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Experimental Liquidus Study of the Binary PbO-CaO and Ternary PbO-CaO-SiO_2 Systems

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Abstract Phase equilibria of the binary PbO-CaO and ternary PbO-CaO-SiO_2 systems have been investigated at 870-1655 °C for oxide liquid in equilibrium with air and solid oxide phases: tridymite or cristobalite SiO_2, pseudowollastonite $CaSiO_3$, dicalcium silicate $(Ca,Pb)_2SiO_4$, tricalcium silicate $(Ca_{1-x}Pb_x)_3SiO_5$ ($x < 0.03$), new phase tricalcium-lead silicate $(Ca_{0.8}Pb_{0.2})_3SiO_5$ ($Ca_{12}Pb_3Si_5O_{25}$), lime CaO, and calcium plumbate Ca_2PbO_4, covering the ranges of concentrations not studied before. High-temperature equilibration on primary phase or inert metal (platinum, gold) substrates, followed by quenching and direct measurement of the Pb, Ca and Si concentrations in the phases with the electron probe x-ray microanalysis (EPMA) has been used to accurately characterize the system. Liquidus phase equilibrium data of the present authors for the PbO-CaO-SiO_2 system are essential to obtain a self-consistent set of parameters of thermodynamic models for all phases.

Keywords lead · lime · phase diagrams · silica · slags

1 Introduction

The present study of the PbO-CaO-SiO_2 system is a part of a wider research program aimed at characterization of phase equilibria and thermodynamic properties of the seven-component PbO-ZnO-FeO-Fe_2O_3-Cu_2O-CaO-SiO_2 gas-slag-solid-metal system for the zinc/lead/copper smelting industry using integrated experimental investigations and thermodynamic modelling. This overall research program has already been described in previous publications of the present authors.[1] Although the pure PbO-CaO-SiO_2 system itself may have limited value for industry, its study provides essential fundamental information for creating an accurate thermodynamic database, as its components combined normally constitute more than half of lead–zinc sinters and slags by molar ratio.

2 Literature Review

2.1 The Pb-Ca-O System

The studies available in literature[2–6] are reviewed in the previous assessment by Jak et al.[7,8] The only stable compound, calcium plumbate Ca_2PbO_4 ($2CaO \cdot PbO_2$), contains lead in highest oxidation state (Pb^{4+}) and therefore its stability depends on $p(O_2)$. Ca_2PbO_4 was confirmed to be unstable at lower $p(O_2)$, < 0.001 atm.[7] Recent studies[9,10] confirm the previous data. No attempt to investigate the liquidus by microanalysis of quenched samples in this system has been found in literature, due to difficulty of quenching of the silica-free glasses, corrosive nature of such slags against platinum, and reactivity with water (usual quenching medium). Development of the phase equilibria study methodology by the authors, described below in detail, makes such investigation possible for the first time.

2.2 The PbO-CaO-SiO_2 System

A literature review and an extensive experimental study of solid–liquid phase equilibria of the "PbO"-CaO-SiO_2

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system in air has been performed by Jak.[7,8] Over one hundred experimental liquidus points over the composition range 0-66 mol.% SiO_2 and 0-42 mol.% CaO in tridymite and quartz SiO_2, wollastonite and pseudowollastonite $CaSiO_3$, dicalcium silicate $(Ca,Pb)_2SiO_4$, ganomalite $Pb_3(Ca,Pb)_2Si_3O_{11}$, calcium barysilite $Pb_8CaSi_6O_{21}$, margarosanite $Ca_2PbSi_3O_9$, and massicot PbO primary phase fields were obtained. Several solid phases reported in the early studies of the PbO-CaO-SiO_2 liquidus[11,12] (3CaO·PbO·SiO_2, 2CaO·3PbO·SiO_2, and solutions along the $PbSiO_3$-$CaSiO_3$ and Pb_2SiO_4-$CaSiO_3$ joins) were not confirmed by Jak.[7] Samples containing lime CaO and calcium plumbate Ca_2PbO_4 were not quenched since the technique of sufficiently fast quenching was not developed yet, so the corresponding samples gave information on the phase assemblage in general but not on compositions of slags. Dicalcium silicate and ganomalite were reported to have wide ranges of solid solutions in the system.

