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Effect of CaO/SiO_2 and Fe/SiO_2 ratios on phase equilibria in $PbO-ZnO-CaO-SiO_2-$“Fe_2O_3” system in air

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Abstract: Experimental studies on phase equilibria and liquidus temperature in the $PbO-ZnO-CaO-SiO_2-$“Fe_2O_3” system, with the mass ratios of CaO/SiO_2=1−1.6 and Fe/SiO_2= 1.3−1.7, and 40% PbO and 8% ZnO, were carried out between 1273 and 1573 K. Slags were equilibrated at 1273 to 1573 K and cooled rapidly by quenching. The XRD and SEM−EDS results showed that the slag compositions are in the franklinite primary phase field. Calcium and lead silicates are formed between 1373 and 1473 K. The Ca/Pb silicate and magnetoplumbite phases are partially formed by an incongruent reaction. The experimental and thermodynamical results showed that the liquidus increased by increasing CaO/SiO_2 mass ratio and decreasing Fe/SiO_2 mass ratio.

Key words: lead slags; phase equilibria; liquidus temperature

1 Introduction

The primary production of lead and zinc metal is mainly undertaken in blast furnaces, which operate in a wide range of temperature. HABASHI [1] showed that the reduction of lead oxide in this furnace produces slags in the multicomponent system $PbO-ZnO-CaO-SiO_2-$“Fe_2O_3”. This system represents the major components of lead/zinc smelting slags in oxidizing conditions. The oxidation roasting of lead/zinc sulfide concentrates requires the fluxes addition of SiO_2 and CaO to form a mixture metallurgically balanced. The CaO/SiO_2 and Fe/SiO_2 ratios must be used according to the composition of lead concentrates. The information of the liquidus temperatures and the mineralogical species formed is useful to optimize the industrial practice.

Experimental studies on phase equilibria in the $PbO-ZnO-CaO-SiO_2-$“Fe_2O_3” system in air using different CaO/SiO_2 ratios were carried out by JAK et al [2]. They studied a slag system with constant basicity CaO/SiO_2 ratio 0.933 and two different $PbO/(CaO+SiO_2)$ ratios (2.0 and 3.2). They used a small quantity of synthetic oxide mixture, pelletized and equilibrated at temperature below the liquidus so that two or more phases were formed. Then the samples were cooled rapidly by quenching. The result was that the phases presented at high temperature and their compositions were retained to room temperature. Their results showed that the liquidus in the pseudoternary $ZnO-$“Fe_2O_3”$-(PbO+CaO+SiO_2)$ system contained primary phase fields of spinel ($Zn_xFe_{3-x}O_{4+y}$), zincite ($Zn_xFe_{1-x}O$), hematite (Fe_2O_3), melilite ($Pb_vCa_{2-v}Zn_wFe_{1-w}Si_2O_7$), magneto-plumbite ($PbFe_{12}O_{19}$) and calcium and lead silicates.

ETTLER et al [3,4] studied the lead and zinc slags produced 100−150 years ago and found that the major constituents were clinopyroxene, melilite, olivine and spinel. ZHAO et al [5] carried out experimental studies in the $ZnO-$“FeO”$-Al_2O_3-CaO-SiO_2-MgO$ system in equilibrium with metallic iron. Their results showed that wustite (Fe,Zn)O and spinel $(Fe,Zn)O\cdot(Al,Fe)_2O_3$ were the major phases. JAK and HAYES [6] carried out experimental studies on the $PbO-ZnO-$“Fe_2O_3”$-CaO-SiO_2$ system in air to characterize the phase relations and reported the liquidus pseudoternary section for slags with mass ratio of CaO/SiO_2 being 0.35 and $PbO/(CaO+SiO_2)$

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being 5.0. JAK and HAYES [7] studied the same system with the ratios of CaO/SiO_2 being 0.1 and 0.6, and $PbO/(CaO+SiO_2)$ being 4.3 and 6.2.

The mineralogical species formed in the lead blast furnace depend on the compositions of the original ores and the plant practice adopted. Thus, there exist significant variations in the microstructures in sintered materials and the solid phases formed from the slag. Systems with high concentrations of $PbO-CaO-SiO_2$ produce a glassy slag phase with a low melting point. The presence of ZnO promotes the formation of melilite phase with platelike crystals which support the sintering and prevent from collapse.

The present study is conducted to provide information on the liquidus temperature and the mineralogical species formed in the slags of the $PbO-ZnO-CaO-SiO_2-$"Fe_2O_3" system with different CaO/SiO_2 and Fe/SiO_2 mass ratios at temperature range from 1273 to 1573 K. A thermodynamic analysis is carried out with the software FACTSage developed by THOMPSON et al [8], to estimate the liquidus temperature of the slags as well as the primary solid phases formed in this system.

2 Experimental

The experimental design was based on the sinter compositions used in Mexican industrial blast furnaces, which includes the $PbO-ZnO-CaO-SiO_2-$"Fe_2O_3" slag system with CaO/SiO_2 mass ratio from 1.0 to 1.6, Fe/SiO_2 mass ratio from 1.3 to 1.7 and 40% (mass fraction) PbO and 8% ZnO. Pure oxide powders (99.5% purity) were used as starting materials to prepare the synthetic slags.

The major difficulty in the experimental procedure was the high vapor pressure of lead species. In order to reduce this problem, master slags with the required amounts of PbO and SiO_2 were prepared. The master slags were then mixed with appropriate addition of the other pure oxide powders (ZnO, CaO and Fe_2O_3) to prepare the final mixtures compositions given in Table 1.

