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Phase Diagram Study for the PbO-ZnO-CaO-SiO_2-“Fe_2O_3” System in Air with CaO/SiO_2 in 1.1 and PbO/(CaO+SiO_2) in 2.4 Weight Ratios

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An experimental study on the phase equilibrium and the liquidus isotherms for the PbO-ZnO-CaO-SiO_2-“Fe_2O_3” system with CaO/SiO_2 in 1.1 and PbO/(CaO+SiO_2) in 2.4 weight ratios, respectively, was carried out in the temperature range 1100-1300ºC (1373-1573 K). High temperature phases were determined by the equilibrium-quenching method. Results are presented in the form of pseudo-ternary sections “Fe_2O_3”-ZnO-(PbO+CaO+SiO_2). X-Ray diffraction (XRD) and SEM-EDS results showed that the phase equilibria in this system are dominated by the high melting temperature spinel and zincite phases. It was observed that if the system is at a temperature below 1300ºC and the total (Fe_2O_3 + ZnO) is greater than 20 wt%, spinel and/or zincite will be present in the slag system. As an application of the phase diagram, the liquid phase compositions below the liquidus surface were estimated, then their viscosities were calculated using FACTSage software.

Keywords: *Phase diagram, Slags, Lead*

1. Introduction

Metallurgical slags have a relevant role to play in the extraction and refining of metals. They are formed by fluxes, added to or included in the charge, which produce a slag with a low melting point. Efficient fluxing requires the knowledge of phase relationships in the slag, and these may be represented graphically on phase diagrams. Zhao[1] has explained that among the various methods for phase diagram determination, the equilibrium-quenching-analysis method is helpful to constructing isothermal sections. This method is based on keeping the high-temperature phase equilibria at room temperature by quenching. The method is appropriate for investigating systems in which the phase transitions are sluggish, and long-term homogenization is thus needed, such as with silica based slags.

The equilibration-quenching method can be explained with reference to Figure 1. Consider a hypothetic A-B-C ternary system with the $A_{(S)}$, $B_{(S)}$, $C_{(s)}$ and $A_2C_{(S)}$ primary phase fields. Boundary lines separate primary phase fields, along which one liquid is in equilibrium with two solid phases as defined by the adjoining primary phase fields. Let us consider that a system of overall composition M is heated at temperatures T_1 and T_2, below the liquidus surface. At temperature T_1, there exists an equilibrium between the liquid phase with a composition of point x and grains of A_2C phase. If the system is kept at temperature T_2, there will be an equilibrium between the liquid phase with a composition of the point y and two solid phases, A_2C and crystals of pure C. When the sample is cooled rapidly by drop quenching directly into water, from temperature T_1 or T_2, the result is that the phases present at those temperatures and their respective compositions are retained at room temperature, as shown in the micrographs in Figure 1. Then, the position of isotherm T_1 and the boundary line at T_2 can be estimated by microanalysis at room temperature.

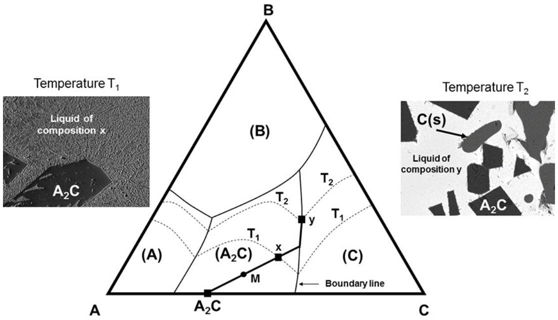

Figure 1. Schematic ternary phase diagram illustrating the use of the equilibration technique.

The production of lead and zinc metals is mainly undertaken in blast furnaces, where the reduction of lead oxide in this furnace produces slags in the multicomponent system PbO-ZnO-“Fe_2O_3”-SiO_2-CaO[2]. This system represents the major components of lead/zinc smelting slags in oxidizing conditions. Depending on the composition of lead concentrates, addition

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of fluxes with different SiO_2, CaO and Fe_2O_3 contents is done, and the information on the liquidus temperatures and the mineralogical species formed is useful for optimizing industrial practice. From the process operations' point of view, the presence of solids in liquid slags increase the viscosity of the system and is likely to result in difficulties in phase separation and slag tapping[3,4].

Jak et al.[5] reported that the liquidus surface for the PbO-ZnO-CaO-SiO_2-"Fe_2O_3" system can be shown graphically if it is projected onto a pseudo-ternary diagram "Fe_2O_3"-ZnO-[PbO+CaO+SiO_2]. In order to describe the system, it is necessary to fix the CaO/SiO_2 ratio and the PbO/(CaO+SiO_2) ratio in the liquid phase. The liquidus isotherms can be plotted on this diagram as would be the case for a normal ternary phase diagram. As $ZnFe_2O_4$ and ZnO primary phases are present in this system, phase equilibria can be treated as a true ternary in these primary phase fields. The composition of the liquid phase and the proportions of solid and liquid phases can be obtained by simple mass balance considerations using the lever rule.