The previous experimental study[7] did not involve the high-temperature, low-PbO parts of the tridymite/cristobalite, pseudowollastonite, and dicalcium silicate primary phase fields. Present study, therefore, is focused on these in the temperature range 1473-1928 K (1200-1655 °C). Another area of the present study includes low-SiO_2 part of the liquid in equilibrium with calcium plumbate, lime, dicalcium silicate and tricalcium silicate.

The dataset[7] has been acquired while the information about systematic deviations of JEOL 8200 EPMA ZAF correction for the PbO-SiO_2[13,14] and PbO-CaO systems was not clearly available yet. For certain slag compositions, these deviations reach 1.5 mol.% overestimation of SiO_2 concentrations. Therefore, an additional purpose of selected experiments for the PbO-CaO-SiO_2 liquidus in the current study is to verify the applicability of the correction to the data measured 25 years ago[7] with the same instrument and at virtually the same conditions, so that the currently accepted correction technique can be applied for the whole dataset, including previous results.[7]

3 Experimental Part

The experimental procedure and apparatus have been described in detail in previous publications by PYROSEARCH.[1,15–17] Initial mixtures were made by mixing high-purity powders of $CaCO_3$ (99.9 wt.% purity), PbO (99.9 wt.% purity), SiO_2 (99.9 wt.% purity), supplied by Alfa Aesar, MA, USA.

Three types of substrates were used for equilibration, depending on the conditions:

1. Pt foil envelopes or wires (> 99.9% purity, 0.05 mm thickness, provided by Johnson Matthew, Australia) were used for the slags in the primary phase fields of pseudowollastonite and dicalcium silicate at 1553-1708 K (1280-1435 °C), cristobalite at 1903-1928 K (1630-1655 °C), and lime at 1373-1573 K (1100-1300 °C).
2. Au foil envelopes (99.99% purity, 0.127 mm thickness, provided by Sigma Aldrich, Australia) were used for the low-SiO_2 PbO-CaO-SiO_2 slag in equilibrium with calcium plumbate and other solids at 1143-1273 K (870-1000 °C).
3. SiO_2 open crucibles (prepared from ampoule sealed by melting with hydrogen–oxygen torch and then with a small hole drilled at the top, to reduce PbO loss due to evaporation and accidental contamination from dust in the furnace) were used for the PbO-CaO-SiO_2 slags in equilibrium with tridymite and cristobalite at 1473-1743 K (1200-1470 °C).

An additional measure to reduce the evaporation of PbO from the samples and to achieve equilibrium was preparation of the PbO-SiO_2 (60 mol.% SiO_2) master-slag by heating the oxide mixture in Pt crucibles at 1173 K (900 °C). The obtained glassy slag was quenched and ground to fine powder in an agate mortar.

The technique of equilibration experiments, quenching, sample preparation, and parameters of electron probe x-ray microanalysis (JEOL 8200L EPMA; Japan Electron Optics Ltd., Tokyo, Japan) is similar to Ref 1. The sample was suspended in the hot zone of the furnace on a support wire made of Kanthal [0.7 or 1-mm diameter, for $T < 1753$ K (1480 °C)] or platinum–rhodium alloy [0.5-mm diameter, for $T > 1753$ K (1480 °C)]. Samples were pre-melted for short time (15-60 min, see Table 1) at 10-50 K above the equilibration temperature, to form a homogeneous slag. This was followed by equilibration at the final target temperature and atmosphere condition for the required time (from 0.75 to 5 h).

