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THERMODYNAMIC OPTIMISATION OF THE SYSTEMS  
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**Abstract**—Phase equilibrium data of the present authors for the CaO-Pb-O and PbO-CaO-SiO<sub>2</sub> system in air, combined with phase equilibrium and thermodynamic data from the literature, were optimised to obtain a self-consistent set of parameters of thermodynamic models for all phases. The modified quasi-chemical model was used for the liquid slag phase. From these model parameters, the optimised ternary phase diagram was back calculated. © 1998 Canadian Institute of Mining and Metallurgy. Published by Elsevier Science Ltd. All rights reserved.

**Résumé**—On a optimisé les données d'équilibre des auteurs ci-dessus, pour la phase de liquidus des systèmes CaO-Pb-O et PbO-CaO-SiO<sub>2</sub>, à l'air libre, en combinaison avec les données d'équilibre de phase et de thermodynamique de la littérature. On a ainsi obtenu un ensemble de paramètres autoconsistants de modèles thermodynamiques pour toutes les phases. On a utilisé le modèle quasi chimique modifié pour la phase de scories liquides. À partir de ces paramètres du modèle, on a calculé à reculons le diagramme de phase ternaire optimisé. © 1998 Canadian Institute of Mining and Metallurgy. Published by Elsevier Science Ltd. All rights reserved.

## INTRODUCTION

The present study of the system CaO-Pb-O and PbO-CaO-SiO<sub>2</sub> is part of a wider research program aimed at characterisation of phase equilibria and thermodynamic properties of the six-component system PbO-ZnO-FeO-Fe<sub>2</sub>O<sub>3</sub>-CaO-SiO<sub>2</sub> for zinc/lead smelting slags and sinters by interactive combination of experimental investigations and thermodynamic modelling. This overall research program has already been described in previous publications of the present authors [1–8].

In the thermodynamic 'optimisation' of a system, all available thermodynamic and phase equilibrium data are evaluated simultaneously in order to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, all of the thermodynamic properties and the phase diagrams can be back-calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can often be resolved, and interpolations and extrapolations can be made in a thermodynamically correct manner.

For the molten slag phase, a modified quasi-chemical model has been used [9–11]. The model has been described in several

publications [2, 3, 7, 9–11]. Parameters for the computer model of the slag system are obtained from thermodynamic and phase equilibrium information on binary and ternary systems. The optimisations for the binary and ternary systems are performed with least-squares optimisation programs which are part of the F\*A\*C\*T computer database system [12]. Binary and ternary phase diagrams are calculated from the optimised parameters with the software of the F\*A\*C\*T system.

In the present study, initial critical evaluations of all available reliable phase diagrams and thermodynamic data for the PbO-SiO<sub>2</sub>, CaO-SiO<sub>2</sub> and PbO-CaO binary systems have been conducted. From these binary parameters, the quasi-chemical model was used to predict the thermodynamic properties of the slag phase in the PbO-CaO-SiO<sub>2</sub> ternary system. The initial computer modelling of the PbO-CaO-SiO<sub>2</sub> ternary system indicated significant discrepancies between the data previously obtained on the binary sub-systems and on this ternary system [13–17]. To resolve these problems a new experimental investigation was carried out [1, 5, 6, 18]. The new [1, 5, 6, 18] and previous experimental information was then used to re-optimize the sub-systems and the ternary system PbO-CaO-SiO<sub>2</sub>.

## PURE COMPONENTS

A selection of the thermodynamic properties of CaO, PbO and SiO<sub>2</sub> from the F\*A\*C\*T databases was reported previously [19, 2]. Values of  $\Delta H_{298}^{\circ}$ ,  $S_{298}^{\circ}$  and  $T_{\text{fusion}}$  as well as  $\Delta H_{\text{fusion}}^{\circ}$  and  $\Delta S_{\text{fusion}}^{\circ}$  at the melting points for the oxides CaO, PbO and SiO<sub>2</sub> and  $\Delta H_{\text{Tr}}^{\circ}$  and  $\Delta S_{\text{Tr}}^{\circ}$  at solid state transformation points

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were taken from selected thermodynamic sources [20–24]. Expressions for  $C_p$  were obtained by fitting the tabulated values. Above the melting point,  $C_p(\text{sol})$  was set equal to  $C_p(\text{liq})$  and below the melting point,  $C_p(\text{liq})$  was set equal to  $C_p(\text{sol})$ . The thermodynamic properties of the component oxides PbO, CaO and SiO<sub>2</sub> are given in Table 1.

### BINARY SUB-SYSTEMS

The binary systems PbO-SiO<sub>2</sub> and CaO-SiO<sub>2</sub> were optimised previously by the present authors [2, 19]. Optimised properties of compounds and quasichemical parameters are listed in

Tables 1 and 2 respectively. The PbO-SiO<sub>2</sub> binary phase diagram is given in Fig. 1.