Experimental studies on phase equilibria in the PbO-ZnO-CaO-SiO_2-"Fe_2O_3" system in air, using different CaO/SiO_2 ratios, have been carried out earlier[5-7] to characterize the phase relations of slag systems used in lead and zinc smelting. They used synthetic oxide mixtures, pelletized and equilibrated at temperatures below the liquidus so that two or more phases were formed. The samples were quenched, and the phases present at high temperature and their compositions were retained at room temperature. Their results showed that the liquidus in the pseudo-ternary "Fe_2O_3"-ZnO-(PbO+CaO+SiO_2) system contains primary phase fields of spinel ($Zn_xFe_{3-x}O_{4+y}$), zincite (ZnO), hematite (Fe_2O_3), melilite ($Pb_vCa_{2-v}Zn_wFe_{1-w}Si_2O_7$), magneto-plumbite ($PbFe_{10}O_{16}$) and calcium and lead silicates.

The present study has been conducted to provide experimental data on the "Fe_2O_3"-ZnO-[PbO+CaO+SiO_2] pseudo-ternary section with the following weight ratios: CaO/SiO_2 = 1.1 and PbO/(CaO+SiO_2) = 2.4, using the equilibrium-quenching method. These composition parameters have been selected because they represent the slags typically encountered in the Mexican lead blast furnaces.

FACTSage thermodynamic software[8] has incorporated an extensive amount of results on the PbO-ZnO-CaO-SiO_2-Fe_2O_3-FeO-Al_2O_3 slag systems in order to obtain one set of model equations for the Gibbs energy of the liquid slag. This software is used in this work as a tool to calculate the boundary line that separates the melilite and silicates' primary phase fields of the phase diagram. This computer program can also calculate the viscosities of liquid silicate slags. The model links the viscosities of silicate melts to their structure and thermodynamic properties. The local structure of the liquid, in terms of the bridging behavior of oxygen, calculated using the thermodynamic model allows to characterize the structure of the liquid semi-quantitatively. The silicon atoms in silicate melts are always tetrahedrally bonded to four oxygen ions. Basic silicate melts consist mainly of M^{n+}, O^{2-}, and SiO_4^{4-} ions. As the silica content increases above the orthosilicate composition, the SiO_4^{4-} tetrahedra start to polymerize, forming more and more bridging oxygens, and gradually, a three-dimensional network is formed. This model has been used extensively for modeling the viscosity of silicate melts containing lead oxide[9].

2. Experimental Procedure

The experimental procedure involves the preparation of synthetic slags from pure oxide powders (above 99.5 wt% purity). One difficulty in the experimental procedure is the high vapor pressure of lead oxide. 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 the appropriate addition of the other pure oxide powders (ZnO, CaO and Fe_2O_3) to prepare the final mixtures. About 31 slag systems were tested, and their compositions are shown in Table 1 and Figure 2.

Table 1. Slag compositions used for experiments (wt%).

Sample number	CaO	SiO_2	PbO	Fe_2O_3	ZnO
1	13.866	12.605	63.529	5	5
2	13.095	11.905	60.000	10	5
3	13.095	11.905	60.000	5	10
4	12.325	11.204	56.471	15	5
5	12.325	11.204	56.471	10	10
6	12.325	11.204	56.471	5	15
7	11.555	10.504	52.941	20	5
8	11.555	10.504	52.941	15	10
9	11.555	10.504	52.941	10	15
10	11.555	10.504	52.941	5	20
11	10.784	9.804	49.412	25	5
12	10.784	9.804	49.412	20	10
13	10.784	9.804	49.412	15	15
14	10.784	9.804	49.412	10	20
15	10.014	9.104	45.882	30	5
16	10.014	9.104	45.882	25	10
17	10.014	9.104	45.882	20	15
18	10.014	9.104	45.882	15	20
19	10.014	9.104	45.882	10	25
20	9.244	8.403	42.353	35	5
21	9.244	8.403	42.353	30	10
22	9.244	8.403	42.353	25	15
23	9.244	8.403	42.353	20	20
24	9.244	8.403	42.353	15	25
25	8.473	7.703	38.824	20	25
26	8.473	7.703	38.824	15	30
27	9.244	8.403	42.353	28	12
28	13.866	12.605	63.529	7.5	2.5
29	13.866	12.605	63.529	2.5	7.5
30	13.557	12.325	62.118	12	0
31	13.557	12.325	62.118	0	12

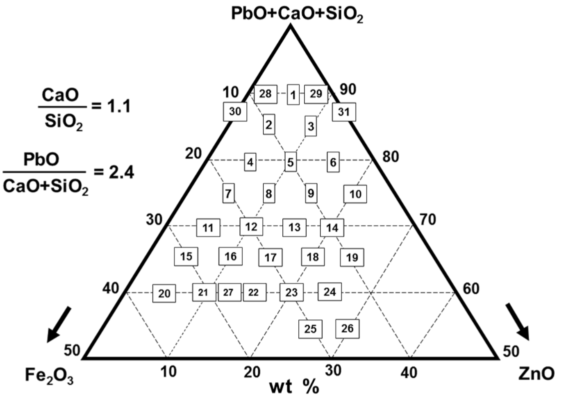

Figure 2. Schematic representation of the slag compositions.

