Phase Equilibrium Study in the Sodium Metasilicate Primary Phase Field of $PbO-Na_2O-SiO_2$ System Between 800 and 1000 °C

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ABSTRACT

In the pyrometallurgical process of secondary lead recycling, a desulfurizing agent, such as Na_2CO_3 is added to minimize the emissions of sulphur into the atmosphere, while silica is introduced into the smelter as a fluxing material. Subsequently, a significant amount of Na_2O and SiO_2 remains in the downstream reverberatory furnace and blast furnace slags. However, there is limited understanding of the thermodynamic behaviour of silicate-based lead slags rich in Na_2O, posing challenges in accurately determining the optimal condition for targeted metal recovery and final slag composition. In this work, the equilibrium phase relations of the $PbO-Na_2O-SiO_2$ system in the primary phase field of Na_2SiO_3 are studied from 800 to 1000 °C via equilibration-quenching method. Samples with different compositions were prepared and held in platinum capsules in air at these temperatures to reach equilibrium. The equilibrated samples were subsequently quenched and the phase compositions were measured by electron probe microanalysis (EPMA). The results were then compared to those of previous studies, and any discrepancies were resolved.

INTROUDCTION

Lead-acid battery (LAB) has a history of over 150 years since its invention in the mid-18th century (Rand and Moseley, 2015). In 2019 (pre-pandemic), the global production of refined lead was around 11.8 million metric tonnes, 80% of which went to the LAB industry. LAB accounts for nearly 50% of the secondary battery market with a market size of \$50 billion USD in 2019 (Zhao *et al.*, 2021). With the growing demand of LAB in automotive industry, the LAB market is forecasted to grow at an annual rate of over 8%, to reach \$116 billion USD in 2030 (Yanamandra *et al.*, 2022). LABs are considered an example of circular economy, evidenced by the fact that the recycling of LABs is economically feasible with a recycling and reuse rate of 99% (EDR Group and EBP Company, 2019; Yanamandra *et al.*, 2022). The recycling of LABs is not only economically significant but also environmentally crucial. If not recycled, the lead contained in LABs might enter landfills and contaminate the water and ecosystems. As a result, the recycling of LABs is an essential and critical practice as it serves both the purpose of conserving finite resources and preventing environmental contamination.

The recycling process of LABs usually includes a critical desulphurization process where lead sulphate is converted to carbonate by a desulfurizing agent such as Na_2CO_3. The representative equation can be written as follows:

$$\mathbf{PbSO_{4(s)} + Na_2CO_{3(aq)} = Na_2SO_{4(aq)} + PbCO_{3(s)}}$$

To maintain the desired low sulphur content, excess Na_2CO_3 is added, which partly makes it to the furnace and is eventually decomposed to Na_2O during the smelting process (Lyakov *et al.*, 2007; Zhang *et al.*, 2016). In a typical two-step smelting process, the desulfurized lead paste and lead grids are firstly melted and partially reduced in a reverberatory furnace, and then charged into a blast furnace. The reverberatory furnace slag contains 45-65 wt% Pb, 5-10% Na and 4-7% Si, while the blast furnace slag generally contains 1-6% Pb, 10-15% Na and 10-18% Si (Nicol *et al.*, 2020). In this complex slag system, some of the subsystems have been extensively studied and their thermodynamics were well established. However, the thermodynamic behaviour of silica-based lead slags that contain Na_2O, represented by the PbO-Na_2O-SiO_2 system remains underexplored.

One of the limited research works conducted on this subject was by Krakau, Mukhin and Geinrich, who studied the phase equilibria of the binary subsystems at different primary phase saturations, including PbO, SiO_2, $PbSiO_3$, Pb_2SiO_4, $Pb_3Si_2O_7$, Pb_3SiO_5 and Na_2SiO_3 using heating and cooling curves method (Krakau *et al.*, 1949). Later, Santoso revisited the work on liquidus temperatures of the PbO-Na_2O-SiO_2 system from 900 to 1100 °C at SiO_2 saturation using quenching method (Santoso, 2017). Their results revealed significantly lower liquidus points than those determined by Krakau *et al.*. Santoso suggested that the difference could be attributed to the limitations of the dynamic method employed by Krakau's group.