20 g of each slag sample was homogenized and equilibrated in platinum crucible in air in two steps. In the first step the samples were melted at 1573 K for 4 h. In the second step the samples were cooled down from 1573 K to a given temperature (1473, 1373 and 1273 K) and kept at high temperature for 4 h in order to reach the equilibrium; then, the samples were quenched into ice water. The furnace temperature variation was controlled within ±3 K with an R-type thermocouple (Pt-Pt, 13%Rh). The estimated maximum lead oxide and zinc oxide losses during equilibration, using the X-ray Fluorescence technique, were 2.5% and 1.1%, respectively.

Table 1 Mixture compositions containing 40% PbO and 8% ZnO used for experiments (mass fraction)

Slag No.	CaO/SiO_2 mass ratio	Fe/SiO_2 mass ratio	Composition/%		
			CaO	SiO_2	Fe_2O_3
1	1.0	1.3	13.48	13.48	25.05
2	1.0	1.7	11.74	11.74	28.53
3	1.2	1.3	15.37	12.81	23.81
4	1.2	1.7	13.48	11.23	27.29
5	1.4	1.3	17.09	12.21	22.69
6	1.4	1.7	15.07	10.76	26.16
7	1.6	1.3	18.66	11.66	21.68
8	1.6	1.7	16.54	10.34	25.12

Samples of each slag were crushed into fine powders and characterized by X-ray diffraction (XRD Bruker D8 Focus) to determine the mineralogical species. The microstructural analysis was carried out by mounting and polishing the samples, then by examination using scanning electron microscopy coupled with an energy-dispersive spectra analyzer, FEI Quanta 600, EDAX EDS, with software GENESIS-MLA (Mineral liberation analysis) to determine the compositions of each phase. The mineral reference standards for EDS analysis were gold, silver, platinum, copper, quartz, galena, sphalerite, chalcopyrite, pyrite and wollastonite. The advantage of this experimental technique is that each experiment provides information on the compositions of the liquid at high temperature and the solid phases formed. The experimental procedure is shown in Fig. 1.

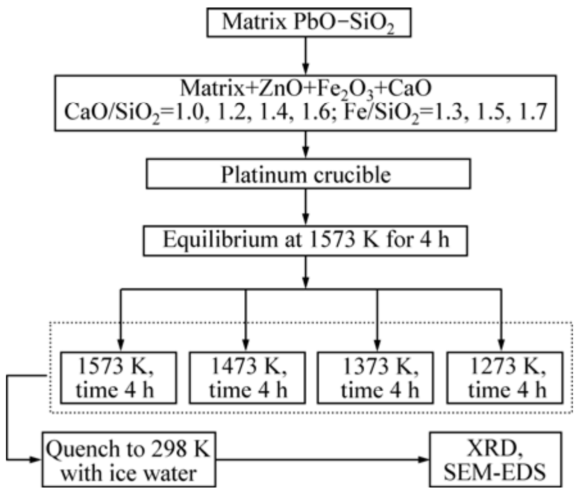


Fig. 1 Experimental procedure

The experimental conditions for the 8 slags were thermodynamically simulated using the software FACTSage (THOMPSON et al [8]) to estimate the liquidus temperature and the phases in equilibrium at high temperature.

3 Results and discussion

3.1 SEM-EDS microanalysis

The results of 32 quenching experiments are given in Table 2. Each phase composition given in this table is the average of up to three compositions measured at various locations within that phase. The results of the EDS microanalysis were compared with the EDS database of minerals, reported by REED [9], and the mineral phases were identified. The main solid phases obtained in the slags can be classified in to three types of compounds: 1) Spinel: $Zn_xFe_{3-x}O_{4+y}$; 2) Calcium and lead silicates: Ca_2SiO_4, Pb_5SiO_7, $Ca_2PbSi_3O_9$; 3) Magnetoplumbite: $PbFe_{12}O_{19}$.

No measurements of the ferric/ferrous ratio were performed in this study, thus iron is represented as ferric oxide for the purposes of describing the composition data.

Table 2 shows that the liquidus temperature is between 1473 K and 1573 K in all the slags and the spinel is the first phase to form during crystallization.

Table 2 Experimental result on samples with CaO/SiO_2 mass ratio of 1.0−1.6 and Fe/SiO_2 of 1.3−1.7