Preliminary FactSage calculation[8] showed that if a bulk composition is selected close to the "PbO"-CaO binary system (74 mol.% PbO, 24% CaO and 2% SiO_2), the liquid phase at 1143-1573 K (870-1300 °C) will contain very low SiO_2 concentrations (~ 0.1 mol.%). Most SiO_2 will form a separate solid phase such as $(Ca,Pb)_2SiO_4$, and the equilibrium of two essentially SiO_2-free phases (liquid and lime or Ca_2PbO_4) will not be affected by the SiO_2-containing phase. Therefore, instead of studying the pure "PbO"-CaO binary system, low-SiO_2 bulk compositions are prepared in the present study, since it allows to obtain additional information on the first SiO_2-containing phase forming at minor addition of SiO_2 to the "PbO"-CaO binary. The highest temperature sample in the PbO-CaO(-low SiO_2) system at 1573 K (1300 °C) was done without premelt and for 20 min only; even then, the evaporation

Table 1 Experimental points on the liquidus surface with compositions of phases in the "PbO"-CaO-SiO_2 system in air

Substrate	Premelt T, °C	Final T, °C	Time, h*	Phase	Corrected, mol.%		
					SiO_2	"PbO"	CaO
Tridymite/cristobalite SiO_2 liquidus							
SiO_2 amp + hole	1350	1300	0.5 + 3	Liquid	64.4	15.8	19.8
				Tridymite	99.96	0.02	0.02
SiO_2 amp + hole	No	1400	2	Liquid	66.9	15.1	18.1
				Tridymite	99.97	0.02	0.02
SiO_2 amp + hole	No	1470	2	Liquid	69.7	13.7	16.6
				Cristobalite	99.95	0.02	0.03
Pt foil	No	1630	1	Liquid	87.6	6.9	5.5
				Cristobalite	99.89	0.01	0.10
Pt foil	No	1655	0.5	Liquid	83.7	5.8	10.5
				Cristobalite	99.97	0.00	0.03
Tridymite SiO_2 + pseudowollastonite $CaSiO_3$ boundary							
SiO_2 amp + hole	1300	1200	0.5 + 5	Liquid	63.7	21.0	15.3
				Tridymite	99.94	0.01	0.05
				Ps-wollastonite	50.1	0.59	49.3
SiO_2 amp + hole	1325	1250	0.5 + 18	Liquid	64.1	19.1	16.8
				Tridymite	99.96	0.02	0.02
				Ps-wollastonite	50.0	0.57	49.4
SiO_2 amp + hole	No	1350	3	Liquid	63.6	9.7	26.7
				Tridymite	99.88	0.01	0.12
				Ps-wollastonite	50.0	0.26	49.8
Pseudowollastonite $CaSiO_3$ liquidus							
Pt foil	1350	1300	0.25 + 3	Liquid	57.5	19.6	22.9
				Ps-wollastonite	50.0	0.53	49.5
Pt foil	1320	1300	0.25 + 1	Liquid	41.2	26.7	32.1
				Ps-wollastonite	49.9	0.41	49.7
Pt foil	No	1370	1	Liquid	42.7	17.1	40.2
				Ps-wollastonite	49.7	0.30	50.0
Pt foil	No	1380	1.5	Liquid	57.2	12.7	30.1
				Ps-wollastonite	49.6	0.32	50.0
Pt foil	No	1380	1.5	Liquid	57.8	12.0	30.2
				Ps-wollastonite	49.6	0.32	50.0
Pt foil	No	1380	1.5	Liquid	60.3	9.3	30.4
				Ps-wollastonite	49.6	0.32	50.0
Pt foil	No	1380	1.5	Liquid	62.2	7.6	30.2
				Ps-wollastonite	49.6	0.32	50.0
Pt foil	No	1380	1.5	Liquid	63.3	6.5	30.2
				Ps-wollastonite	49.6	0.32	50.0
Pseudowollastonite $CaSiO_3$ + dicalcium silicate $(Ca,Pb)_2SiO_4$ boundary							
Pt foil	No	1280	0.5	Liquid	40.2	28.4	31.4
				Ps-wollastonite	50.0	0.39	49.6
				$(Ca,Pb)_2SiO_4$	33.4	17.2	49.4
Pt foil	No	1350	0.5	Liquid	41.8	16.5	41.7
				Ps-wollastonite	49.8	0.29	49.9
				$(Ca,Pb)_2SiO_4$	33.3	11.5	55.2
Pt foil	No	1425	1	Liquid	43.4	5.1	51.5
				Ps-wollastonite	50.2	0.11	49.7