In this work, the phase equilibria of PbO-Na_2O-SiO_2 system in the primary phase field of Na_2SiO_3 was studied in air between 800 and 900 °C using equilibration-quenching-microanalysis technique. The results are compared with the above two studies.

METHODOLOGY

The current work utilizes the static method, also known as the equilibration-quenching technique. In this approach, samples are equilibrated at specific temperatures until reaching equilibrium. Subsequently, the samples are quenched to room temperature to preserve the phase assemblage present at high temperatures. The composition of the equilibrium phases is then determined with Electron Probe Micro-Analysis (EPMA).

Samples were prepared by mixing various amounts of PbO (99.0 % purity, Fisher Scientific), Na_2SiO_3 (200 level quality, Sigma Aldrich) and SiO_2 (99.5% purity, Sigma Aldrich) in an agate mortar and pestle. The well-mixed powders were pressed into Pt capsules of 6 mm in diameter, 6 mm long, and 0.15 mm in thickness. The two ends of the capsule were folded to minimize the loss of volatile material at high temperatures. The capsules were then put in an alumina tray and suspended in the hot zone of a vertical resistance heating furnace under an air atmosphere. The sample temperature was continuously monitored by a type K thermocouple, the tip of which comes into contact with the Pt capsule. The schematic of the experimental setup is shown in FIG 1.

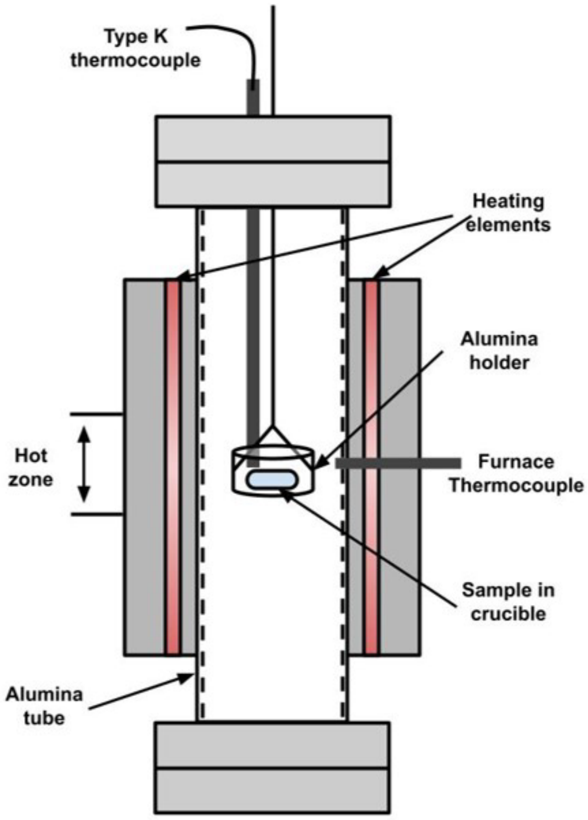


FIG 1 Schematic diagram of equilibrium test setup.

After the test, the specimens were quenched in oil due to the hygroscopic nature of the Na_2O-containing products. Solidified samples were mounted in epoxy and were then grinded and polished using ethylene glycol as lubricant to avoid reaction between water and Na_2O. The samples were quickly transferred to the EPMA (JEOL, Japan) employing a JXA8230 probe. Compositions of each phase were measured by Wavelength-Dispersive Spectrometry (WDS) function at an accelerating voltage of 15 KV, 20 nA beam current, 20 μm beam size, 40 s on-peak counting time, and 20s on each side of the background. Albite ($NaAlSi_3O_8$) was used as reference material for Na and Si and crocoite ($PbCrO_4$) was used as reference material for the determination of Pb. The average was taken from at least 10 measurements on each phase of the sample.