Slag No.	Temperature/K	Phases in equilibrium	Phase name	Phase composition (mass fraction)/%				
				Fe_2O_3	SiO_2	CaO	ZnO	PbO
1	1573	Liquid	Liquid	31.41	8.89	7.04	9.91	42.75
	1473	Liquid + Spinel	Liquid	25.17	10.06	8.95	6.75	49.07
			Spinel	67.86	0.88	0.74	26.99	3.53
	1373	Liquid + Spinel	Liquid	20.17	14.44	10.21	5.7	49.48
			Spinel	57.04	4.55	2.49	23.59	12.33
	1273	Liquid+ Spinel +Silicate	Liquid	10.46	12.06	9.23	0.58	67.67
			Silicate	11.35	19.6	17.12	0.66	51.27
			Spinel+Silicate	46.17	4.57	6.92	19.71	22.63
2	1573	Liquid	Liquid	33.85	8.42	3.84	10.42	43.47
	1473	Liquid + Spinel	Liquid	27.13	8.34	4.93	5.44	54.16
			Spinel	60.25	1.05	7.72	28.23	2.75
	1373	Liquid + Spinel	Liquid	27.05	9.92	5.94	3.95	53.14
			Spinel	68.47	0.73	0.43	29.89	0.48
	1273	Liquid + Spinel + Silicate	Liquid	18.1	6.97	1.65	1.62	71.66
			Spinel	59.60	7.66	4.48	26.28	1.98
			Silicate	2.03	47.68	44.58	0.0	5.71
3	1573	Liquid	Liquid	24.2	13.26	12.94	8.2	41.4
	1473	Liquid + Spinel	Liquid	24.41	14.73	15.37	7.08	38.41
			Spinel	69.56	0.14	0.5	29.8	0.0
	1373	Liquid + Spinel	Liquid	19.36	15.02	11.74	4.1	49.78
			Spinel	50.05	7.35	6.21	19.93	16.46
	1273	Liquid+Spinel +Silicate + $PbFe_{12}O_{19}$	Liquid	12.89	17.14	13.16	1.56	55.25
			Silicate	10.73	21.78	17.61	0.87	49.01
			Spinel+Silicate+ $PbFe_{12}O_{19}$	44.06	11.4	11.61	17.65	15.28
4	1573	Liquid	Liquid	28.3	12.32	14.0	8.5	36.88
	1473	Liquid + Spinel	Liquid	29.33	14.42	13.98	7.33	34.94
			Spinel	66.1	3.45	2.43	25.69	2.33
	1373	Liquid+Spinel +Silicate+ $PbFe_{12}O_{19}$	Liquid	23.04	16.35	11.85	3.92	44.84
			Spinel+Silicate+ $PbFe_{12}O_{19}$	46.73	11.99	12.97	18.0	10.31
	1273	Liquid+Spinel + Silicate+ $PbFe_{12}O_{19}$	Liquid	19.95	12.29	5.73	1.2	60.83
			Silicate	6.59	39.68	33.63	1.05	19.05
			Spinel+Silicate+ $PbFe_{12}O_{19}$	37.76	12.79	11.46	12.8	25.19

(To be continued)

(Continued)

Slag No.	Temperature/K	Phases in equilibrium	Phase name	Phase composition (mass fraction)/%				
				Fe_2O_3	SiO_2	CaO	ZnO	PbO
5	1573	Liquid	Liquid	25.0	11.95	14.12	9.54	39.39
	1473	Liquid+ Spinel	Liquid	26.09	10.86	12.18	9.27	41.6
			Spinel	47.85	10.35	13.32	21.14	7.34
	1373	Liquid + Spinel + Silicate	Liquid	16.19	10.23	2.52	3.48	67.58
			Spinel	46.83	8.96	14.77	20.8	8.64
			Silicate	6.95	18.84	27.4	0.98	45.83
	1273	Liquid + Spinel+ Silicate	Liquid	16.56	7.0	2.83	1.25	72.36
			Spinel	63.24	0.88	0.47	30.85	4.56
			Silicate	0.56	23.79	32.23	0.04	43.38
6	1573	Liquid	Liquid	30.06	9.98	12.14	9.57	38.25
	1473	Liquid + Spinel	Liquid	29.02	10.96	11.52	9.51	38.99
			Spinel	68.21	1.27	0.51	29.2	0.81
	1373	Liquid + Spinel+ Silicate	Liquid	20.29	8.08	4.8	1.61	65.22
			Spinel	60.42	5.25	9.12	21.25	3.96
			Silicate	0.67	25.29	42.91	0.0	31.13
	1273	Liquid + Spinel+ Silicate	Liquid	16.72	8.94	6.07	0.7	67.57
			Spinel	67.0	1.35	0.31	29.0	2.34
			Silicate	0.85	29.5	42.45	0.0	27.2
7	1573	Liquid	Liquid	29.57	12.98	16.04	9.37	32.04
	1473	Liquid + Spinel + Silicate	Liquid	24.34	15.45	18.34	7.92	33.95
			Spinel	64.4	1.55	3.07	29.69	1.29
			Silicate	1.23	34.22	55.74	1.09	7.72
	1373	Liquid + Spinel+ Silicate	Liquid	17.0	8.84	1.85	2.98	69.33
			Spinel	67.76	0.99	0.63	28.21	2.41
			Silicate	0.72	32.19	47.14	0.32	19.63
	1273	Liquid + Spinel+ Silicate	Liquid	12.22	3.39	0.85	1.39	82.15
			Silicate	2.09	27.73	36.99	0.62	32.57
			Spin+Silic	45.99	11.41	16.32	19.63	6.65
8	1573	Liquid	Liquid	26.02	12.4	15.79	9.02	36.77
	1473	Liquid + Spinel+ Silicate	Liquid	24.19	11.05	12.17	6.84	45.75
			Spinel	58.3	6.69	8.37	24.59	2.05
			Silicate	2.48	29.45	53.63	0.55	13.89
	1373	Liquid + Spinel+ Silicate	Liquid	22.36	6.47	7.54	1.92	61.71
			Spinel	61.23	1.11	0.84	22.22	14.6
			Silicate	0.68	28.84	49.04	0.0	21.44
	1273	Liquid + Spinel+ Silicate	Liquid	17.76	6.15	4.32	0.93	70.84
			Spinel	65.04	1.67	3.2	29.08	1.01
			Silicate	2.7	23.47	35.81	0.76	37.26

During cooling further calcium/lead silicates start to precipitate. Measurements of the spinel composition indicate that in air and in the range of temperatures investigated, this phase is close to franklinite composition ($ZnFe_2O_4$: 33.76% ZnO in mass fraction and 66.23% Fe_2O_3). The concentration results show that the liquid composition becomes rich in PbO as temperature is diminished from 1573 to 1273 K. There are also crystals observed in a combination of franklinite, calcium/lead silicates and magnetoplumbite. It is possible that in such crystals calcium/lead silicates and magnetoplumbite are formed as a result of an incongruent reaction between liquid and franklinite.