#### The CaO-Pb-O system

The system CaO-Pb-O was investigated by Kuxman and Fischer [25] in air and in a pure nitrogen atmosphere by DTA experiments of mixtures of 4, 8, 14, 21, 30 and 35 wt% CaO and by equilibration of melts in lime crucibles. These workers reported the existence of the intermediate compound Ca<sub>2</sub>PbO<sub>3</sub> (2CaO.PbO) which melts incongruently at 822 °C and has a eutectic with PbO at 815 °C and the liquid mole ratio Ca/(Ca + Pb) = 0.134.

Table 1. Thermodynamic properties of stoichiometric compounds in the PbO-CaO-SiO<sub>2</sub> system

A	B	a (0)	b (1)	c (-2)	d (-3)	e (-0.5)	f (2)	g (3)	h (-1)
CaO(s)									
-635090	37.750	58.791	0	-1147146	102978788	-133.904	0	0	0
CaO(l)									
578235	41.161	62.760	0	0	0	0	0	0	0
PbO(s)									
-218062	68.699	47.639	0.0122549	0	-45546016	-65.753	0	0	0
PbO(l)									
-202243	73.384	64.998	0	0	0	0	0	0	0
SiO <sub>2</sub> (Quartz)									
-908627	44.207	80.012	0	-3546684	491568369	-240.276	0	0	0
SiO <sub>2</sub> (Tridymite)									
-907045	45.524	75.373	0	-5958095	958246123	0	0	0	0
SiO <sub>2</sub> (Cristobalite)									
-906377	46.029	83.514	0	-2455360	280072194	-374.693	0	0	0
SiO <sub>2</sub> (l)									
-926636	9.917	85.772	0	0	0	0	0	0	0
PbSiO <sub>3</sub>									
-1149194	109.926	140.482	-0.0015355	-10439214	1789401320	0	0	0	0
Pb <sub>2</sub> SiO <sub>4</sub>									
-1366819	186.263	205.522	-0.0036610	-15460813	2823840390	0	0	0	0
Pb <sub>3</sub> SiO <sub>6</sub>									
-1798583	331.080	222.672	0.0874456	-1690336	0	0	0	0	0
Ca <sub>3</sub> SiO <sub>5</sub>									
-2933326	167.796	321.190	0	-994800	97529998	-2450.200	0	0	0
Ca <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>									
-3942846	210.874	339.908	0	-10659995	1373589130	-985.100	0	0	0
β-Ca <sub>2</sub> SiO <sub>4</sub>									
-2306046	127.610	209.680	0	-7989400	1297479950	-701.900	0	0	0
α'-Ca <sub>2</sub> SiO <sub>4</sub>									
-2307009	123.637	209.680	0.0520524	-7989400	1297479950	-701.900	-1.058*10 <sup>-04</sup>	5.38*10 <sup>-08</sup>	0
α-Ca <sub>2</sub> SiO <sub>4</sub>									
-2281887	143.248	209.680	0	-7989400	1297479950	-701.900	0	0	0
CaSiO <sub>3</sub> , wollastonite									
-1632579	81.810	149.073	0	-3659348	484349421	-690.295	0	0	0
CaSiO <sub>3</sub> , pseudowollastonite									
-1628506	85.279	141.156	0	-5857595	940734953	-417.232	0	0	0
Ca <sub>2</sub> PbO <sub>4</sub>									
-1623488	147.297	203.699	0.0065635	-2033547	205957576	-267.808	-4.937*10 <sup>-6</sup>	0	-8767.3
Pb <sub>3</sub> Ca <sub>2</sub> Si <sub>3</sub> O <sub>11</sub>									
-1141456	422.120	500.535	0.0367648	-12934344	1544024636	-1185.896	0	0	0
Pb <sub>2</sub> Si <sub>3</sub> O <sub>7</sub>									
-3900850	480.145	478.231	0.0612747	-10640052	1246975028	-1049.594	0	0	0
PbCa <sub>2</sub> Si <sub>3</sub> O <sub>8</sub> , margarosonite									
-4416138	274.937	405.257	0.0122549	-12934344	1635116667	-1054.389	0	0	0
Pb <sub>3</sub> CaSi <sub>4</sub> O <sub>21</sub> , Ca-Pb barysilite									
-8077849	857.686	919.975	0.0980395	-22427250	2688020876	-2101.586	0	0	0

$$H \text{ (J mol}^{-1}\text{)} = A + \int_{298.15}^T C_p dT \text{ (relative to elements at 298.15 K)}$$

$$S \text{ (J mol}^{-1}\text{K}^{-1}\text{)} = B + \int_{298.15}^T (C_p/T) dT$$

$$C_p \text{ (J mol}^{-1}\text{K}^{-1}\text{)} = a + bT + cT^2 + dT^{-3} + eT^{-0.5} + fT^2 + gT^3 + hT^{-1}$$

Table 2. Optimised binary quasichemical parameters for the liquid phase in the PbO-SiO<sub>2</sub>, CaO-SiO<sub>2</sub> and CaO-PbO systems.