RESULTS AND DISCUSSION

Samples with various $PbO:Na_2O:SiO_2$ ratios were equilibrated at 800, 900 and 1000 °C under an air atmosphere. The material was held in platinum crucibles and quenched in oil. The bulk composition of samples was determined to lie in the sodium metasilicate primary phase field based on previous research by Krakau, Mukhin and Geinrich (Krakau *et al.*, 1949). The composition of starting materials, experimental conditions, product phases, and their compositions are listed in TABLE 1. The backscattered electron (BSE) images of typical samples at different temperatures are presented in FIG 2. The isothermal sections of the ternary phase diagram including the data from the present work and the previous studies are shown in FIG 3.

TABLE 1 – Test conditions and compositions of each phase

Temperature (°C) and sample number	**Sample Composition (PbO:Na_2O:SiO_2 mol%)**	**Sample Composition (PbO:Na_2O:SiO_2 wt%)**	**Duration (h)**	**Phase**	**Composition (PbO:Na_2O:SiO_2 mol%)**	**Composition (PbO:Na_2O:SiO_2 wt%)**	**Raw EPMA (sums before normalisation wt%)**	**Standard deviation (PbO:Na_2O:SiO_2 wt%)**
800-S1	11:36:53	16:34:50	40	Liquid	20:24:56	48:16:35	98.9	1:0.4:0.7
				Na_2SiO_3	0:48:52	0:49:48	97.2	0:2:1.6
800-S2	16:34:50	41:24:35	40	Liquid	26:23:51	55:14:29	98.5	1:0.2:0.6:
				Na_2SiO_3	0:49:51	0:48.5:49	97.7	0:0.4:0.2
800-S3	23:36:41	52:23:25	40	Liquid	60:13:27	85:5:10	101.6	1.7:0.7:1
				Na_2SiO_3	0:48:52	0:48:50	98	0:0.8:0.2
900-S1	8:8:84	24:7:69	40	Liquid	12.5:12:75.5	34:9:55	97.3	0.3:0.1:0.2
				SiO_2 (tridymite)	0:0:100	0:0:97.4	97.4	0:0:0.6
900-S2	2.5:43:54.5	9:41:50	20	Liquid	7:32:61	21:27:50	97	2:2.8:1.1
				Na_2SiO_3	0:49:51	0:48:49	97	0:1:0.5
900-S3	10:40:50	29:32:39	20	Liquid	24:26:50	53:16:30	99.1	0.8:1:0.6
				Solid Na_2SiO_3	0:48:52	0:48.4:49	100.2	0:3:2.7
900-S4	16:42:42	41:30:29	20	Liquid	33:31:36	64:17:19	100.2	3.7:2.3:1.6
				Solid Na_2SiO_3	0:49:51	0:48:49	97	0:0.6:0.3
1000-S1	4:45:51	13:41:45	10	Liquid	16.5:29:54.5	41:21:37	99	5:4:2
				Solid Na_2SiO_3	0:50:50	0:50:50	100.04	0:0.5:0.4

Sample 900-S1 is a comparison test with previous studies in the SiO_2 primary phase field by holding the sample in Pt capsule under air atmosphere at 900 °C for 40 hours. The BSE images show that the liquid phase is in equilibrium with the needle-like solid tridymite (FIG 1). The composition of the liquid phase in 900-S1 closely aligns with the data reported by Santoso (Santoso, 2017), shown in FIG 2-(b), who employed a different methodology involving the use of quartz crucibles to establish a silica-saturated composition. The consistency between the results obtained from distinct approaches underscores the reliability of the approach employed in this work. The compositions determined by Santoso (Santoso, 2017) and the current study both measured higher SiO_2 content in the liquid phase compared to Krakau, Mukhin and Geinrich (Krakau *et al.*, 1949). This discrepancy likely arose from the difference between static and dynamic techniques. Samples especially those with high SiO_2 content, might not have reached equilibrium in dynamic experiments.