3.2 Microstructure

The microstructures of slags quenched at different temperatures for slag number 2 (CaO/SiO_2=1.0 and Fe/SiO_2=1.7) are shown in Fig. 2. It is observed that at 1573 K the slag is completely melted and the rapid cooling to room temperature produces a dendritic

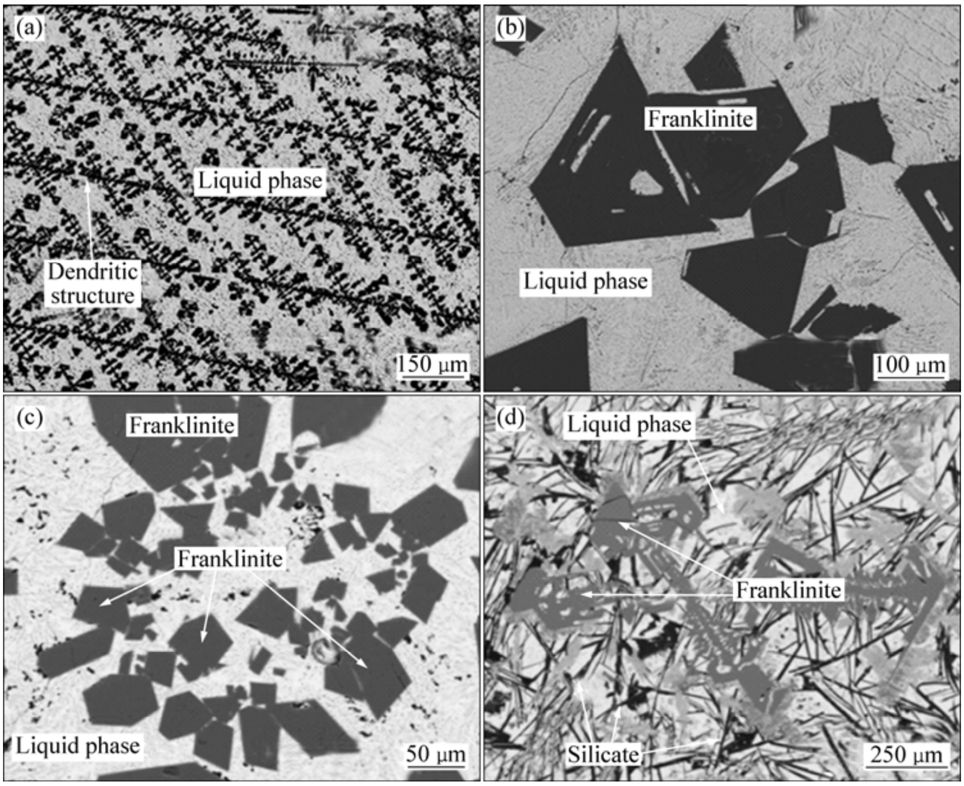


Fig. 2 Morphologies of slag samples with CaO/SiO_2 mass ratio of 1.0 and Fe/SiO_2 mass ratio of 1.7 quenched from different temperatures: (a) 1573 K; (b) 1473 K; (c) 1373 K; (d) 1273 K

structure. The microanalysis carried out in the arms of dendrites showed zinc and iron segregation which produced precipitation of spinel phase at low temperature.

The micrographs of the samples equilibrated at 1373 K and 1473 K shows dark angular crystals of the spinel phase. The present experiments indicate that the composition of spinel in equilibrium with the liquid phase approaches the franklinite composition ($ZnFe_2O_4$) in air in the range of temperatures investigated. The sample equilibrated at 1273 K shows spinel crystal together with elongated crystals which, according to their microanalysis, correspond to calcium and lead silicates. Figure 2 also shows white regions that correspond to liquid slag in equilibrium with the solid phases at high temperature. The microstructures shown in Fig. 2 illustrate the crystallization sequences that can take in the real lead slags.

Figure 3 shows the X-ray mapping images of Pb, Ca, Si, Fe and Zn elements for the sample number 2 quenched from 1273 K. The X-ray mapping image shows a contrast due to element concentration gradient. For example, in the X-ray image for calcium, the bright areas correspond to calcium-rich zones and the dark areas correspond to calcium-poor zones. This figure shows that the irregular polygons mainly contain iron and zinc; thus, it is believed that these correspond to the spinel-type phase ($ZnFe_2O_4$). The X-ray mapping shows that the elongated crystals contain silicon and calcium and correspond to calcium silicates. It is also observed that the main amount of lead is present in the white zone in this sample which corresponds to the liquid phase at 1273 K.

Figure 4 shows the microstructures of sample 3 (mass ratio of CaO/SiO_2=1.2 and Fe/SiO_2=1.3). The dendritic structure in Fig. 4(a) shows again that at 1573 K the slag was completely liquid. The sample equilibrated at 1473 K shows that spinel is the first solid to form. There are crystals with combined phases, franklinite, silicates and magnetoplumbite, as shown in Fig. 4(d) and reported in Table 2.