Table 1 continued

Substrate	Premelt T, °C	Final T, °C	Time, h*	Phase	Corrected, mol.%		
					SiO_2	“PbO”	CaO
			$(Ca,Pb)_2SiO_4$	33.5	4.2	62.3	
Pt foil	No	1435	1	Liquid	43.0	3.6	53.3
				Ps-wollastonite	49.3	0.09	50.6
				$(Ca,Pb)_2SiO_4$	33.5	3.0	63.5
Calcium plumbate Ca_2PbO_4 + tricalcium-lead silicate $(Ca_{0.8}Pb_{0.2})_3SiO_5$ boundary							
Au foil	1010	870	0.2 + 2	Liquid	0.01	94.3	5.7
				Ca_2PbO_4	0.00	33.2	66.8
				$(Ca_{0.8}Pb_{0.2})_3SiO_5$	24.5	15.7	59.8
Au foil	1030	910	0.2 + 1	Liquid	0.00	90.3	9.7
				Ca_2PbO_4	0.00	33.3	66.7
				$(Ca_{0.8}Pb_{0.2})_3SiO_5$	24.9	15.3	59.8
Au foil	1020	950	0.2 + 0.5	Liquid	0.00	88.9	11.1
				Ca_2PbO_4	0.00	33.1	66.9
				$(Ca_{0.8}Pb_{0.2})_3SiO_5$	25.2	15.4	59.4
Lime CaO + tricalcium-lead silicate $(Ca_{0.8}Pb_{0.2})_3SiO_5$ boundary							
Au foil	1020	1000	0.2 + 0.5	Liquid	0.00	87.3	12.7
				CaO	0.00	0.49	99.51
				$(Ca_{0.8}Pb_{0.2})_3SiO_5$	25.1	15.4	59.6
Lime CaO + dicalcium silicate $(Ca,Pb)_2SiO_4$ boundary							
Pt foil	1130	1100	0.2 + 0.7	Liquid	0.00	86.0	14.0
				CaO	0.00	0.63	99.37
				$(Ca,Pb)_2SiO_4$	n.a.		
Pt foil	1220	1200	0.1 + 0.3	Liquid	0.00	84.7	15.3
				CaO	0.00	0.51	99.49
				$(Ca,Pb)_2SiO_4$	33.4	0.34	66.3
Lime CaO + tricalcium silicate $(Ca,Pb)_3SiO_5$ boundary							
Pt foil	No	1250	0.25	Liquid	0.00	83.8	16.2
				CaO	0.00	0.69	99.31
				$(Ca,Pb)_3SiO_5$	24.9	2.2	72.9
Pt foil	No	1300	0.25	Liquid	0.08	83.4	16.5
				CaO	0.00	0.83	99.17
				$(Ca,Pb)_3SiO_5$	25.1	2.1	72.7

*Time is presented as (preheat time) + (equilibration time)

loss of PbO was significant, that delineates the upper temperature limit of silica-free PbO-rich slags to be investigated with the current technique.

Wollastonite ($CaSiO_3$) (supplied by Charles M. Taylor Co., Stanford, CA) and K-456 lead silicate glass (71 wt. pct. PbO, supplied by NIST) standards were used for Si, Pb and Ca calibration of the EPMA. $PbSiO_3$ and Pb_2SiO_4 (obtained as a part of experimental study of the PbO-SiO_2 system[14]), and Ca_2PbO_4 were used as additional reference points in the PbO-SiO_2 and Ca-Pb-O systems. Additional correction was developed and applied for the values after the JEOL 8200 EPMA ZAF correction:

$$x(\mathrm{SiO_2})^{\mathrm{corrected}} = x(\mathrm{SiO_2}) - x(\mathrm{SiO_2}) \cdot x(\mathrm{PbO}) \left(-0.0129 - 0.0206 \cdot x(\mathrm{SiO_2}) + 0.421 \cdot x(\mathrm{SiO_2})^2 - 0.4066 \cdot x(\mathrm{SiO_2})^3\right), \tag{Eq 1}$$

$$x(\mathrm{CaO})^{\mathrm{corrected}} = x(\mathrm{CaO}) - 0.0192 \cdot x(\mathrm{PbO}) \cdot x(\mathrm{CaO}), \tag{Eq 2}$$

$$x(\mathrm{PbO})^{\mathrm{corrected}} = 1 - x(\mathrm{SiO_2})^{\mathrm{corrected}} - x(\mathrm{CaO})^{\mathrm{corrected}}. \tag{Eq 3}$$

4 Results and Discussion

Examples of micrographs of quenched PbO-CaO-SiO_2 samples are given in Fig. 1(a), (b), (c), and (d).

