_3-"FeO"-CaO-SiO_2 system in equilibrium with metallic iron (reference 8).

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Table 1. Compositions of copper smelting slags, and process conditions for various smelting processes (3).

Table 1. **Compositions of copper smelting slags, and process conditions for various smelting processes (3).**

	Smelter	Process	Cu	SiO_2	Fe Total	Fe^{3+}	Al_2O_3	CaO	MgO	S	SiO_2/Fe	CaO/SiO_2	Slag T [^{O}C]
A	Magma	Outokumpu Flush	2.75	32	44	2	4	1		1	0.73	0.03	1250
B	Chino	Inco Flash	0.9	33	44	1	3	1		1	0.75	0.03	1240
C	Ilo	Reverberatory Furnace	0.6	33	36	2	8	5		1	0.92	0.15	1200
D	Mufulira	Electric Furnace	0.7	37	24	1	5	14	5	0.3	1.54	0.38	1300
E	Southern Copper	Noranda Furnace	2.6	29	44	5	2	1	3	1	0.65	0.03	1230
F	Caletones	Teniente Furnace	7	25	40	4	6	1		5	0.63	0.04	1240
G	Mt Isa	Isasmelt	0.5	32.6	37.6	5.6	4.3	7.4	1.9	1	0.86	0.22	1200
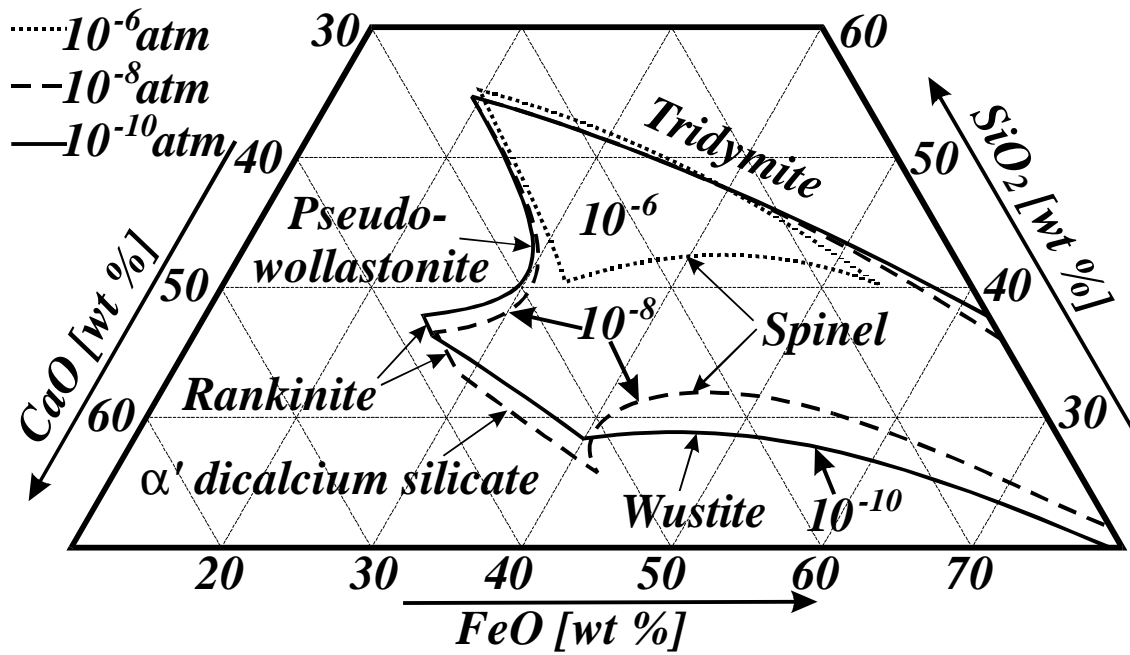
Figure 1. Liquidus isotherms at 1250°C in the FeO-Fe$_2$O$_3$-CaO-SiO$_2$ system at oxygen partial pressures of 10^{-10}(solid line), 10^{-8} (dashed) and 10^{-6} atm (dotted line) (predicted by the FACT model).