Figure 5 shows the evidence that Ca/Pb silicates and magnetoplumbite are partially formed as a result of an incongruent reaction between liquid and franklinite. An incongruent reaction can be carried out when a pre-existing solid is consumed or resorbed in the process. Figure 5(a) shows franklinite crystals before the incongruent reaction, for a slag with mass ratio of CaO/SiO_2=1.0 and Fe/SiO_2=1.7, equilibrated at 1373 K. Figure 5(b) shows a franklinite crystal which has been partially transformed in a slag with the same global composition and equilibrated at 1273 K.

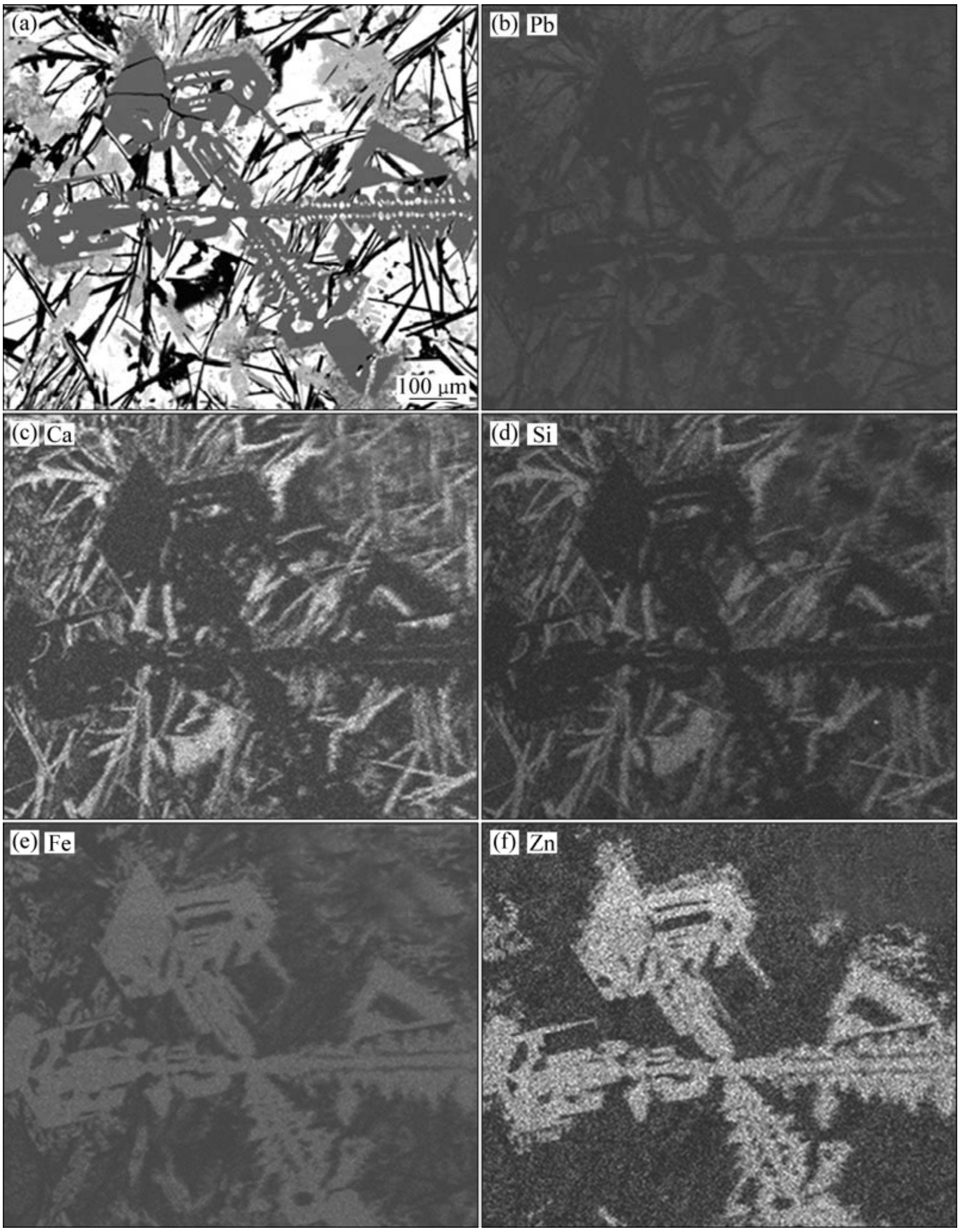


Fig. 3 X-ray mapping images of Pb, Ca, Si, Fe and Zn elements for slag with mass ratio of CaO/SiO_2 being 1.0 and Fe/SiO_2 being 1.7 quenched from 1273 K

Figure 6 shows the SEM-EDS analysis of a franklinite crystal which has been partially transformed for a slag with mass ratio of CaO/SiO_2=1.0 and Fe/SiO_2=1.7. These EDS results confirm that the former crystals correspond to franklinite $ZnFe_2O_4$ (white zones), while the gray zones mainly correspond to a combination of Ca/Pb silicate (obtained from CaO, SiO_2 and PbO) and magnetoplumbite (obtained from Fe_2O_3 and PbO).

JAK et al [2] reported the liquidus surface for the ZnO−"Fe_2O_3"−(PbO+CaO+SiO_2) system projected onto a pseudo-ternary diagram with the mass ratios of CaO/SiO_2 being 0.933 and PbO/(CaO+SiO_2) being 2.0. This pseudo-ternary diagram shows that there exists an incongruent reaction according to the following expression:

Liquid + Franklinite = Magnetoplumbite + Ca/Pb silicate

The slags shown in Figs. 5 and 6 have the CaO/SiO_2 mass ratio of 1.0 and PbO/(CaO+SiO_2) of 1.7, which are close to those values of the slags reported by JAK et al [2]. Then, it is possible that Ca/Pb silicates and magnetoplumbite are produced in the former franklinite crystals by the above mentioned incongruent reaction.