About 20 g of each slag sample were homogenized and equilibrated in platinum crucible (25 mm inner diameter and 35 height) in air in two steps, the first involving the melting of the sample at 1300ºC over 6 h, and the second equilibration at the predetermined temperatures of 1300, 1200 and 1100ºC over 4 h. After equilibrium was achieved, the samples were quenched in iced water. The furnace temperature was controlled within ± 3ºC 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. The experimental procedure is shown in Figure 3.

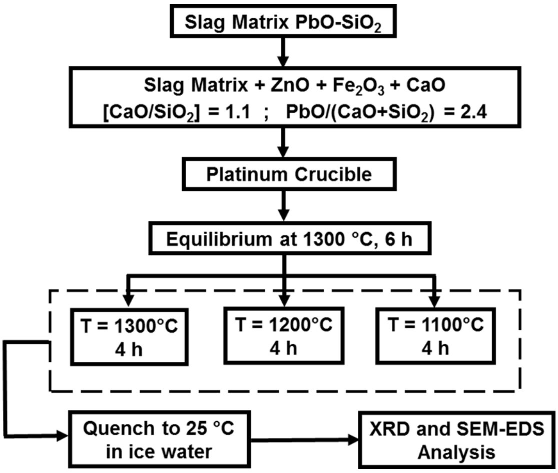

Figure 3. Experimental procedure.

Samples of each slag were characterized by X-ray diffraction (XRD Bruker D8 Focus) using Cu K_α (λ=1.5406 Å) radiation over a 2θ of 10º to 120º at a speed of 2 min^{-1}. A microstructural analysis was performed by first mounting and polishing the samples, then by examination using scanning electron microscopy coupled with an energy-dispersive spectra analyzer (FEI Quanta 600, EDAX EDS) and GENESIS-MLA software (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. Attention was paid to the morphology, shape and compositions of the solid crystallized phases; the presence of crystals was homogeneous in composition. It must be stressed that it is possible to confirm the equilibrium achievement by changing the equilibration time variation to confirm that no further changes take place with time. Another test of the equilibrium achievement is by confirming the chemical homogeneity of phases and samples[10].

3. Results and Discusion

3.1. Phase diagram of the pseudoternary system

The compositions results of the quenching experiments between 1100ºC and 1300ºC are given in Table 2. The advantage of this experimental technique is that each experiment provides information on the liquidus composition and on the compositions of the solid phases formed. Each phase composition given in Table 2 is an average of up to three compositions measured in various locations within that phase.

It must be stressed that in practice, there is always a mixture of two iron cations Fe^{2+} and Fe^{3+} present in slags and the Fe^{2+}/Fe^{3+} ratio depends on both temperature and oxygen partial pressure. It has been reported[6] that when the oxygen partial pressures is high, approaching that of air, at 1100-1300ºC, the Fe^{2+}/Fe^{3+} ratio is about 1/9; i.e., there is little Fe^{2+} in this phase. As the FeO concentrations in the present system in air are small all iron is represented as ferric oxide in this article ("Fe_2O_3").

The liquidus surface for part of the pseudo-ternary section "Fe_2O_3"-ZnO-(PbO+CaO+SiO_2) with the CaO/SiO_2 weight ratio of 1.1 and the PbO/(CaO+SiO_2) weight ratio of 2.4 is shown in Figure 4. This pseudo-ternary section has the following primary fields:

1. Spinel: $Zn_xFe_{3-x}O_{4+y}$
2. Zincite: ZnO
3. Melilite: $Pb_vCa_{2-v}Zn_wFe_{1-w}Si_2O_7$
4. Calcium and lead silicates: Ca_2SiO_4, Pb_5SiO_7, $Ca_2PbSi_3O_7$, etc.

Jak and Hayes[6] also reported primary fields of hematite (Fe_2O_3) and magneto-plumbite ($PbFe_{10}O_{16}$) in some diagrams with different CaO/SiO_2 and Pb/(CaO+SiO_2) ratios and with less than 5 wt% ZnO in the slag; however, our research was carried out with slags containing higher amounts of ZnO, and so we did not observe the presence of such phases.

Figure 4 shows that the phase equilibria in this system is dominated by the phases of high melting point, spinel and zincite. It can be seen that if the system is below 1300ºC, and if the total (Fe_2O_3 + ZnO) is greater than 20 wt%, spinel and/or zincite will be present in the slag system. As spinel and zincite do not contain significant amounts of PbO,

Table 2. Experimental data on the Section with a CaO/SiO_2 weight ratio of 1.1 and $PbO/(CaO+SiO_2)$ weight ratio of 2.4.