The experimental results are reported in Table 1 and compared to the optimized thermodynamic model predictions[18] for the binary "PbO"-CaO and ternary "PbO"-CaO-SiO_2 liquidus in Fig. 2, 3, and 4. As there is one phase (Ca_2PbO_4) based on PbO_2 instead of PbO, the diagrams are strictly projections from the oxygen corner onto the "PbO"-CaO line and "PbO"-CaO-SiO_2 plane, respectively.

The results of the present work for the "PbO"-CaO system agree with the most recent data[10] for invariant reactions: eutectic Liquid + O_2 (0.21 atm) = PbO + Ca_2PbO_4 at 1129 ± 2 K (856 ± 2 °C) and peritectic Liquid + CaO + O_2 (0.21 atm) = Ca_2PbO_4 at 1258 ± 5 K (985 ± 5 °C).

Although the FactSage model[18] predicts a significant range of two immiscible liquids over the cristobalite primary phase field, the experiment at the highest temperature, 1928 K (1655 °C) and 6 mol.% PbO still gave single liquid in equilibrium with cristobalite. Therefore, the immiscibility range is much more narrow than expected, i.e. less than 6 mol.% PbO addition suppresses the immiscibility in the CaO-SiO_2 system.

Four solid phases in the PbO-CaO-SiO_2 system show significant ranges of solid solutions:

$$C_2S = (Ca_{1-x}Pb_x)_2SiO_4,\ 0 < x < 0.43;$$

$$\text{Ganomalite} = Pb_3(Ca_{1-x}Pb_x)_2Si_3O_9,\ 0.01 < x < 0.39;$$

$$C_3S = (Ca_{1-x}Pb_x)_3SiO_5,\ 0 < x < 0.03;$$

$$\text{Wollastonite and pseudowollastonite} = (Ca_{1-x}Pb_x)SiO_3,\ 0 < x < 0.04.$$

Among those, C_3S is identified as a solution stable in equilibrium with liquid above ~ 1225 °C in present study for the first time. Analysis of the dataset[7] shows no difference in solubility behavior of PbO in wollastonite and pseudowollastonite.

A new phase $(Ca_{0.8}Pb_{0.2})_3SiO_5$ or $Ca_{12}Pb_3Si_5O_{25}$ has been discovered. Its primary phase field occupies a narrow range between the Ca_2PbO_4 and C_2S fields at 1143-1273 K (870-1000 °C) at low SiO_2 concentrations. It does not form a continuous solution with C_3S, as the latter dissolves no more than 3 mol.% PbO (compared to 15% in

