Density measurements of low silica $CaO\text{-}SiO_2\text{-}Al_2O_3$ slags: slag structure discussions

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Abstract: The density of low silica $CaO\text{-}SiO_2\text{-}Al_2O_3$ slags with silica content varying from 5 – 14 % was measured using Archimedes Principle. A Pt-30%Rh bob which hung from a balance was then immersed in the slag and the change in mass was measured at temperatures 1410 and 1460 ^oC. The density values obtained from the measurements were later compared with the model developed by Persson et al. Density values of the corresponding binary silicates as well as higher silica ternary slags were then estimated and compared with the experimental works of other researchers. Some density measurements were also carried out using the X-ray sessile drop technique at higher temperatures which showed good agreement with the results of Archimedes method.

Later the density decrease at high temperatures was interpreted based on the silicate structure. As the mole percent of SiO_2 was below the 33 pct required for the orthosilicate composition, discrete SiO_4^{-4} tetrahedral units in the silicate melt would exist along with O^{2-} ions. The expansivity curve for the ternary system was plotted against the alumina content. The drooping expansivity curve suggested that the predominant expansions in the bonding were due to Ca-O bonds. The change in melt expansivity may be attributed to the ionic expansions in the order of Al^{3+} - O^{2-} $<Ca^{2+}$-O^{2-} $<Ca^{2+}$-O^- Structural changes in the ternary slag also could be correlated to a drastic change in the value of enthalpy of mixing. Similar trend also can be found in the sulphide capacity study of $CaO\text{-}SiO_2\text{-}CrO_x$ system at 1873K. The sulfide capacity shows a decreasing trend as Cr^{2+} replaces Ca^{2+} in the slag. With further increase of Cr^{2+} content, there are indications of the occurrence of a minimum point beyond which the sulfide capacities show a slight increasing trend. The latter is attributed, on the basis of slag structure analysis of Gaskell and coworkers, to the increasing extent of the polymerization reaction releasing oxygen ions for sulfide reactions.

Keywords: Density Measurements, Expansivity, Archimedes Principle, Slag structure

1. Introduction

Density is probably the most fundamental thermophysical property that is of immense importance to predict the structure correlations of molten slags. Apart from this it is also a prime variable required for fluid static and dynamics calculations at high temperatures. Molar volume which is the reciprocal of density is a thermochemical property and has direct reflections of Gibbs energies of the slag system. It is possible, using mutually compatible thermochemical and thermophysical data in the same model [1], to establish a relation between the two[2]. The key to the model developed was that the cation-anion attraction forces should be reflected both in the relative integral molar enthalpies of mixing as well as the molar volume of the silicate melts [3]. A direct relationship could be made between the two as they are directly correlated to the bonding between the nearest and next nearest neighbor ions in the silicate system.

There are various methods to measure density of slag systems at high temperatures. Table I shows a comparison between the popular techniques. From the comparison, it can be seen that the Archimedes Technique is a reasonable method in terms of both accuracy of the result as well as operating easiness.

Table I: Comparison between popular techniques for density measurement.

Method	Advantages	Disadvantages
Maximum Bubble Pressure Technique [4]	High accuracy	Controlling atmosphere is difficult
Levitation Technique [5]	Most accurate	Expensive
Sessile Drop Technique [6,7]	Relatively easiest technique	Error is high
Archimedes Technique [8]	Better control of gas atmosphere Higher accuracy	Methods required to minimize error

CaO-SiO_2-Al_2O_3 ternary is the most extensively studied silicate system, with several researchers carrying out density measurements at various compositions [9-12]. However, very few have made measurements in the low silica region [4, 13]. Silicate structure variations with change in temperature have been successfully explained by Lee and Gaskell[4].

The aim of the present work is to determine the density of CaO-SiO_2-Al_2O_3 slags in the low silica region. The Experimental values obtained would then be compared with the corresponding values obtained from the density model developed by Persson et al.[1] as well as with experimental works of Zielinski and Sikora[13]. Attempt would also be made to find the corresponding binary silicate densities and provide an approximate estimation of the density of pure CaO from the experimental values obtained. Further, based on enthalpy and expansivity variations, some approximations to the silicate structure variation with change in temperature would also be suggested.

The changes in the silicate structure also affect other slag properties like sulfide capacity. This is explained by the experiments conducted on the CaO-SiO_2-Cr_2O_3 slag system in the metasilicate region [14]. The variation of sulfide capacity shows a decrease as Cr^{2+} replaces Ca^{2+} in the slag, then increasing with further increase in the Cr^{2+} content. Hence using the experimental values of density (orthosilicate composition) and sulfide capacity measurements (metasilicate composition), the effect of polymerization on the slag structure and later on the corresponding properties were explained using the structural analysis of Gaskell and coworkers.

2. Experimental

For high temperature density measurements, the material selection for the crucible as well as bob and wire arrangement is of crucial importance for high temperature measurements especially in the case of slag systems. Platinum-30% Rhodium bob and wire were used as this alloy is inert to the chemical attack by the slag and functions without any mechanical break-down at the experimental temperatures. Armco iron crucibles were used for the measurement; hence there was a limitation to the maximum temperature for the density measurement. The measurement temperature range was 1683-1733 K. The CaO-Al_2O_3-SiO_2 slag was prepared from pure raw materials supplied by Alfa Aesar, Germany, shown in Table II. The raw materials were dried in a muffle furnace maintained at 1273 K for 24 hours before mixing thoroughly. The slag compositions were selected from Slag Atlas[15] and their melting points were verified by Thermo-Calc® so that the slags in the homogeneous liquid phase region above 1673 K. The experimental set-up and procedure has been explained elsewhere [16].