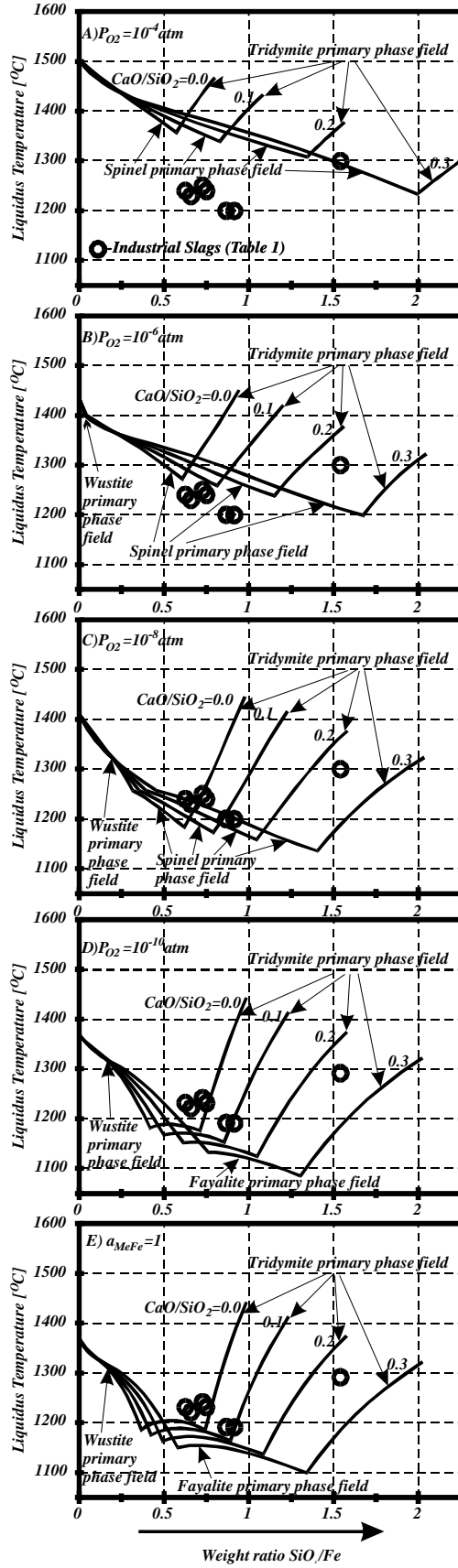
Figure 2. Slag liquidus as a function of SiO₂/Fe weight ratio
   for CaO/SiO₂ weight ratios of 0.0, 0.1, 0.2 and 0.3
   at oxygen partial pressures A)10⁻⁴, B)10⁻⁶, C) 10⁻⁸, D)10⁻¹⁰ atm
   and E)in equilibrium with metallic iron