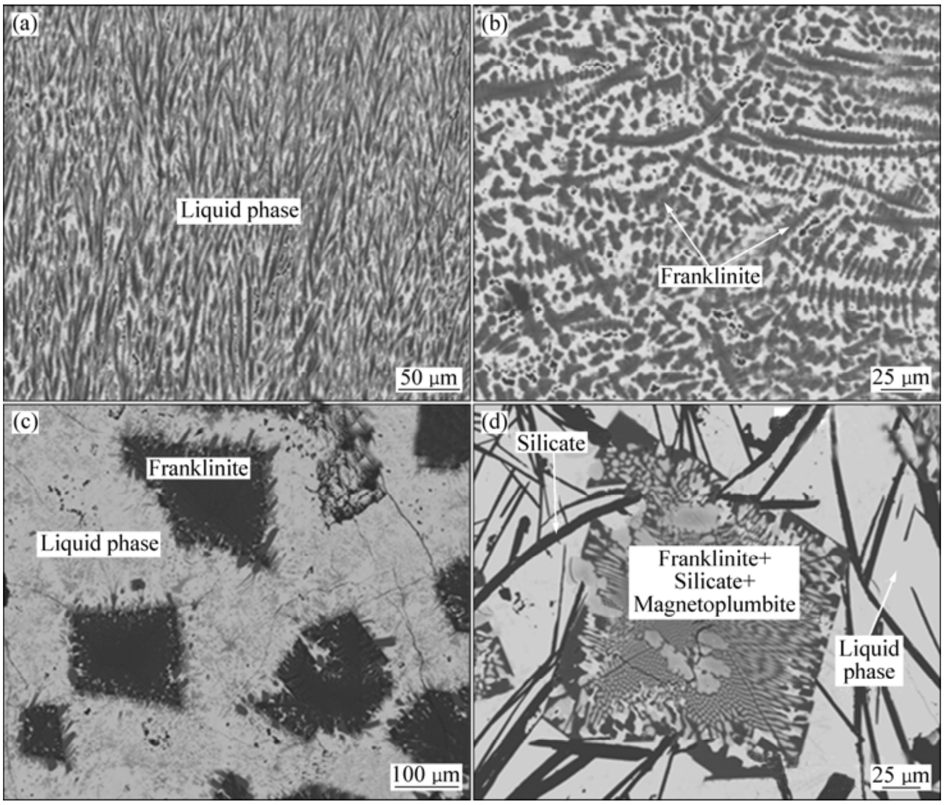


Fig. 4 Morphologies of slags with mass ratio of CaO/SiO_2 being 1.2 and Fe/SiO_2 being 1.3 quenched from different temperatures: (a) 1573 K; (b) 1473 K; (c) 1373 K; (d) 1273 K

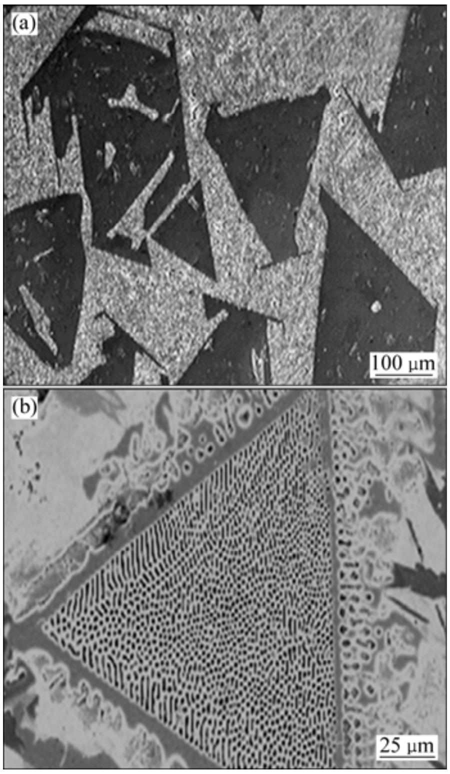
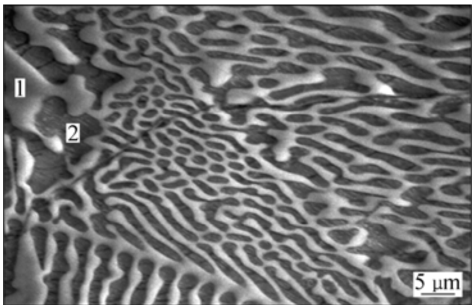


Fig. 5 Franklinite crystals before incongruent reaction at 1373 K (a) and after reaction at 1273 K (b) for slag with mass ratio of CaO/SiO_2 being 1.0 and Fe/SiO_2 being 1.7



Zone	Composition (mass fraction)/%				
	Fe_2O_3	SiO_2	CaO	ZnO	PbO
1	67.68	0.59	1.16	29.74	0.83
2	14.69	15.62	42.35	5.97	21.37

Fig. 6 SEM−EDS analysis of franklinite crystal partially transformed into magnetoplumbite and Ca/Pb silicate