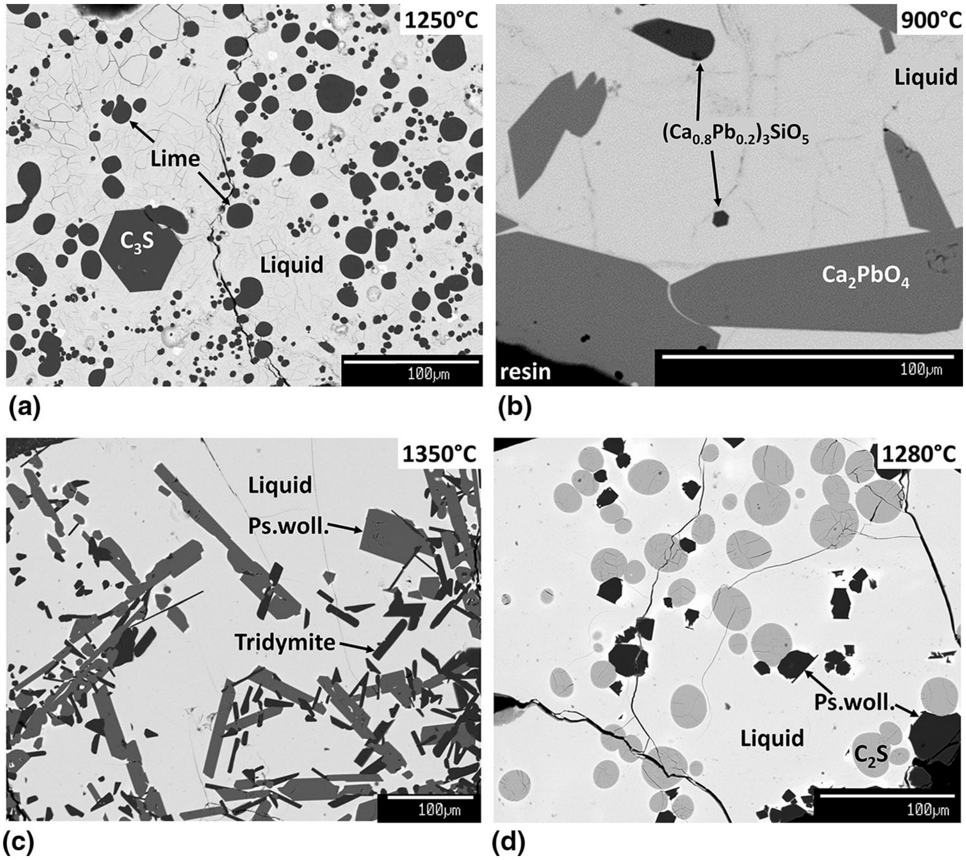


Fig. 1 Microstructures of quenched samples of the "PbO"-CaO-SiO_2 system in air. (a) Liquid + lime(CaO) + Ca3SiO5, (b) liquid + Ca2PbO4 + (Ca0.8Pb0.2)3SiO5, (c) liquid + pseudowollastonite + tridymite, (d) liquid + pseudowollastonite + (Ca,Pb)2SiO4

Fig. 2 “PbO”-CaO phase diagram in air (high-PbO part) with present experimental points at 1143-1573 K (870-1300 °C), compared to a recent model[18]