Mixture No	Temp (ºC)	Phases in equilibrium	Phase Name	Phase Composition (wt%)					
				Fe_2O_3	ZnO	PbO	CaO	SiO_2	wt%
1	1100	L + $Ca_{3-x}Pb_xSi_2O_7$	L	6.27	5.97	72.02	5.81	9.93	87.75
			CSP	0.00	0.00	44.48	33.34	22.18	
1	1200	L + $Ca_{3-x}Pb_xSi_2O_7$	L	5.91	5.85	71.58	6.04	10.61	88.24
			CSP	0.00	0.00	43.63	34.56	21.81	
10	1050	L + ZnO + Melilite	L	7.15	9.01	73.75	2.73	7.36	83.85
			Z	0.00	100.00	0.00	0.00	0.00	
			M	0.00	20.50	5.40	44.29	29.81	
10	1100	L + ZnO + Melilite	L	7.01	8.94	76.35	3.01	4.70	84.06
			Z	0.00	100.00	0.00	0.00	0.00	
			M	0.00	19.34	5.04	45.66	29.96	
10	1130	L + ZnO	L	6.16	11.45	70.71	4.50	7.18	82.39
			Z	0.00	100.00	0.00	0.00	0.00	
10	1170	L + ZnO	L	5.45	13.02	64.82	7.39	9.31	81.53
			Z	0.00	100.00	0.00	0.00	0.00	
10	1200	L + ZnO	L	10.91	4.11	40.55	8.37	36.06	84.98
			Z	0.00	100.00	0.00	0.00	0.00	
10	1300	L + ZnO	L	5.45	14.19	64.35	7.56	8.45	80.36
			Z	0.00	100.00	0.00	0.00	0.00	
11	1200	L + Spinel	L	24.32	3.17	58.20	6.30	8.01	72.51
			S	69.01	30.99	0.00	0.00	0.00	
12	1200	L + Spinel	L	13.43	7.71	63.59	4.57	10.70	78.86
			S	68.54	31.46	0.00	0.00	0.00	
13	1200	L + Spinel	L	13.03	11.65	59.57	6.86	8.90	75.32
			S	67.42	32.34	0.00	0.25	0.00	
14	1200	L + Spinel	L	9.71	16.55	58.86	6.13	8.75	73.74
15	1100	L + Spinel + $PbFe_{10}O_{16}$	L	24.14	1.41	56.69	8.59	9.16	74.45
			S	71.22	28.16	0.00	0.62	0.00	
			MP	75.22	0.87	23.49	0.42	0.00	
15	1200	L + Spinel	L	24.83	1.25	58.40	6.76	8.76	73.92
			S	71.93	27.48	0.00	0.59	0.00	
15	1300	L + Spinel	L	29.76	5.18	47.95	8.00	9.10	65.05
			S	73.58	25.99	0.00	0.44	0.00	
16	1100	L + Spinel	L	15.04	3.32	66.27	7.28	8.09	81.64
			S	67.11	32.89	0.00	0.00	0.00	
16	1200	L + Spinel	L	17.76	5.30	60.79	7.18	8.97	76.94
			S	68.01	31.99	0.00	0.00	0.00	
16	1300	L + Spinel	L	20.10	8.43	54.64	7.33	9.51	71.47
			S	69.53	29.95	0.00	0.52	0.00	
17	1200	L + Spinel	L	13.33	11.21	55.25	8.09	12.11	75.45
			S	67.03	32.97	0.00	0.00	0.00	
17	1300	L + Spinel	L	12.22	14.68	51.82	9.04	12.24	73.10
			S	67.97	32.03	0.00	0.00	0.00	

Table 2. Experimental data on the Section with a CaO/SiO_2 weight ratio of 1.1 and PbO/($CaO+SiO_2$) weight ratio of 2.4.