3.3 X-ray diffraction results

The X-ray diffraction (XRD) analysis was used to confirm phase identification. Figure 7 shows the XRD patterns for slags 1 and 3 with mass ratio of CaO/SiO_2 being 1.0 and Fe/SiO_2 being 1.3 and 1.7, respectively, equilibrated at 1273 K and quenched to room temperature. Franklinite $ZnFe_2O_4$ (JCPD file 22−1012), margarosanite $Ca_2PbSi_3O_9$ (JCPD file 20−0219) and hardystonite $Ca_2ZnSi_2O_7$ (JCPD file 35−0745) are the

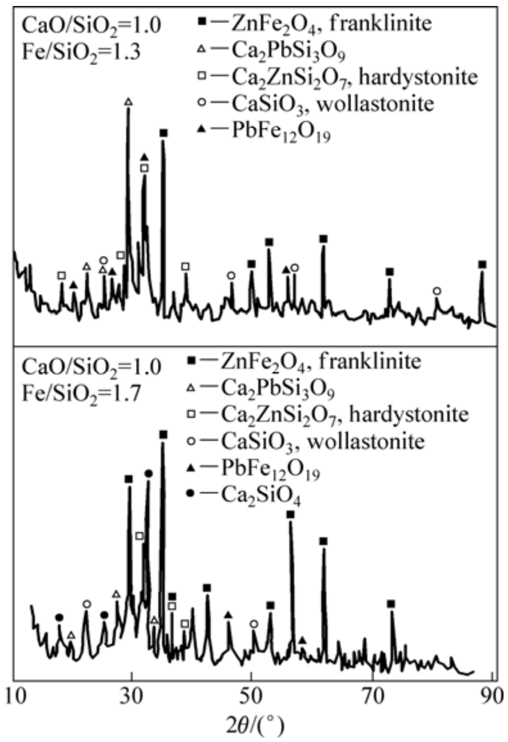


Fig. 7 XRD patterns for slags with mass ratio of CaO/SiO_2 being 1.0 and Fe/SiO_2 being 1.3 (a) and 1.7 (b), equilibrated at 1273 K and quenched to room temperature

main species present in both slags; however, the peaks of franklinite increase in intensity and those of hardystonite diminishes as the Fe/SiO_2 is increased.

The X-ray diffraction analysis also shows the presence of wollastonite ($CaSiO_3$) (JCPD file 27—1064) and lead iron oxide whose composition is close to the stoichiometry of the magnetoplumbite compound $PbFe_{12}O_{19}$ (JCPD file 310686) which was reported by JAK et al [2]. It is worth noting that the presence of crystals of hardystonite ($Ca_2ZnSi_2O_7$) and lead iron oxide ($PbFe_{12}O_{19}$) were not clearly observed in the SEM-EDS microanalysis.

3.4 Thermodynamic calculation

The thermodynamic modeling was carried out using the FACTSage computer system (THOMPSON et al [8]) which used a modified quasichemical model for the molten slag phase. A polynomial model was used for solid solutions with one sublattice. A compound energy model was used for more complex solid solutions with several sublattices. This software was used to estimate the phase distribution and liquidus temperatures for the slags in terms of slag basicity from 1.0 to 1.6 and Fe/SiO_2 ratios from 1.3 to 1.7, and temperatures from 1273 K to 1673 K (1000 °C to 1400 °C).

The phases considered in this calculation were the liquid slag phase, the spinel solid solution ($Zn_xFe_{3-x}O_{4+y}$), melilite, which is a family of species with general formula ($Pb_vCa_{2-v}Zn_wFe_{1-w}Si_2O_7$), magnetoplumbite ($PbFe_{12}O_{19}$) and a solid solution of silicates (M_2SiO_4, where M = Ca, Pb, Fe and Zn).

In the calculations, we considered the initial slag composition given in Table 1. Figure 8 shows that these slags are in the spinel primary phase field and the liquidus temperatures, which were deduced from FACTSage model predictions, are between 1523 and 1613 K (1250 and 1340 °C). This information is of particular importance to lead blast furnace. It must be stressed that the experimental results showed that the liquidus temperatures were below 1573 K (1300 °C) for all the slags. The calculated liquidus temperature decreases as the slag basicity is increased at a given Fe/SiO_2 ratio, whilst the liquidus increases when the Fe/SiO_2 ratio is increased. The minimum liquidus temperature was predicted at about 1523 K (1250 °C) for the slag with mass ratio of CaO/SiO_2 being 1.6 and Fe/SiO_2 being 1.3.

Melilite was included in the calculations as a solid solution; however, the FACTSage results showed that the composition of this phase was close to hardystonite compound ($Ca_2ZnSi_2O_7$). This phase was obtained at low mass values of CaO/SiO_2 and low temperatures. Magnetoplumbite was also formed at low slag basicities.

4 Conclusions

1) The SEM results showed dendritic structures for all the slags equilibrated at 1573 K, which indicates that the slag is completely liquid. However, XRD analysis showed the presence of solid phases as franklinite. It is likely that this phase is formed within the “arms” of the dendrites during cooling.

2) The liquidus temperature is between 1473 K and 1573 K. Franklinite is the first phase to form on crystallization in all the slags. During cooling further, franklinite precipitation takes place and when the liquid composition reaches a given composition, Ca/Pb silicates start to precipitate.

3) Calcium and lead silicates and magnetoplumbite are partially formed as a result of an incongruent reaction between liquid and franklinite between 1273 K and 1373 K.

4) The calculated liquidus temperature for the franklinite primary field increases as the Fe/SiO_2 mass ratio is increased at a given CaO/SiO_2 mass ratio.