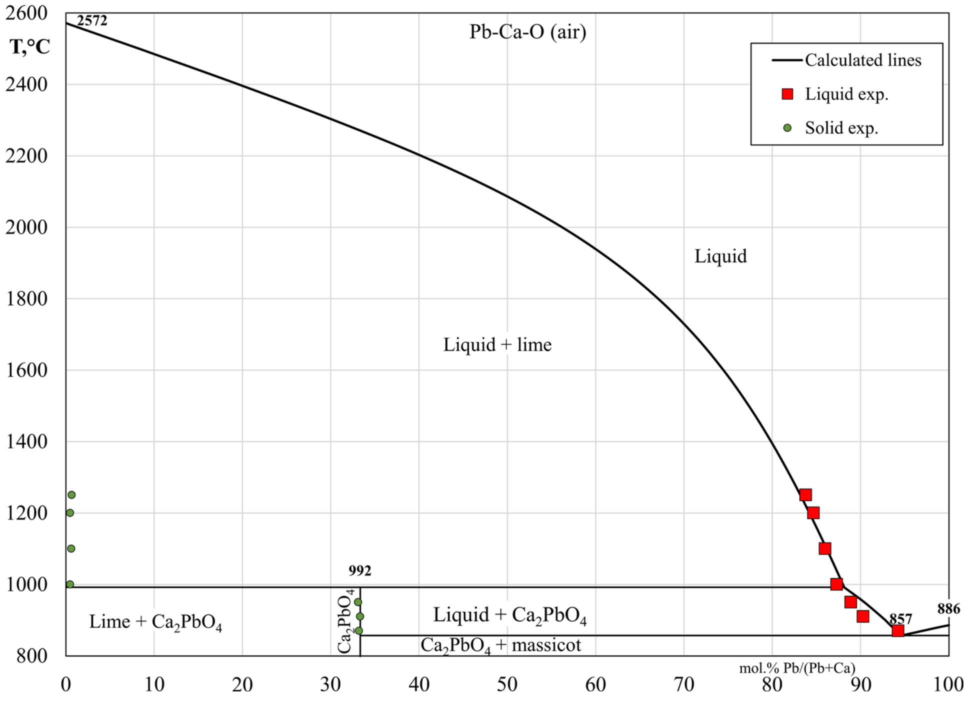
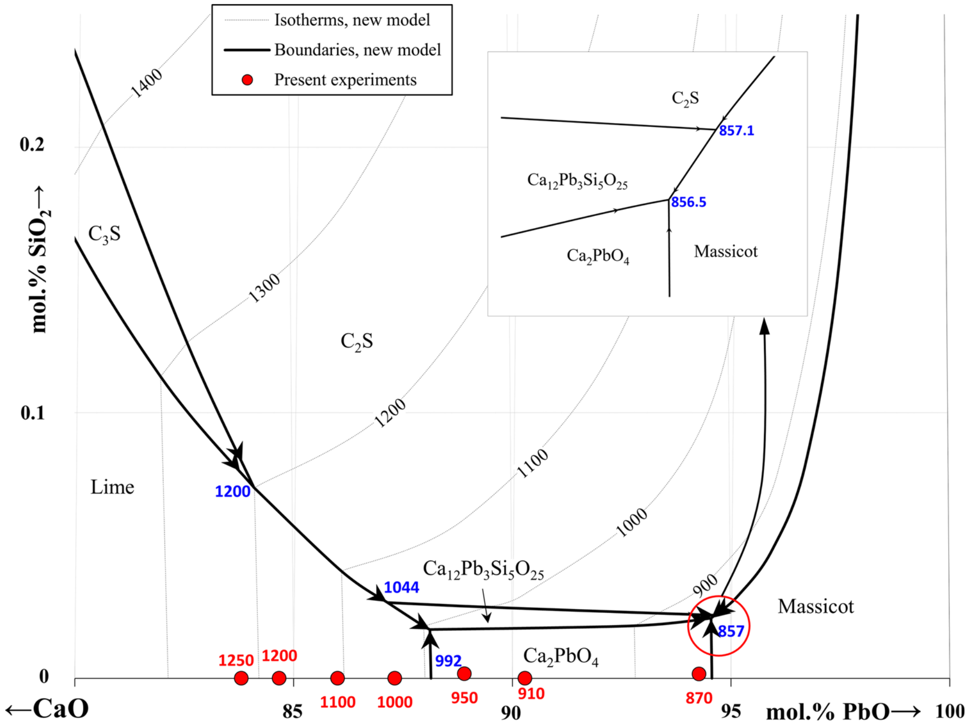


Fig. 3 “PbO”-CaO-SiO2 phase diagram in air (low-SiO2, high-PbO part) with present experimental points at 1143-1573 K (870-1300 °C), compared to a recent model.[18] Note that Pb is present as PbO in slag and all solid phases except Ca2PbO4 (2CaO·PbO2)



$Ca_{12}Pb_3Si_5O_{25}$), and is stable only above ~ 1225 °C. In the intermediate range at 1323-1473 K (1050-1200 °C) the low-SiO_2 liquid is in equilibrium with lime and C_2S. In all low-SiO_2 experiments at 870-1300 °C, the concentration of SiO_2 in liquid, lime and Ca_2PbO_4 was below the EPMA uncertainty limit (0.1 mol.%), confirming the initial FactSage prediction and allowing to plot these points on the “PbO”-CaO binary diagram.