18	1200	L	+	Spinel	L	11.60	17.14	51.98	8.91	10.37	71.26
					S	73.80	25.68	0.00	0.52	0.00	
18	1300	L	+	Spinel	L	15.13	20.81	45.39	8.29	10.38	64.06
19	1200	L	+	ZnO	L	14.62	11.84	59.93	5.24	8.37	73.53
					Z	0.00	100.00	0.00	0.00	0.00	
19	1300	L	+	ZnO	L	9.66	20.16	50.24	8.56	11.38	70.18
					Z	0.00	100.00	0.00	0.00	0.00	
20	1100	L	+	Spinel	L	21.31	0.00	58.74	9.04	10.91	78.69
					S	71.32	28.26	0.00	0.42	0.00	
20	1200	L	+	Spinel	L	27.70	2.47	53.40	7.54	8.89	69.84
					S	73.03	26.97	0.00	0.00	0.00	
20	1300	L	+	Spinel	L	33.58	4.49	46.55	6.46	8.91	61.93
					S	75.55	23.99	0.00	0.47	0.00	
21	1100	L	+	Spinel	L	17.33	2.49	60.89	8.39	10.91	80.19
					S	68.20	31.24	0.00	0.56	0.00	
21	1200	L	+	Spinel	L	17.01	4.04	60.94	8.60	9.42	78.95
					S	68.34	31.26	0.00	0.40	0.00	
21	1300	L	+	Spinel	L	27.44	7.94	48.76	6.62	9.24	64.62
					S	70.03	29.97	0.00	0.00	0.00	
22	1100	L	+	Spinel + Melilite	L	10.92	6.31	73.91	3.40	5.46	82.77
					S	66.61	33.39	0.00	0.00	0.00	
					M	2.59	24.05	4.08	33.24	36.04	
22	1200	L	+	Spinel	L	17.10	8.20	58.80	8.19	7.71	74.70
					S	68.50	30.97	0.00	0.53	0.00	
22	1300	L	+	Spinel	L	20.62	14.81	46.77	7.82	9.98	64.57
					S	68.31	31.69	0.00	0.00	0.00	
23	1100	L	+	Spinel + ZnO + Melilite	L	9.30	9.66	72.93	3.55	4.56	81.04
					S	65.41	34.59	0.00	0.00	0.00	
					Z	0.00	100.00	0.00	0.00	0.00	
					M	0.00	28.37	0.00	34.31	37.32	
23	1200	L	+	Spinel + Melilite	L	11.32	18.31	52.31	7.98	10.07	70.37
					S	67.42	32.34	0.00	0.25	0.00	
					M	0.00	43.35	0.00	32.15	24.50	
23	1300	L	+	Spinel	L	18.46	18.90	45.87	7.84	8.92	62.63
					S	65.02	34.98	0.00	0.00	0.00	
24	1100	L	+	Spinel + ZnO + Melilite	L	9.39	9.28	72.80	2.79	5.74	81.34
					Z	0.00	100.00	0.00	0.00	0.00	
					S	64.80	35.20	0.00	0.00	0.00	
					M	0.00	28.10	0.00	34.19	37.71	
24	1200	L	+	ZnO + Spinel	L	12.73	17.12	52.93	7.51	9.70	70.15
					Z	0.00	100.00	0.00	0.00	0.00	
					S	68.06	31.94	0.00	0.00	0.00	
24	1300	L	+	Spinel	L	15.19	22.27	46.20	7.46	8.89	62.54
					S	7.26	92.74	0.00	0.00	0.00	
25	1300	L	+	Spinel	L	17.72	24.67	44.31	5.67	7.63	57.60
					S	64.24	35.76	0.00	0.00	0.00	

Table 2. Experimental data on the Section with a CaO/SiO_2 weight ratio of 1.1 and PbO/(CaO+SiO_2) weight ratio of 2.4.

26	1300	L	+	ZnO	L	9.17	13.42	59.46	7.67	10.28	77.41
					Z	0.00	100.00	0.00	0.00	0.00	
27	1100	L	+	Spinel	L	14.90	3.29	67.96	5.86	7.99	81.80
					S	64.93	35.07	0.00	0.00	0.00	
27	1200	L	+	Spinel	L	14.22	7.26	60.34	8.12	10.06	78.52
					S	66.84	33.16	0.00	0.00	0.00	
28	1100	L	+	$Ca_{3-x}Pb_xSi_2O_7$	L	8.33	3.71	72.54	5.56	9.86	87.96
					CSP	0.00	0.00	82.99	11.58	5.43	
28	1200	L	+	$Ca_{3-x}Pb_xSi_2O_7$	L	7.89	2.85	68.63	8.53	12.09	89.26
					CSP	0.00	0.00	43.23	34.72	22.05	
29	1100	L	+	$Ca_{3-x}Pb_xSi_2O_7$	L	2.55	2.66	76.20	7.16	11.43	94.79
					CSP	0.00	0.00	43.32	33.99	22.69	
29	1200	L	+	$Ca_{3-x}Pb_xSi_2O_7$	L	2.52	8.58	68.93	7.91	12.06	88.90
					CSP	0.00	0.00	43.03	34.58	22.39	
29	1300	L	+	$Ca_{3-x}Pb_xSi_2O_7$	L	5.07	6.64	63.54	11.40	13.35	88.29
30	1100	L	+	$Ca_{3-x}Pb_xSi_2O_7$	L	13.60	0.00	70.58	6.27	9.56	86.40
					CSP	0.00	0.00	43.32	33.99	22.69	
31	1100	L	+	ZnO	L	0.00	9.60	83.39	2.17	4.84	90.40
					Z	0.00	93.64	6.36	0.00	0.00	