System A-B	$k$	$\omega k(\text{AB})$ [J]	$\eta k(\text{AB})$ [J/K]
PbO-SiO <sub>2</sub>	0	-24351	
	6	-174076	
	7	183069	-20.83
CaO-SiO <sub>2</sub>	0	-152217	-19.46
	1	-37932	
	5	-90148	
	7	439891	133.89
PbO-CaO	0	-103014	-52.30

Kitaguchi *et al.* [26] investigated this system in air using TG-DTA. The intermediate compound was reported [26] to be Ca<sub>2</sub>PbO<sub>4</sub> (2CaO.PbO<sub>2</sub>); no Ca<sub>2</sub>PbO<sub>3</sub> was found.

The existence of Ca<sub>2</sub>PbO<sub>4</sub> has been confirmed by others [27-29] and indicates that lead may be present in the 4+ as well as the 2+ states. This means that the system in air is not a true binary but part of the Pb-Ca-O ternary system. No information was found in relation to the presence and amount of Pb<sup>4+</sup> in the liquid phase. In the present study it is assumed that there is negligible Pb<sup>4+</sup> in the liquid.

Kitaguchi *et al.* [26] reported the eutectic (liquid → Ca<sub>2</sub>PbO<sub>4</sub> + PbO) in air to be at 847 ± 6 °C and the liquid mole ratio Ca/(Ca + Pb) = 0.04. The peritectic (liquid + Ca<sub>2</sub>PbO<sub>4</sub> → liquid + CaO) was reported to be at 980 ± 2 °C with liquid having mole ratio Ca/(Ca + Pb) = 0.14.

Araten [27] reported the solubility of CaO in the PbO liquid to be of the order of 5 wt% (mole ratio Ca/(Ca + Pb) = 0.173) at a temperature around 1000 °C (temperature is not clearly

stated). This is consistent with both versions of the diagram [25, 26].

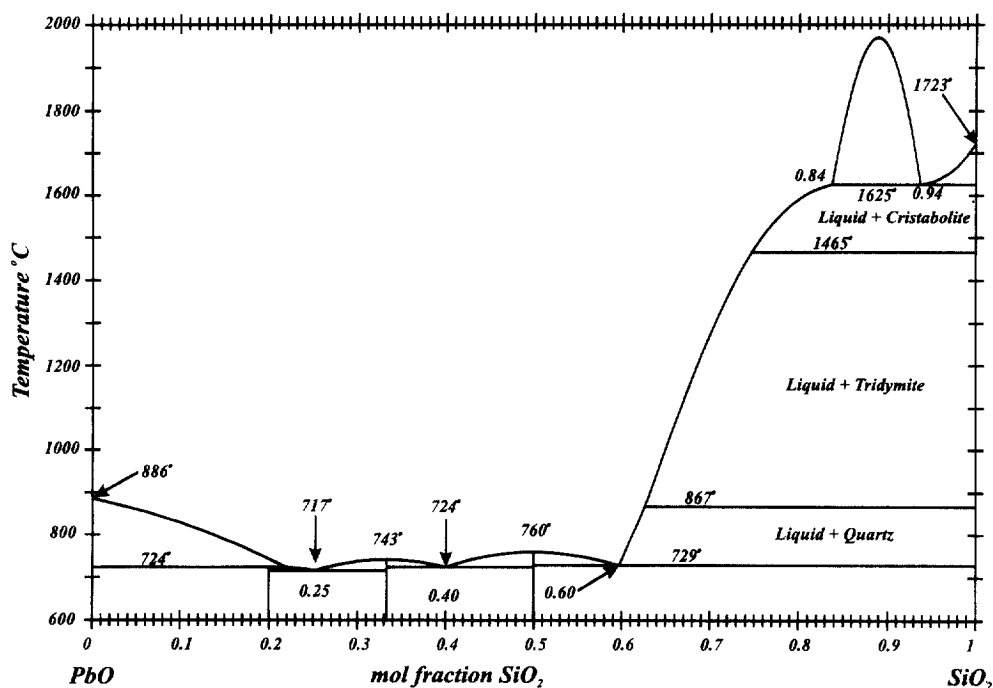
A new experimental investigation was undertaken by the present authors to characterise this system [18]. Quenching experiments were carried out in equilibrium with air as well as at lower oxygen partial pressures. It was confirmed that the incongruently melting compound has the formula Ca<sub>2</sub>PbO<sub>4</sub>. It was found that the compound Ca<sub>2</sub>PbO<sub>4</sub> decomposes into liquid and lime in air at a temperature above 1000 °C. The temperature of the eutectic (liquid → Ca<sub>2</sub>PbO<sub>4</sub> + PbO) was found to be above 850 °C in air. At 825 °C and oxygen partial pressures above 0.01 atm, the compound Ca<sub>2</sub>PbO<sub>4</sub> is stable and at oxygen partial pressures below 0.001 atm, it decomposes into PbO and CaO.

$S_{298}$  and  $C_p$  values for the compound Ca<sub>2</sub>PbO<sub>4</sub> were calculated using the increment method [30]. The  $\Delta H_{298}$  value was optimised to fit the liquidus data [18] in the primary field of this compound. These thermodynamic properties are given in Table 1.

From the experimental information [18] the system CaO-PbO was optimised. The binary quasichemical parameters for the liquid phase obtained during optimisation are given in Table 2.