   (predicted by the FACT model).
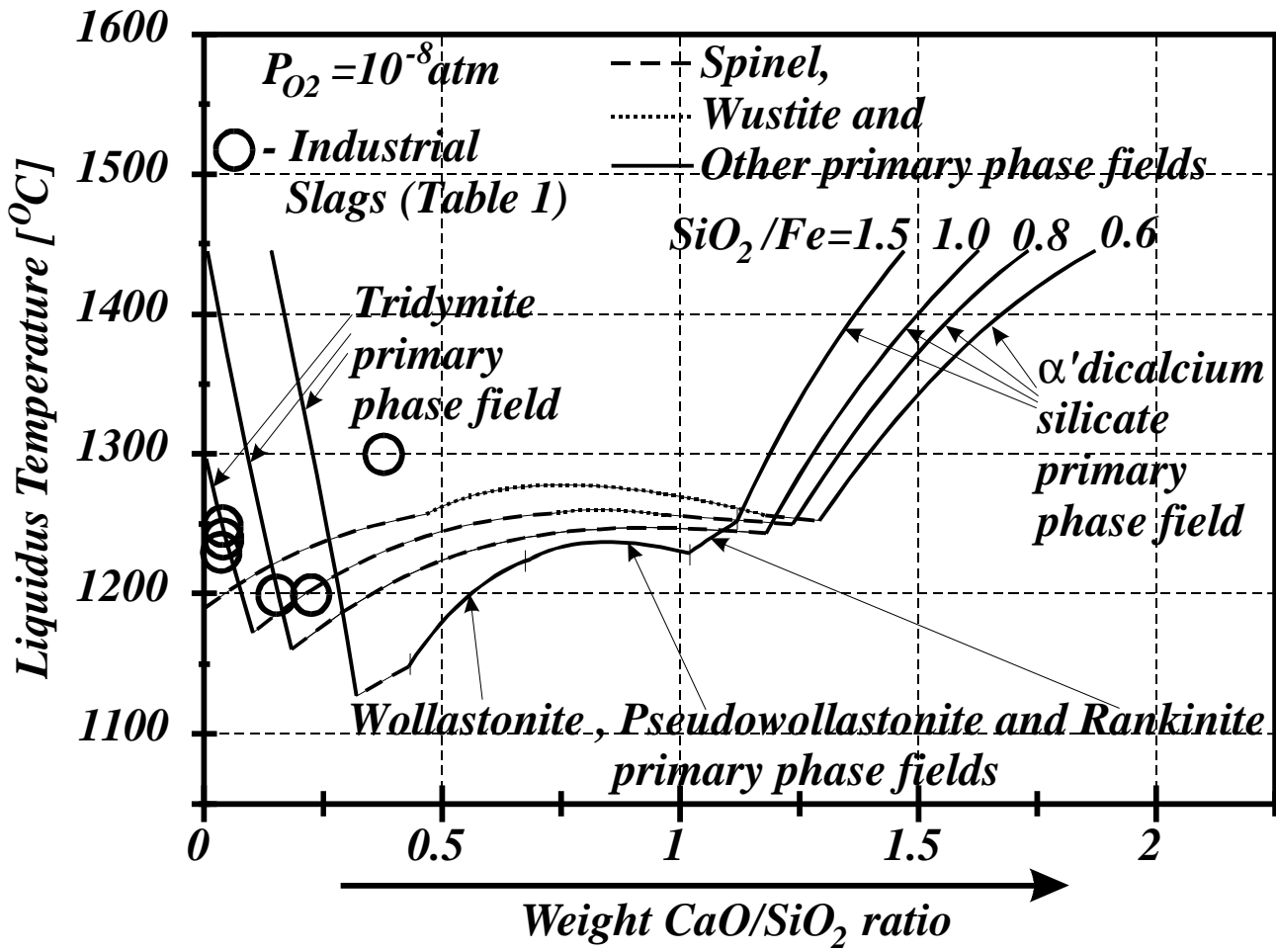
Figure 3. Slag liquidus as a function of CaO/SiO$_2$ weight ratio for SiO$_2$/Fe of 0.6, 0.8, 1.0 and 1.5 at an oxygen partial pressure of 10^{-8} atm (predicted by the FACT model).
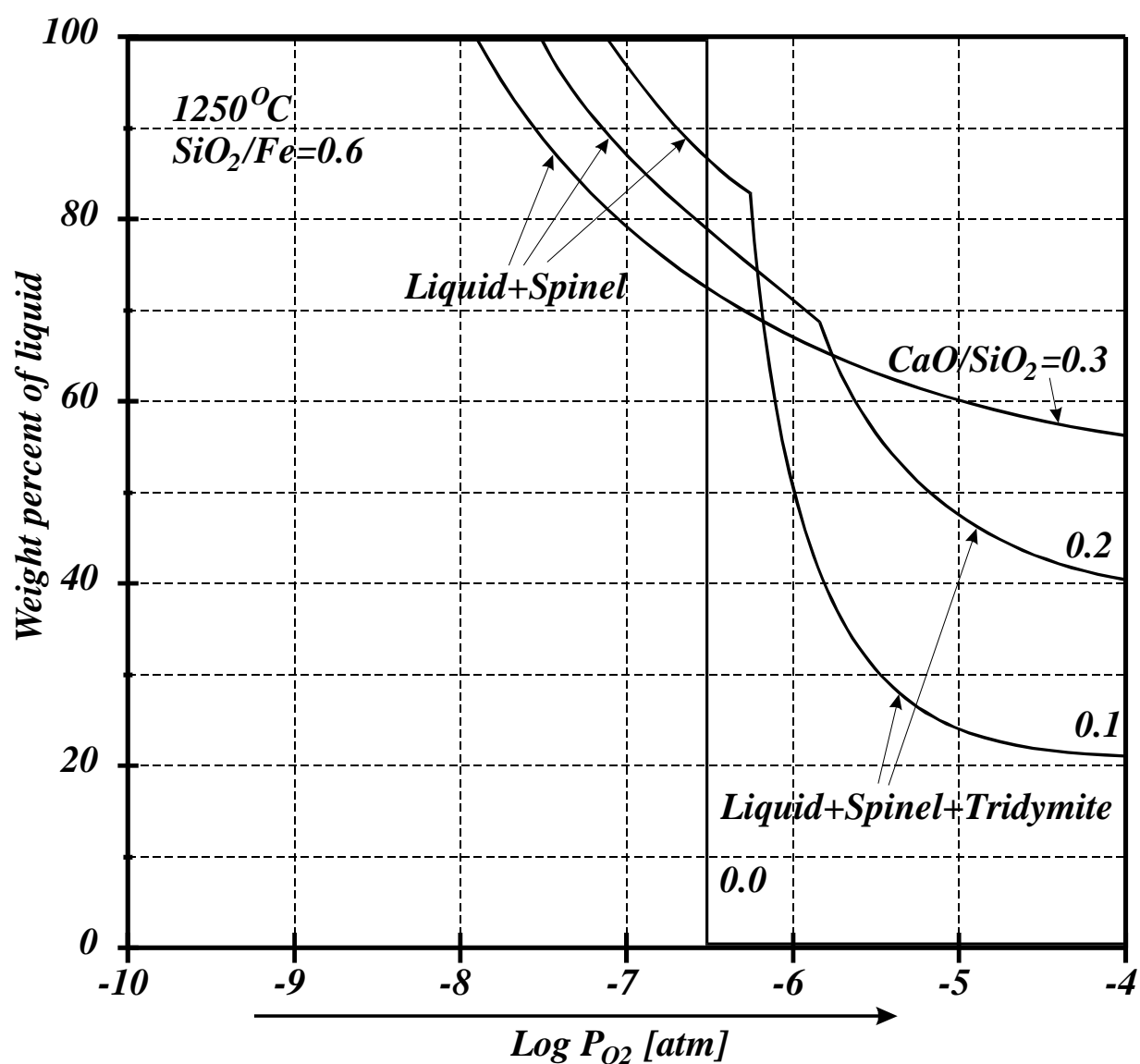