PCS: PbO + CaO + SiO_2

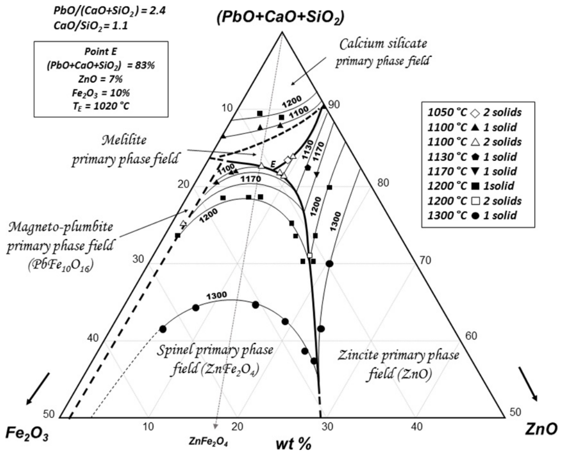

Figure 4. Experimentally determined liquidus surface on the pseudo-ternary section of "Fe_2O_3"-ZnO-(PbO-CaO-SiO_2) for slags with CaO/SiO_2 and PbO/(CaO+SiO_2) weight ratios of 1.1 and 2.4, respectively.

CaO or SiO_2 in solid solution, then the CaO/SiO_2 and PbO/(CaO+SiO_2) ratios in the liquid phase do not change. The SEM-EDS measurements of the glass compositions were sufficient to construct liquidus surfaces in these primary phase fields.

As indicated, the general ternary phase diagram rules can be applied to the zincite and spinel primary phase fields of the pseudo-ternary section; then, the compositions and proportions of the phases present in a slag of a particular overall composition can be derived from the diagram for any temperature using tie-line. Using these rules, we were able to estimate the position of the isotherms at 1100, 1200 and 1300ºC in Figure 4.

The ternary phase diagram rules cannot be applied in the melilite and calcium silicate primary fields, as the liquid and solid compositions do not lie on the pseudo-ternary section; however, the liquidus temperatures for compositions in these primary fields can be defined. Figure 4 shows the isotherms at 1100 and 1200ºC obtained experimentally in the calcium silicate primary field. There is uncertainty about the spinel/melilite and melilite/silicate boundary lines; therefore, this part of the diagram was deduced from experimental and FACTSage predictions[8]. The special point E was experimentally determined at 1020ºC, 10% Fe_2O_3, 7% ZnO and 83% (PbO+CaO+SiO_2), which represents the intersection of the spinel/zincite, spinel/melilite and zincite/melilite boundary lines, with the minimum liquidus temperature.

The SEM-EDS measurements in Table 2 show that all the zinc and iron are present in the liquid, zincite, spinel and melilite phases. These are the primary phase fields directly relevant to lead and zinc sinters. As the systems are cooled to temperatures below the liquidus, the remaining liquid phase becomes enriched in PbO and the liquid compositions approach those described by the PbO-CaO-SiO_2 ternary system.

3.2. Microstructure

Examples of microstructures observed at different temperatures for slag sample number 23 are presented in Figure 5. The crystallization of this sample shows that the first

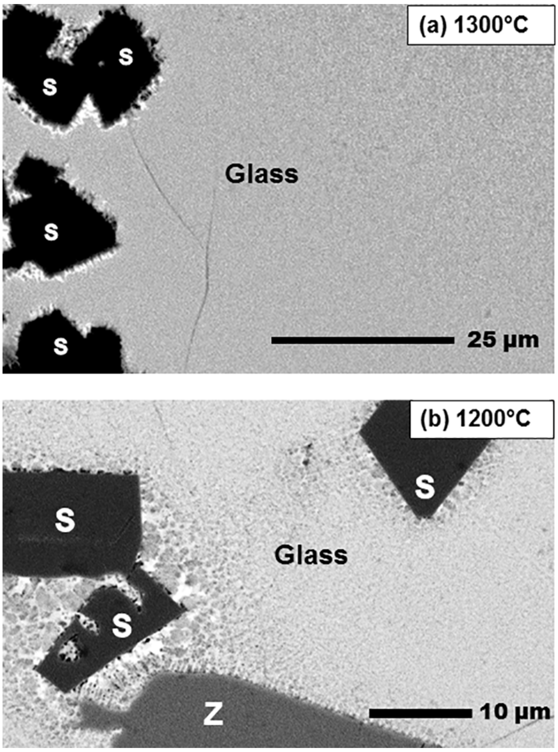

Figure 5. Micrographs of the slag sample 23 equilibrated and quenched from (a) 1300ºC and (b) 1200°C. S: spinel, Z: zincite.

solid to form is spinel, when the liquid compositions reach the boundary line of spinel-zincite there is a coprecipitation of spinel and zincite. As the cooling of the sample continues to point E in the phase diagram, melilite starts to precipitate and the liquid composition leaves the composition of the pseudo-ternary section.