The calculated optimised phase diagram in air along with experimental points [18, 26] is given in Fig. 2. The eutectic (liquid → Ca<sub>2</sub>PbO<sub>4</sub> + PbO) was calculated to be at 861 °C and a liquid mole ratio Ca/(Pb + Ca) = 0.05(4). The peritectic (liquid + CaO → Ca<sub>2</sub>PbO<sub>4</sub>) was calculated to be at 1001 °C with the liquid having a mole ratio Ca/(Pb + Ca) = 0.14.

At lower oxygen partial pressures, the compound Ca<sub>2</sub>PbO<sub>4</sub> is not stable. Figure 3 presents the pseudo-binary diagram CaO-PbO at an oxygen partial pressure equal to 0.001 atm. The system at this low oxygen partial pressure was calculated to have a eutectic (liquid → PbO + CaO) at 826 °C at a liquid molar ratio Ca/(Pb + Ca) = 0.12.

Fig. 1. The phase diagram of the system PbO-SiO<sub>2</sub> as previously optimised [2].

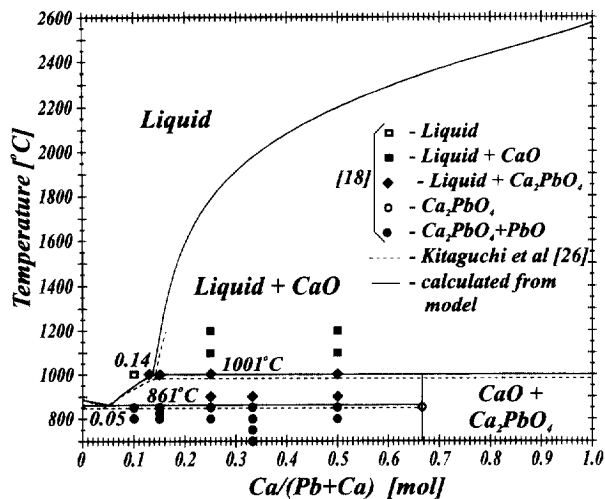


Fig. 2. The phase diagram of the system CaO-Pb-O in air.

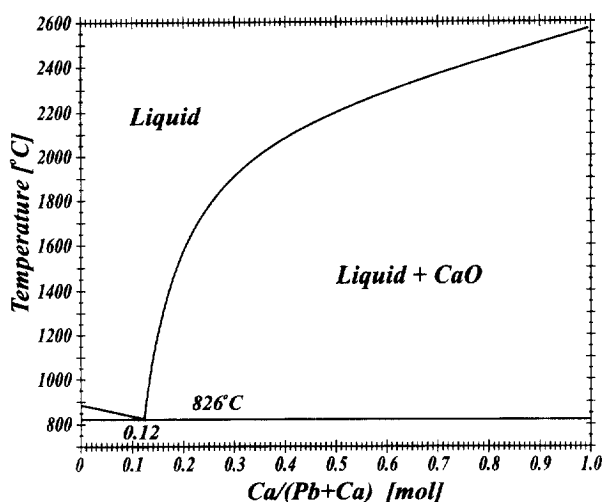


Fig. 3. The phase diagram of the system CaO-Pb-O calculated at  $P_{O_2} = 0.001$  atm.

Figure 4 presents the variation of the temperature of the eutectic (liquid  $\rightarrow$  PbO + CaO/Ca<sub>2</sub>PbO<sub>4</sub>) as a function of the oxygen partial pressure. The minimum oxygen partial pressure at which the compound Ca<sub>2</sub>PbO<sub>4</sub> is stable was calculated to be 0.0018 atm. At oxygen partial pressures below 0.0018 atm, this eutectic reaction involves liquid, lead oxide and lime and the eutectic temperature is not dependent on the oxygen partial pressure. As oxygen partial pressure increases above 0.0018 atm, the eutectic involves liquid, PbO and Ca<sub>2</sub>PbO<sub>4</sub> and the temperature of the eutectic increases with increasing oxygen partial pressure (from 826°C at 0.0018 atm to 861°C in equilibrium with air).

#### THE PbO-CaO-SiO<sub>2</sub> SYSTEM

EMF measurements with a solid electrolyte (stabilised zirconia) oxygen concentration cell were used by Taskinen *et al.*

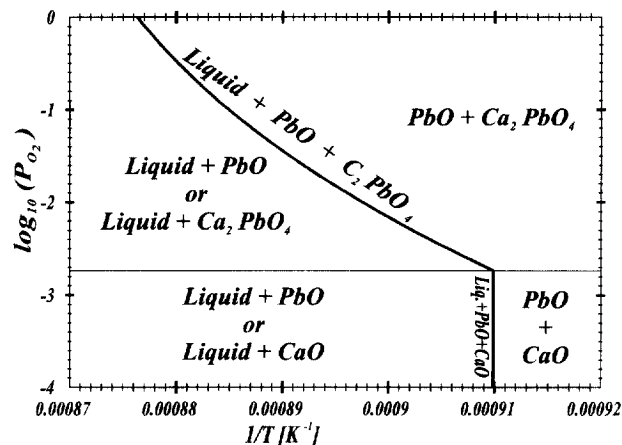


Fig. 4. Calculated temperature of the eutectic (liquid  $\rightarrow$  PbO + CaO/Ca<sub>2</sub>PbO<sub>4</sub>) as a function of oxygen partial pressure.