Figure 4. Weight percent of liquid at $1250^O C$ as a function of oxygen partial pressure for SiO_2/Fe weight ratio of 0.6 and CaO/SiO_2 weight ratios of 0.0, 0.1, 0.2 and 0.3 (predicted by the FACT model).
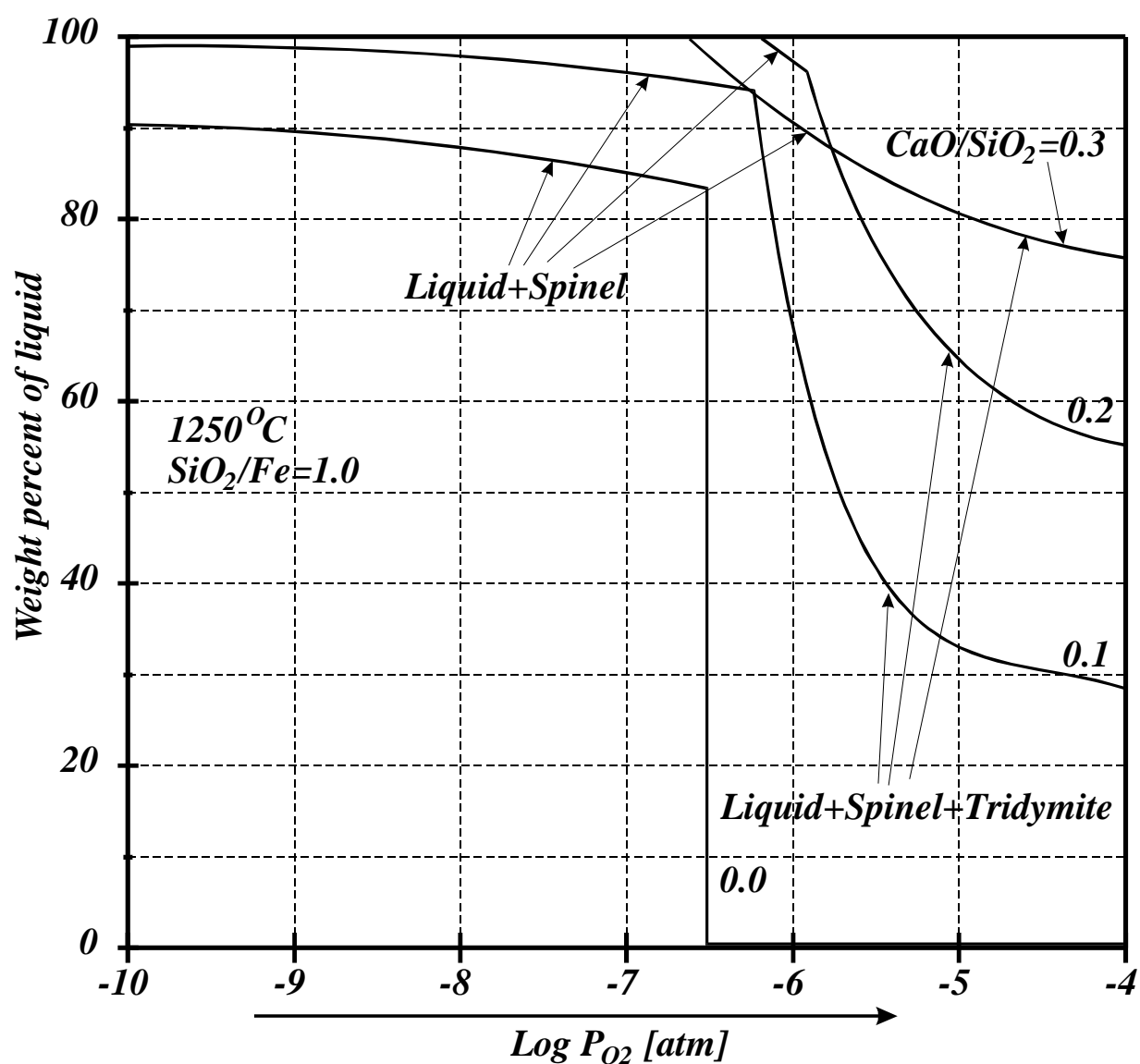