Figure 5a shows that at 1300 ºC the slag system is constituted of two clearly different phases; the dark angular crystals (S) correspond to spinel with a composition close to that of franklinite (ZnFe$_2$O$_4$: 33.67 wt% ZnO and 66.33 wt% Fe$_2$O$_3$), and the gray background corresponds to the liquid converted into glass during the quenching process. The composition of the glass phase in this sample, measured with EDS, gives one point that lies in the 1300ºC isotherm of the pseudo-ternary phase diagram. The equilibrium phases at 1200ºC are shown in Figure 5b. It is observed that there are three phases in equilibrium: spinel (S), glass, and gray oval precipitates corresponding to zincite (Z). At 1200ºC the composition of glass is on the boundary line of spinel and zincite primary phase fields.

The crystallization of sample 24 is illustrated in Figure 6. Zincite is the first solid to form (Figure 6a). On cooling further, the liquid composition reaches the boundary line spinel/zincite and coprecipitation of zincite and spinel begins (Figure 6b).

It is worth mentioning that at high temperatures (1100-1300ºC) the stable phases are liquid and one or more solids; however, after cooling the samples the glass phase obtained together with the solid phases can be considered as metastable phases at room temperature.

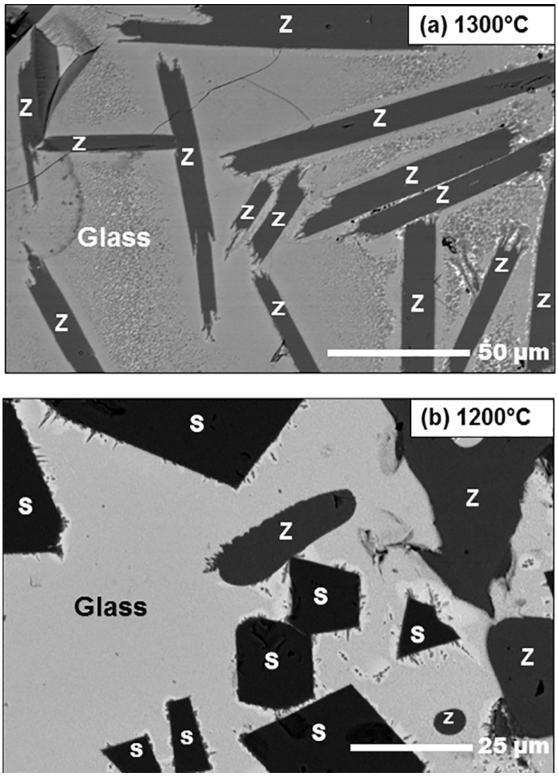

Figure 6. Micrographs of the slag sample 24 equilibrated and quenched from (a) 1300°C and (b) 1200°C. S: spinel, Z: zincite.

3.3. X-Ray diffraction results

XRD analysis was used to confirm the phase identification. Figure 7 shows the XRD patterns obtained from the slag number 23 equilibrated at three temperatures (1300, 1200 and 1100ºC) and quenched to room temperature. Figure 7a shows that at 1300ºC, the spinel ZnFe$_2$O$_4$ (JCPD file 22-1012) is the only crystalline phase, which is in agreement with the SEM-EDS results shown in Figure 5a. When the liquid composition reaches the spinel/zincite boundary line, spinel and zincite ZnO (JCPD file 003-0888) coprecipitate, as shown in the XRD pattern of Figure 7b. At 1100ºC, the XRD pattern of Figure 7c shows that the slag contains spinel (ZnFe$_2$O$_4$), zincite and melilite with the composition Ca$_2$ZnSi$_2$O$_7$ (JCPD file 012-0453).

3.4. Application to plant practice

The lead blast furnace is a reactor where the charge moves through a vertical shaft in counter-current to the ascending reducing gas flow. The produced liquid phases (slag, matte, speiss and bullion) are collected in the furnace