Except for sample 900-S1, all other samples were measured to be in the two-phase region where liquid was in equilibrium with solid Na_2SiO_3. In samples tested at 800 and 900 °C, the solid grains displayed two distinct structures: polygonal and lath-shaped, both of which had identical compositions, suggesting that these crystalline structures were Na_2SiO_3. The polygonal shape is likely a cross-section of the crystal, whereas the larger lath-like structure may result from viewing the lateral section of the solid phase. According to the isothermal sections in FIG 2, tie lines pass through the starting points in all samples, suggesting negligible sample loss during high temperature tests, and negligible Na loss during the electron beam analysis. Compared to the results reported by Krakau *et al.*(Krakau *et al.*, 1949), the liquid phase with much higher PbO content was observed. The liquid-solid two-phase region of Na_2SiO_3 primary phase field is much larger, indicating a higher melting point of mixture in this region. From practical point of view, when the slag composition falls between the liquidus lines established by Krakau *et al.* and the current study, it is likely that slag might not achieve complete melting at the designated temperature. This incomplete melting can result in increased viscosity, thereby causing challenges during the tapping process. Consequently, it is essential to determine an accurate liquidus and other associated properties.

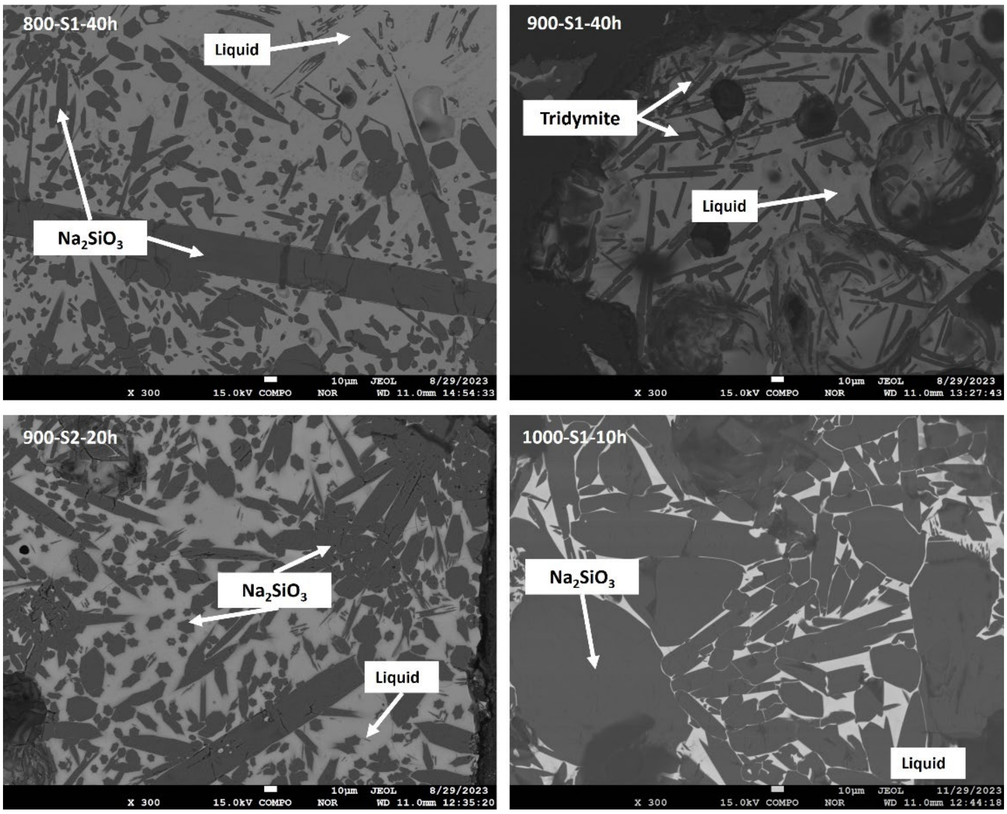
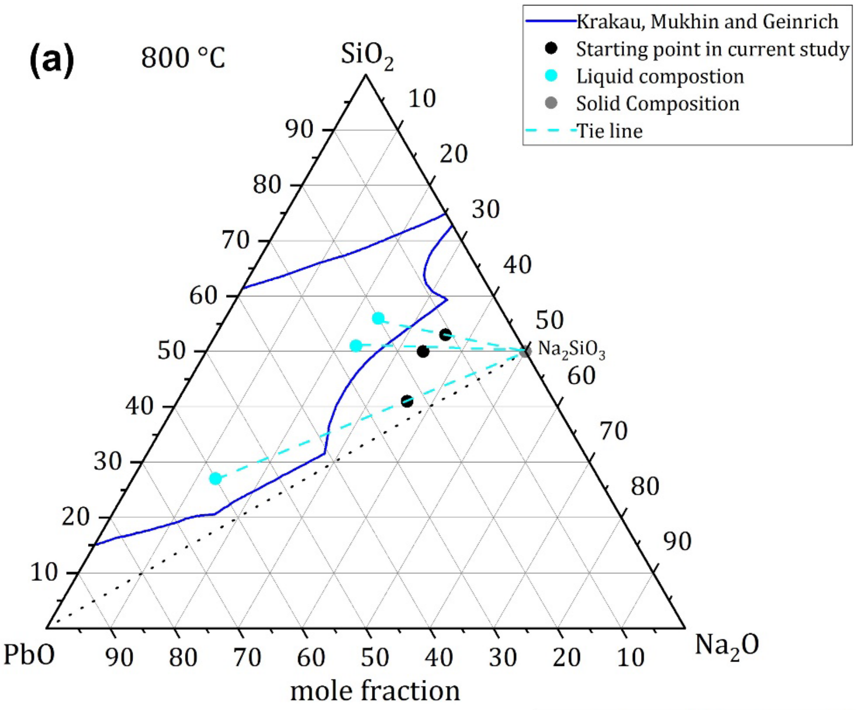
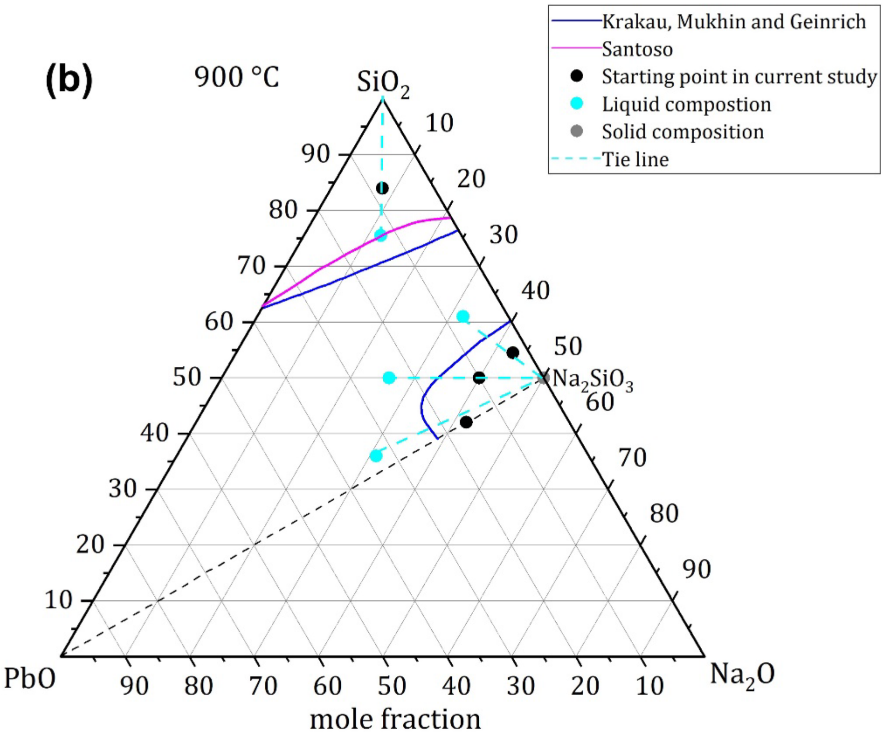


FIG 2 – Backscattered electron images of samples 800-S1, 900-S1, 900-S2 and 1000-S1.