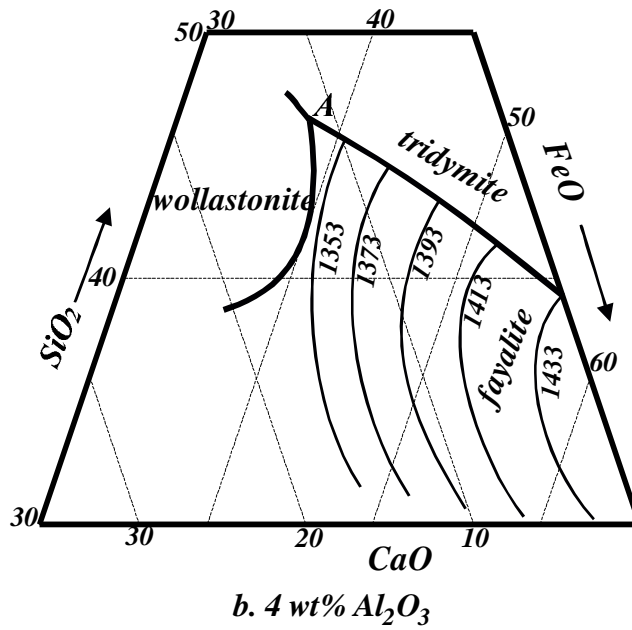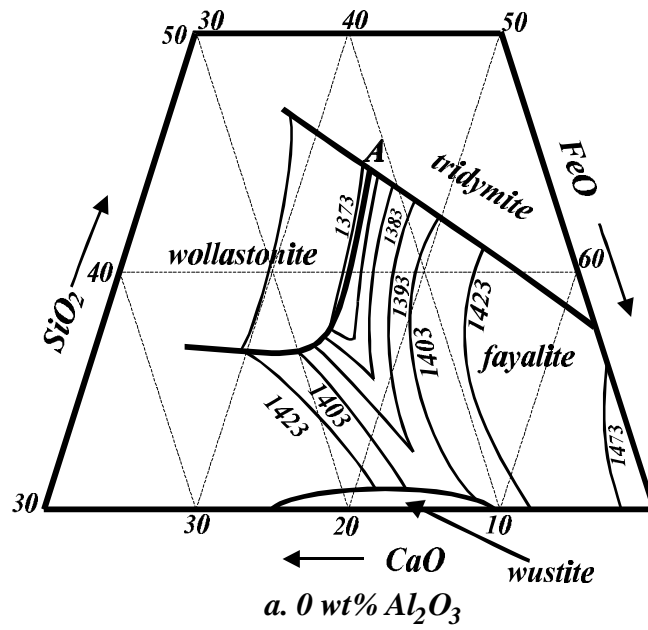
Figure 5. Weight percent of liquid at 1250°C as a function of oxygen partial pressure for SiO$_2$/Fe weight ratio of 1.0 and CaO/SiO$_2$ weight ratios of 0.0, 0.1, 0.2 and 0.3 (predicted by the FACT model).