[13] and Sugimoto and Kozuka [16] to determine PbO activities in the ternary CaO-PbO-SiO<sub>2</sub> liquid phase. Sugimoto and Kozuka [16] investigated the temperature range from 900 to 1100°C. Taskinen, Taskinen and Holappa [13] investigated the temperature range from 900 to 1000°C. Richardson and Pillay [14] measured the activity of PbO in the low lime region of the ternary CaO-PbO-SiO<sub>2</sub> liquid in the temperature range from 1000 to 1200°C by a study of the equilibrium  $(PbO) \rightleftharpoons [Pb] + [O]$ , where (PbO) is lead oxide, either pure or dissolved in the silicate, [Pb] is molten lead metal and [O] is oxygen dissolved in the lead metal. Slag and lead metal were equilibrated under nitrogen, quenched and the oxygen concentration in the lead metal phase was analysed chemically. Ouchi and Kato [15] measured PbO activities in liquid CaO-PbO-SiO<sub>2</sub> solutions using a Knudsen cell-mass spectrometer technique in the temperature range from 1050 to 1250°C.

Phase relations in the ternary system were investigated by Samanta and Hummel [17] by a quenching technique with optical microscopy and XRD. Some samples were examined with the electron probe.

The initial computer modelling of the PbO-CaO-SiO<sub>2</sub> ternary system indicated significant discrepancies between the data reported by Samanta and Hummel [17] and other previously obtained data on the binary sub-systems [2, 19, 25–29] and on this ternary system [13–16]. To resolve these problems, a new extensive experimental study of the PbO-CaO-SiO<sub>2</sub> ternary system was undertaken by the present authors [6, 18] using the quenching technique followed by electron probe X-ray microanalysis. Liquidus and solidus data were reported for most of the primary phase fields [6, 18]. It is these recent experimental results which were mainly used for the optimisation. Over 200 experimental liquidus points over the composition range 0–65 mol% SiO<sub>2</sub> and 0–42 mol% CaO in most of the primary phase fields were used.

Binary quasichemical parameters for the liquid phase from the optimisations of the binary sub-systems (see Table 2) and three additional ternary parameters were required to reproduce the reported [6, 18] ternary liquidus surface and other available thermodynamic data [13–16]. The ternary terms  $+56417Y_{CaO}(Y_{PbO} + Y_{CaO})J$  and  $+137285Y_{CaO}^2J$  were added to

the value of  $\omega_{(\text{Pb-Si})}$  and the ternary term  $-71785 Y_{\text{SiO}_2} Y_{\text{PbO}} / (Y_{\text{PbO}} + Y_{\text{CaO}}) \text{J}$  was added to the value of  $\omega_{(\text{Ca-Si})}$ .

All solid phases with the exception of the  $\alpha'$  dicalcium silicate  $\text{Ca}_2\text{SiO}_4$  and lead calcium silicate  $\text{Ca}_2\text{Pb}_3\text{Si}_3\text{O}_{11}$  were assumed to be pure stoichiometric compounds.  $S_{298}^\circ$  and  $C_p$  values for the stoichiometric compounds margarosanite  $\text{Ca}_3\text{PbSi}_3\text{O}_9$  and Pb-Ca barysilite  $\text{CaPb}_8\text{Si}_6\text{O}_{21}$  were calculated using the increment method [30].  $\Delta H_{298}^\circ$  values were optimised to fit the liquidus data [6, 18] in the primary fields of these compounds. Thermodynamic properties of the stoichiometric compounds are given in Table 1.

Dicalcium silicate  $\text{Ca}_2\text{SiO}_4$  ( $\alpha'$  polymorph) and lead calcium silicate  $\text{Ca}_2\text{Pb}_3\text{Si}_3\text{O}_{11}$  were found to form extensive solid solutions [6, 18]. For instance,  $\alpha'$  dicalcium silicate  $\text{Ca}_2\text{SiO}_4$  dissolves up to 45 mol%  $\text{Pb}_2\text{SiO}_4$ . The chemical compositions of these solid solutions in equilibrium with liquids at the various temperatures indicate that  $\text{Pb}^{2+}$  substitutes for  $\text{Ca}^{2+}$  cation.

The thermodynamic properties of the  $\alpha'$  dicalcium silicate  $\text{Ca}_2\text{SiO}_4$  and lead calcium silicate  $\text{Ca}_2\text{Pb}_3\text{Si}_3\text{O}_{11}$  solid solutions were described by a sub-regular solution model. The selection of the  $S_{298}^\circ$ ,  $C_p$  and  $\Delta H_{298}^\circ$  values for the compounds  $\alpha'$   $\text{Ca}_2\text{SiO}_4$  and  $\text{Pb}_2\text{SiO}_4$  is described by Eriksson *et al.* [19] and Jak *et al.* [2] respectively.  $S_{298}^\circ$ ,  $C_p$  and  $\Delta H_{298}^\circ$  values for the compounds  $\text{Ca}_2\text{Pb}_3\text{Si}_3\text{O}_{11}$  and  $\text{Pb}_2\text{Si}_3\text{O}_{11}$  (which is unstable as a stoichiometric compound) were calculated using the increment method [30] (see Table 1). The  $\Delta H_{298}^\circ$  value for the compound  $\text{Ca}_2\text{Pb}_3\text{Si}_3\text{O}_{11}$  was then adjusted to fit the liquidus data.