(a)
800 °C
SiO_2
PbO
Na_2O
Na_2SiO_3
10
20
30
40
50
60
70
80
90
mole fraction
Krakau, Mukhin and Geinrich
Starting point in current study
Liquid compostion
Solid Composition
Tie line


(b)
900 °C
SiO_2
PbO
Na_2O
Na_2SiO_3
10
20
30
40
50
60
70
80
90
mole fraction
Krakau, Mukhin and Geinrich
Santoso
Starting point in current study
Liquid compostion
Solid composition
Tie line

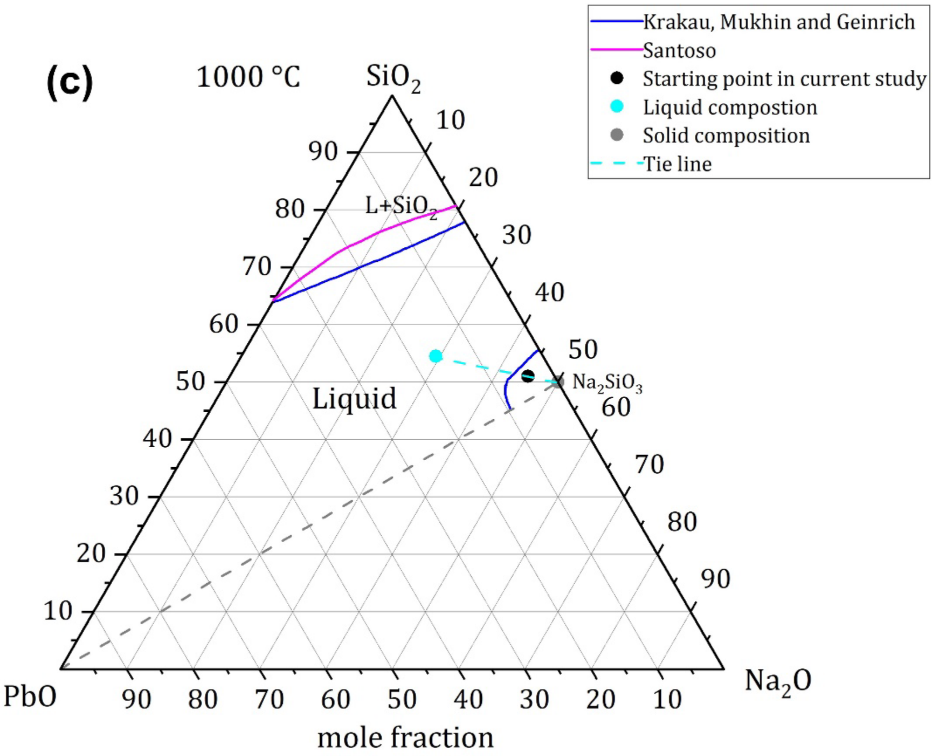


FIG 3 – Isothermal sections of $PbO-Na_2O-SiO_2$ system at (a): 800 °C, (b): 900 °C and (c): 1000 °C.

CONCLUSIONS

The current work studied the liquidus temperatures of the Na_2SiO_3 primary phase field between 800 and 1000 °C on the $PbO-Na_2O-SiO_2$ system using the equilibration-quench-analysis method. The liquid-solid two-phase region established in the current study is significantly larger than the one observed by Krakau, Mukhin and Geinrich, suggesting a higher melting point within this primary phase field.

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