5) The highest value of the calculated liquidus temperature for the franklinite primary field is obtained for the slags with the lowest basicity (CaO/SiO_2=1.0) at a given Fe/SiO_2 mass ratio.

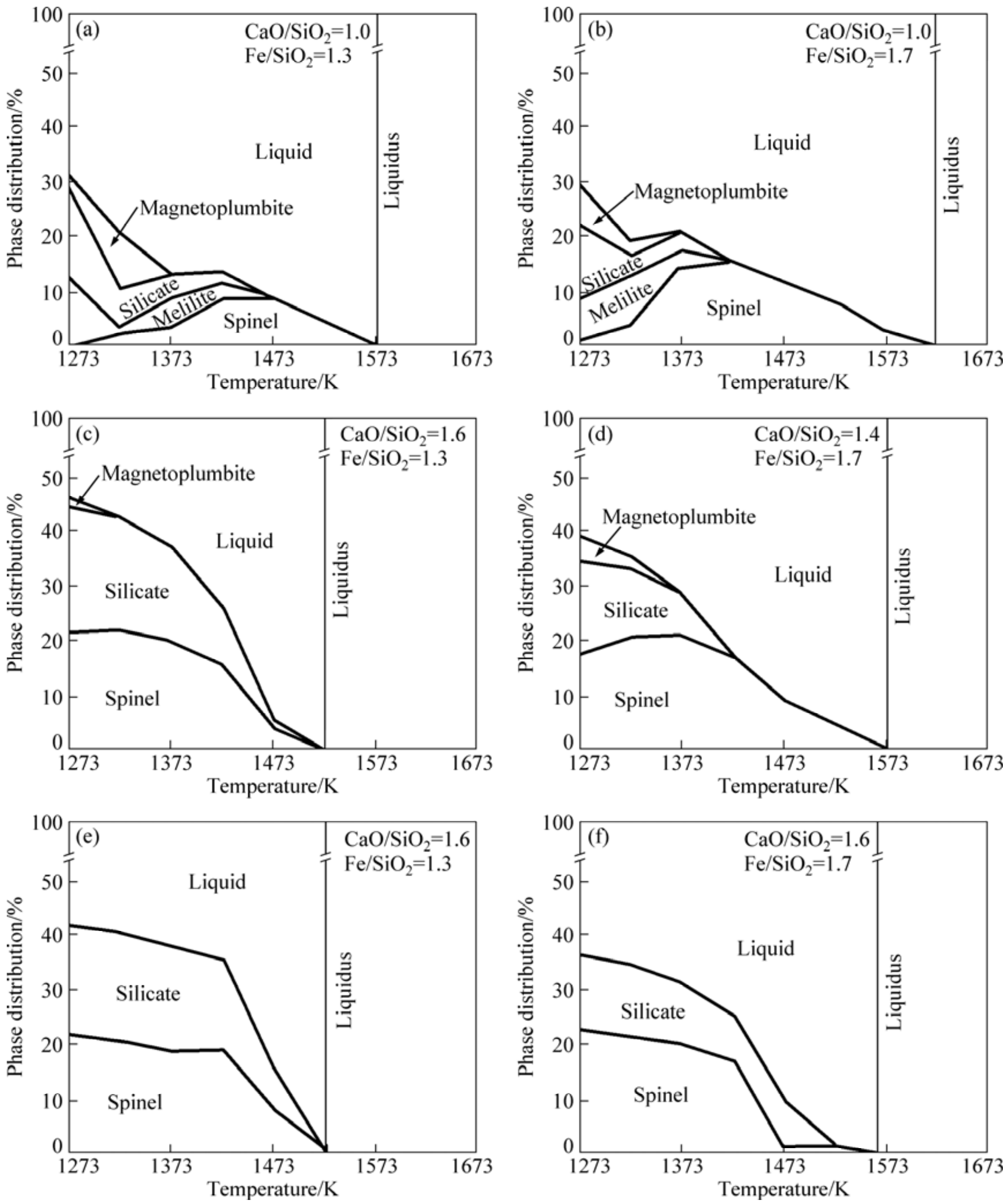


Fig. 8 Calculated phase distribution and liquidus temperature for slags in terms of CaO/SiO_2 and Fe/SiO_2 mass ratios

6) Hardystonite ($Ca_2ZnSi_2O_7$) and magnetoplumbite ($PbFe_{12}O_{19}$) are calculated to form at a low CaO/SiO_2 mass ratio and low temperature.

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CaO/SiO_2 和 Fe/SiO_2 比对空气中 PbO−ZnO−CaO−SiO_2−"Fe_2O_3"系相平衡的影响

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摘　要：实验测定了 CaO/SiO_2 和 Fe/SiO_2 质量比分别为 1~1.6 和 1.3~1.7、含 40% PbO 和 8% ZnO 的 PbO−ZnO−CaO−SiO_2−"Fe_2O_3"渣系的相平衡和液相线温度。将该渣系在 1273~1573 K 达到平衡，然后快速淬火冷却。XRD 和 SEM−EDS 分析结果表明，该渣的成分位于锌铁尖晶石相的初始成相区，在 1273~1473 K 生成硅酸钙/铅，部分硅酸钙/铅和磁铁铅矿相是通过转熔反应生成的。实验结果和热力学计算结果表明，液相线温度随着渣中 CaO/SiO_2 比的增加和 Fe/SiO_2 比的降低而增加。

关键词：铅渣；相平衡；液相线温度

(Edited by YUAN Sai-qian)