The optimised Gibbs energy of the solid solution of  $\text{Pb}_2\text{SiO}_4$  in the  $\alpha'$   $\text{Ca}_2\text{SiO}_4$  is:

$$G = X_{\text{C}_{2\text{S}}} G_{\text{C}_{2\text{S}}} + X_{\text{P}_{2\text{S}}} (G_{\text{P}_{2\text{S}}} + 3331) + 2RT(X_{\text{C}_{2\text{S}}} \ln X_{\text{C}_{2\text{S}}} + X_{\text{P}_{2\text{S}}} \ln X_{\text{P}_{2\text{S}}}) + X_{\text{C}_{2\text{S}}} X_{\text{P}_{2\text{S}}} (-2335 - 9498 X_{\text{P}_{2\text{S}}}) [\text{J/mol}], \quad (1)$$

where  $X_{\text{C}_{2\text{S}}}$ ,  $X_{\text{P}_{2\text{S}}}$ ,  $G_{\text{C}_{2\text{S}}}$  and  $G_{\text{P}_{2\text{S}}}$  are mole fractions and standard Gibbs energies of  $\alpha'$ - $\text{Ca}_2\text{SiO}_4$  and  $\text{Pb}_2\text{SiO}_4$  respectively.

The optimised Gibbs energy of the solid solution of  $\text{Pb}_3\text{Si}_3\text{O}_{11}$  in lead calcium silicate  $\text{Ca}_2\text{Pb}_3\text{Si}_3\text{O}_{11}$  is:

$$G = X_{\text{C}_{2\text{P}_{3\text{S}}}} G_{\text{C}_{2\text{P}_{3\text{S}}}} + X_{\text{P}_{3\text{S}}} (G_{\text{P}_{3\text{S}}} + 24330) + 2RT(X_{\text{C}_{2\text{P}_{3\text{S}}}} \ln X_{\text{C}_{2\text{P}_{3\text{S}}}} + X_{\text{P}_{3\text{S}}} \ln X_{\text{P}_{3\text{S}}}) - 37731 X_{\text{C}_{2\text{P}_{3\text{S}}}} X_{\text{P}_{3\text{S}}} [\text{J/mol}], \quad (2)$$

where  $X_{\text{C}_{2\text{P}_{3\text{S}}}}$ ,  $X_{\text{P}_{3\text{S}}}$ ,  $G_{\text{C}_{2\text{P}_{3\text{S}}}}$  and  $G_{\text{P}_{3\text{S}}}$  are mole fractions and standard Gibbs energies of  $\text{Ca}_2\text{Pb}_3\text{Si}_3\text{O}_{11}$  and  $\text{Pb}_3\text{Si}_3\text{O}_{11}$  respectively.

The resultant ternary phase diagram calculated by the F\*A\*C\*T computer software is presented in Fig. 5. When the liquidus is relatively flat, an agreement with the experimental data [6, 18] of  $\pm 15 \text{K}$  at a given composition is obtained and when the liquidus is steep, the experimental [6, 18] and the calculated values agree within  $\pm 1 \text{mol}\%$  at a given temperature. The agreement between the calculated and experimental [6, 18] liquidus in the ternary system is illustrated in Fig. 6. Figure 7 presents the low-lime region of the diagram.

The calculated optimised ternary phase diagram is consistent with the ternary activity data [13–16] at the low lime contents up to the liquidus isotherm. Comparison of the calculated and reported [13, 14, 16] activities of  $\text{PbO}$  in  $\text{PbO-CaO-SiO}_2$  liquid

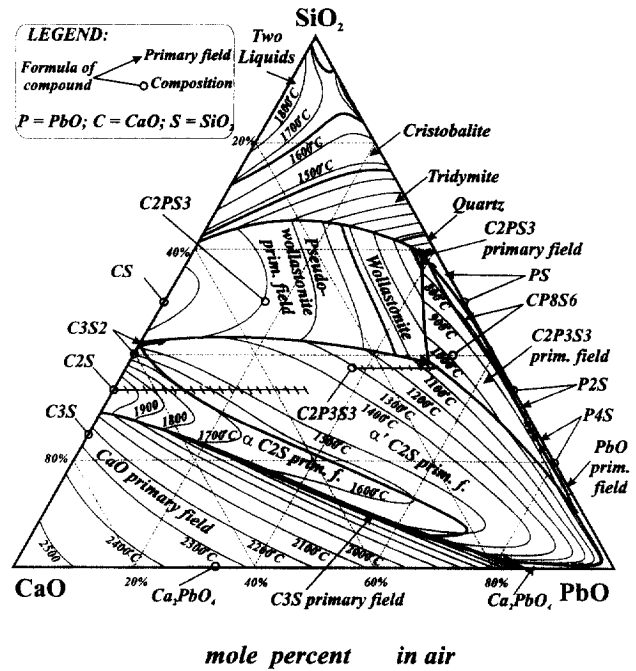


Fig. 5. The calculated optimised phase diagram of the system  $\text{PbO-CaO-SiO}_2$  in air (temperature in degrees Celsius).