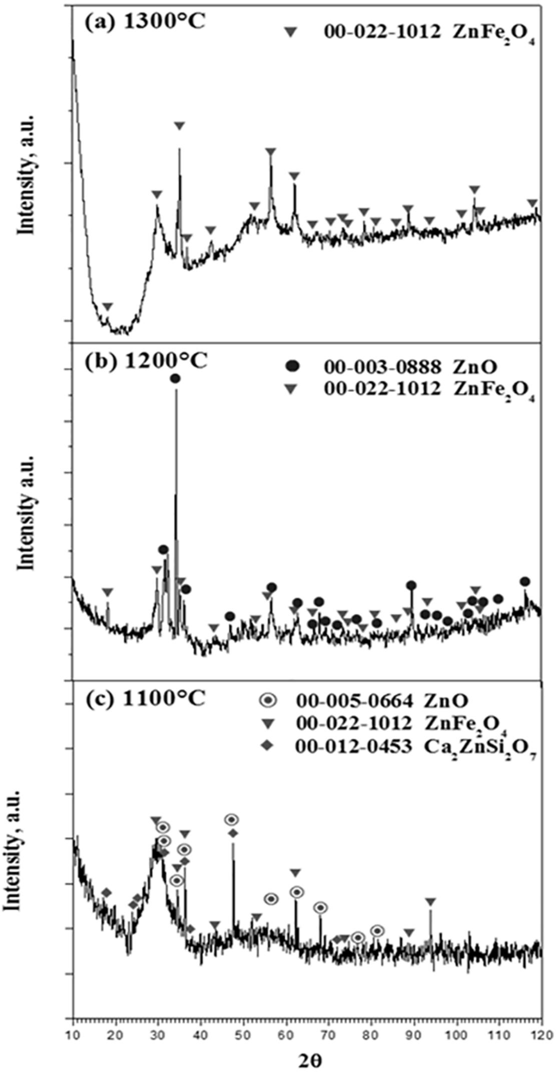

Figure 7. X-Ray diffraction patterns for slag sample 23 equilibrated at different temperatures.

crucible and separated by density gradient. The sinter produced in Mexico has historically been different from that form around the world in that the Mexican sinter contains high concentrations of silver and bismuth. The recovery of precious metals during lead production in a blast furnace makes this process more profitable. Losses of silver and lead are common in this process and can be due to both physical and chemical phenomena. Lead can be trapped as metallic particles in the slag[11], due to its composition and viscosity.

The information provided in the pseudo-ternary section of the slag system can be used in practical applications to predict the effect on the slag viscosity of increasing ZnO content. Figure 8 shows the composition of the slags in the Mexican plant which have ZnO compositions of 14 and 22 wt%. This figure also shows the cooling paths for the slags with low (14 wt% ZnO) and high (22 wt% ZnO) together with the point compositions of the liquids in equilibrium with spinel at temperatures under the liquidus surface. The compositions of the liquid phase were used to estimate their viscosity using the FACTSage program[8].

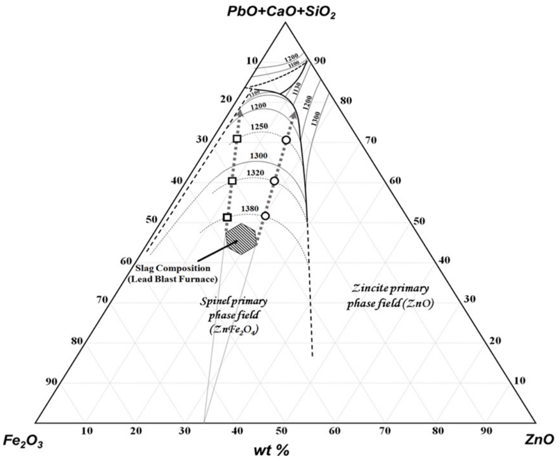

Figure 8. Pseudo-ternary section of "Fe_2O_3"-ZnO-(PbO-CaO-SiO_2) with the cooling path of two different slags in a commercial lead blast furnace.

Figure 9 shows the changes during cooling in the viscosity of the liquid phase, in terms of temperature and ZnO content, for both slags, with low and high ZnO content. It is evident that increasing the ZnO content in the slag increases the viscosity and, therefore, the possibility that valuable metals can be trapped in the slags during the tapping stage is also increased.

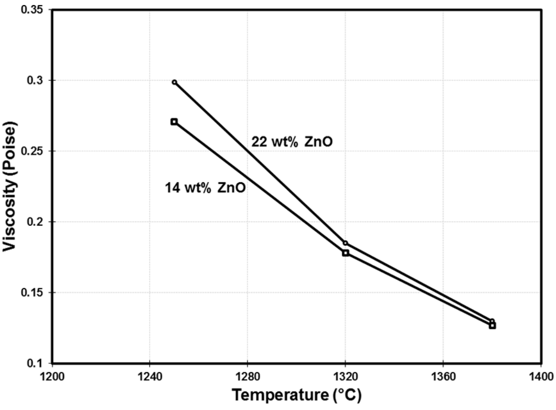

Figure 9. Effect of temperature and ZnO content on the liquid slag viscosity calculated with FACTSage software[8].

4. Conclusions

An experimental study of quenched synthetic slag samples in the system PbO-ZnO-CaO-SiO_2-"Fe_2O_3" with the weight ratios CaO/SiO_2 = 1.1 and PbO/(CaO+SiO_2) = 2.4 was carried out. The XRD and SEM-EDS techniques were used to identify the solid phases that were formed in equilibrium with the liquid at a high temperature.

The experimental data was used to construct the liquidus in the pseudoternary section "Fe_2O_3"-ZnO-(PbO-CaO-SiO_2)

in the temperature range of 1100-1300ºC. The isotherms in the spinel, zincite and silicates primary phase fields were experimentally obtained, as well as the boundary lines for spinel/zincite and zincite/melilite. The thermodynamic software FACTSage was used to calculate the boundary line of melilite/silicates in the (PbO+CaO+SiO_2) rich region.

An application of the phase diagram is the estimation of the composition of the liquid phase that remains once the crystallization process begins; then, its viscosity can be calculated by commercial software.

5. Acknowledgements

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