a. 0 wt% Al₂O₃

b. 4 wt% Al₂O₃

Figure 6. Experimentally determined liquidus
in the Al₂O₃-"FeO"-CaO-SiO₂" system
in equilibrium with metallic iron (ref. 8).

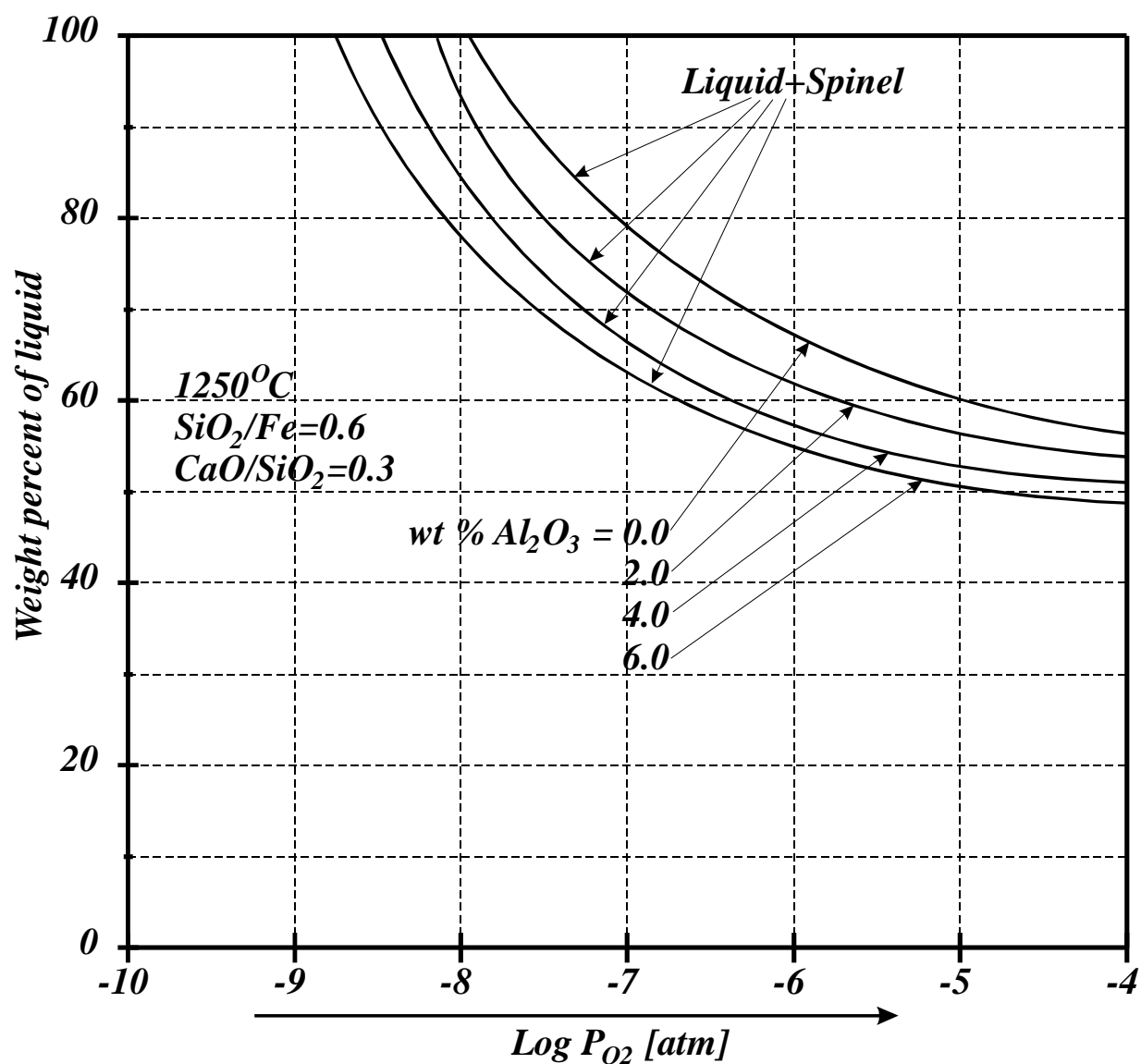*Figure 7. Weight percent of liquid at 1250°C as a function of oxygen partial pressure*
for SiO$_2$/Fe weight ratio of 0.6 and CaO/SiO$_2$ weight ratio of 0.3
and Al$_2$O$_3$ of 0.0, 2.0, 4.0 and 6.0 wt % (predicted by the FACT model).