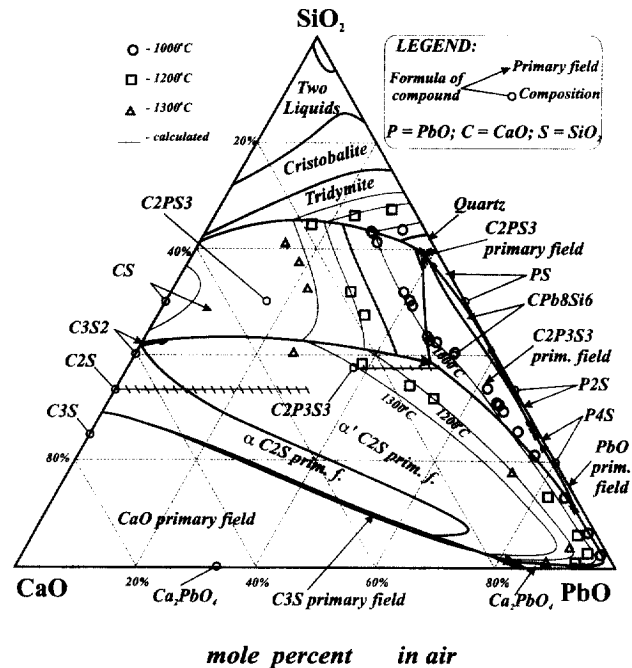


Fig. 6. Calculated and experimental liquidus isotherms in the  $\text{PbO-CaO-SiO}_2$  ternary system in air.

solutions is shown in Fig. 8. Authors [13, 14, 16] reported activities of  $\text{PbO}$  in the  $\text{PbO-CaO-SiO}_2$  liquid at  $\text{CaO}$  concentrations higher than the liquidus reported by Jak *et al.* [6, 18], the latter, more recent data were given preference during optimisation.

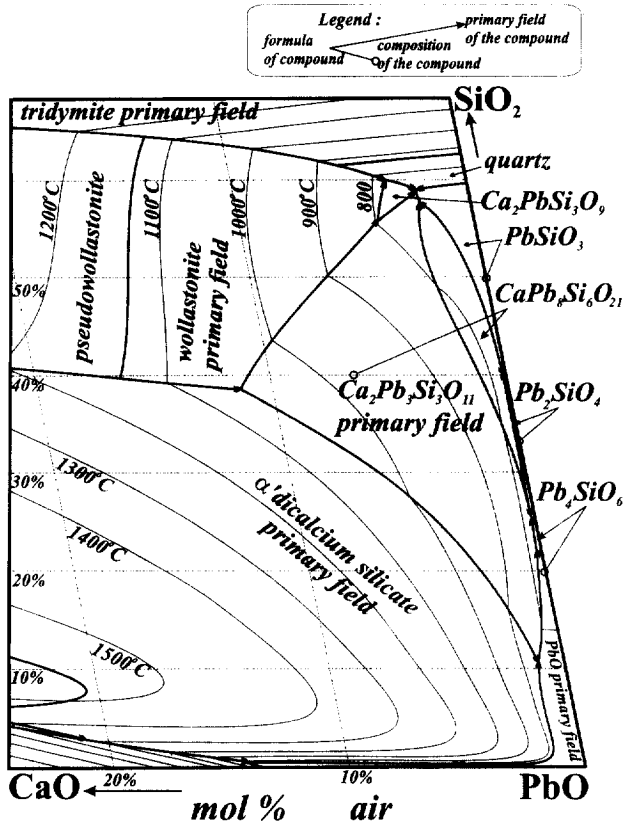


Fig. 7. The calculated liquidus surface of the PbO-rich region of the system PbO-CaO-SiO<sub>2</sub> in air.

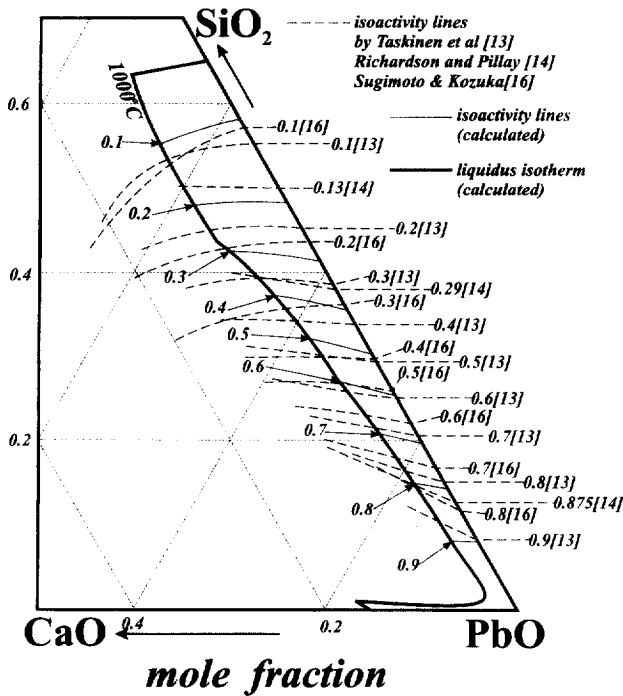


Fig. 8. Comparison of the experimental and calculated activities of PbO in liquid PbO-CaO-SiO<sub>2</sub> solutions at 1000°C (pure liquid standard state).