Attempts to reach the primary phase of rankinite were not successful, since at 1708 K (1435 °C) liquid was still observed in equilibrium with pseudowollastonite and C_2S. This indicates that addition of PbO lowers stability of

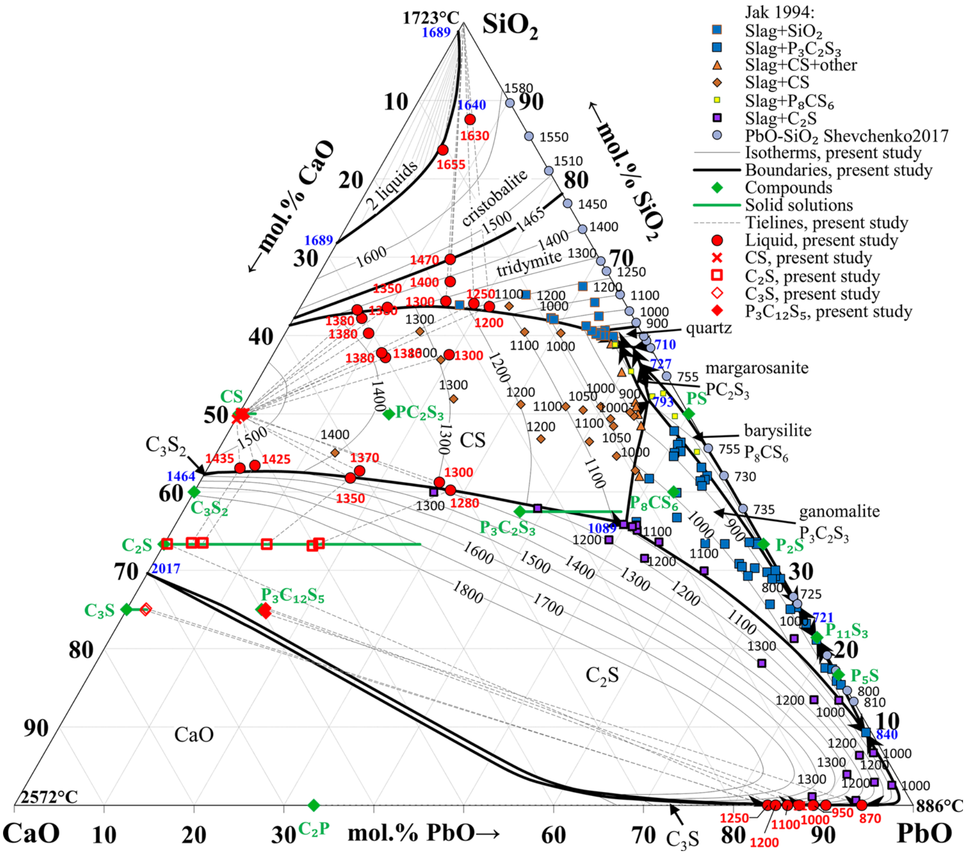


Fig. 4 Liquidus projection of the "PbO"-CaO-SiO2 system in air, with data[7] (recalculated using newly established correction for EPMA measurement) and current experimental results. Isotherms and boundary lines outside the experimentally studied range of compositions are calculated using a recent optimised thermodynamic model.[18] Note that Pb is present as PbO in slag and all solid phases except Ca2PbO4 (2CaO·PbO2)

rankinite compared to pseudowollastonite and C$_2$S, and the primary phase field of rankinite is limited by a narrow and short range close to the CaO-SiO$_2$ binary.

5 Conclusions

New phase equilibria information in the "PbO"-CaO and the "PbO"-CaO-SiO$_2$ systems in air has been obtained. The studied range of temperatures covered 1173-1928 K (870-1655 °C), and included the equilibria of slag with one or two crystalline phases: tridymite, cristobalite SiO$_2$, pseudowollastonite (Ca,Pb)SiO$_3$, dicalcium silicate (Ca,Pb)$_2$SiO$_4$, tricalcium silicate (Ca,Pb)$_3$SiO$_5$, lime CaO, calcium plumbate Ca$_2$PbO$_4$, and a new phase (Ca$_{0.8}$Pb$_{0.2}$)$_3$SiO$_5$. This is an important update of the previous study of this system[7] that allows to create a more accurate thermodynamic model of this system as well as a foundation for the thermodynamic database of the multicomponent system Pb-Zn-Fe-Cu-Si-Ca-Al-Mg-O, essential for the lead smelting and recycling industries.

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