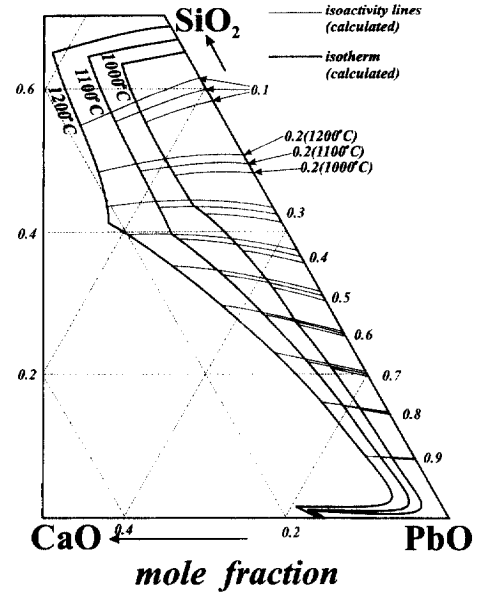


Fig. 9. Calculated activities of PbO in liquid PbO-CaO-SiO<sub>2</sub> solutions at 1000, 1100 and 1200°C (pure liquid standard state).

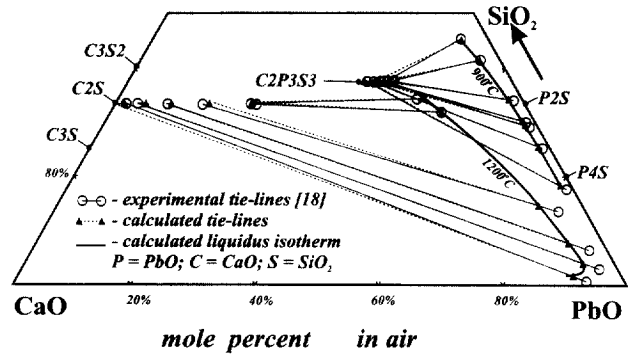


Fig. 10. Comparison of the experimental and calculated tie-lines between liquid and α'-dicalcium silicate at 1200°C and between liquid and lead calcium silicate Ca<sub>2</sub>Pb<sub>2</sub>Si<sub>3</sub>O<sub>11</sub> solid solution at 900°C.

The variation of the activities of PbO in PbO-CaO-SiO<sub>2</sub> liquid solutions at 1000°C, 1100°C and 1200°C as a function of composition is presented in Fig. 9.

The calculations also well reproduce the solid solubility data. Comparison of the experimental [6, 18] and calculated tie-lines between liquid and α'-dicalcium silicate at 1200°C and between liquid and lead calcium silicate Ca<sub>2</sub>Pb<sub>2</sub>Si<sub>3</sub>O<sub>11</sub> solid solution at 900°C is shown in Fig. 10.

From this set of thermodynamic parameters, all thermodynamic properties can be calculated including the activities of all components present in the system. Extrapolation into multi-component systems can be conducted provided other sub-ternary systems are also reviewed and optimised using the procedures described in this paper.

CONCLUSIONS

An initial evaluation of the thermodynamic data and phase diagrams currently available for the CaO-Pb-O and PbO-CaO-

SiO<sub>2</sub> systems was conducted. It was demonstrated that previous information was not thermodynamically consistent. To resolve these discrepancies further experimental work was carried out to determine phase relations at the liquidus.

From experimental data provided from the present research program [6, 18] the thermodynamic properties in the ternary system have been re-optimised, with the quasichemical model being used for the liquid phase, such that agreement between the experimental and calculated liquidus is within  $\pm 15$  K at a given composition when the liquidus is relatively flat and  $\pm 1$  mol% at a given temperature when the liquidus is steep. The binary and ternary thermodynamic parameters which have been derived from this study allow not only the construction of the liquidus but also the calculation of all thermodynamic properties including activities of components as a function of temperature and composition.

These results were used at further stages of the program to develop a self-consistent database for the prediction of phase relations and thermodynamic properties of the six-component system PbO-ZnO-SiO<sub>2</sub>-CaO-FeO-Fe<sub>2</sub>O<sub>3</sub> which represents the major components of the lead and zinc smelting slags and sinters. The model will provide a tool to enable the thermodynamic properties and phase equilibria in these complex systems to be predicted accurately for a wide range of compositions. The characterisation and accurate modeling of this six-component system is of particular importance to a wide range of the lead and zinc smelting processes.

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