Table II: Details of materials used for preparing the slag.

Material	Purity (metals basis)
CaO	99.95 %
SiO_2	99.8 %
Al_2O_3	99.97%

3. Results

The density measurements were obtained at 1683 K and 1733 K. The various slag compositions investigated in the present work and the results obtained are presented in Table III. It could be observed that, as the silica content of the slags studied increased, the density decreased significantly. A similar trend has been verified in the measurements with binary FeO-SiO_2 slags studied by Lee and Gaskell [4], CaF_2-SiO_2 melts by Yakobashvili [17], ternary CaO-Al_2O_3-SiO_2 slags studied by Bochorishvili *et al.*[12] and Zieliński *et al.*[13] and in quaternary Al_2O_3-CaO-MgO-SiO_2 slags studied by Winterhager *et al.* [11].

Table III: Density, Temperature coefficient and Volumetric expansion of low silica CaO-SiO_2-Al_2O_3 ternary slags. Experimental errors (due to reproducibility and other factors) have been shown.

Sl No.	CaO (mass %)	Al_2O_3 (mass %)	SiO_2 (mass %)	ρ_{1683} (g/cm^3)	ρ_{1733} (g/cm^3)	Temperature Coefficient x 10^5 (m^3/kg K)	Expansivity x 10^3 (K^{-1})
1	51.5	43.5	5.0	3.09±0.08	2.88±0.07	-9.52	1.46
2	51.5	38.9	9.6	3.00±0.03	2.79±0.03	-9.52	1.50
3	51.5	34.5	14	2.98±0.04	2.76±0.03	-9.09	1.59

The experimental error was calculated in accordance with the probable measurement errors occurring, i.e.

a) The error due to the measurement of the mass of the bob and

b) The measurement of the height of the molten slag.

The error occurring due to the mass measurement using the balance would depend on the inherent error provided by the instrument and by the number of readings that could possibly be taken at a particular temperature. In each case, the mass measurement error was in line with the calibration error (±0.025g) of the instrument. The error due to the estimation of molten slag level using the bob-thermocouple arrangement was of the order of 1 mm. This was taken on an assumption that the minimum error which could be possible during height estimation was of the same order of magnitude. This error in measurement would result in a volumetric error of 0.028 cm^3.

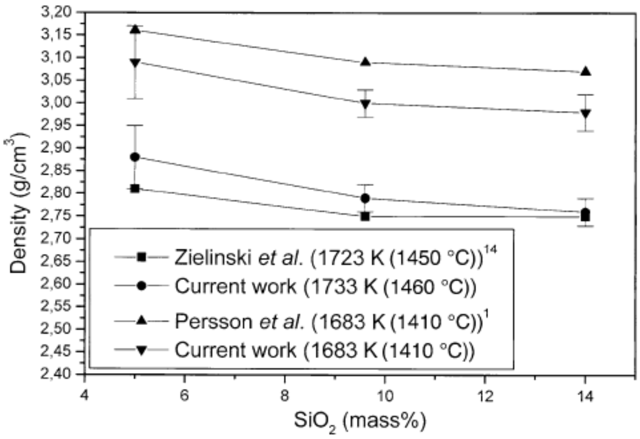

Figure 1: Comparison between density values of the current work with the model proposed by Persson et al at 1683 K [1] and the results of Zielinski et al at 1723 K [13]. Experimental error bar values are shown for the current work indicating good agreement with both model and experimental results.

Figure 1 shows the comparison of the experimental results with those predicted using the model developed by Persson *et al.*[3] It is to be noted that the model values have an error inherent in them as it is difficult to incorporate fixed density values for pure CaO, Al_2O_3 and SiO_2. Persson *et al.*[3] have mentioned that there were difficulties in retrieving reliable experimental data required for precise model calculations. The authors also mention that, for systems containing CaO as a component, a marked deviation from experimental data was to be expected owing to the unreliable molar volume value of CaO in super-cooled state, which induced uncertainties in the measurements of densities for binary systems like CaO- SiO_2 and Al_2O_3-CaO within +/- 10% and +/- 5% error limits respectively. Taking this into consideration, the agreement between the present experimental data and those predicted by the model can be considered reasonable.

The experimental values obtained at 1733 K were compared to those obtained with similar compositions carried out by Zielinski and Sikora [13] using maximum bubble pressure method. Good agreement between the values can be observed in Figure 1. Some density measurements were also carried out by the present authors using X-ray sessile drop method at higher temperatures. These values were also in agreement with the extrapolated densities obtained by the Archimedes method.

4. Discussion

Prediction of binary densities

The model developed by Persson *et al.*[1] actually estimates the molar volumes /densities of ternary slag melts from the corresponding binary slag systems. Conversely, it could be possible to find the densities of the binary slags from the experimental values. As the experiment was carried out at a fixed weight percentage of calcium oxide, the predictions of the densities of binary slag sub systems *viz:* CaO- SiO_2 and CaO- Al_2O_3 were facilitated. The density values for the CaO- Al_2O_3- SiO_2 slag was plotted with varying SiO_2 content for a given temperature as shown in Figure 2. A linear fit was made to the graph obtained as an approximation which showed the variation of the density as a function of silica content. Similar methods were used in the present work to find the densities of the binary CaO- SiO_2 and CaO- Al_2O_3

slag systems by extrapolating from the ternary to the silica rich as well as silica deficient zones respectively. The values obtained were compared with density values from the model mentioned above as well as other references[13, 18].

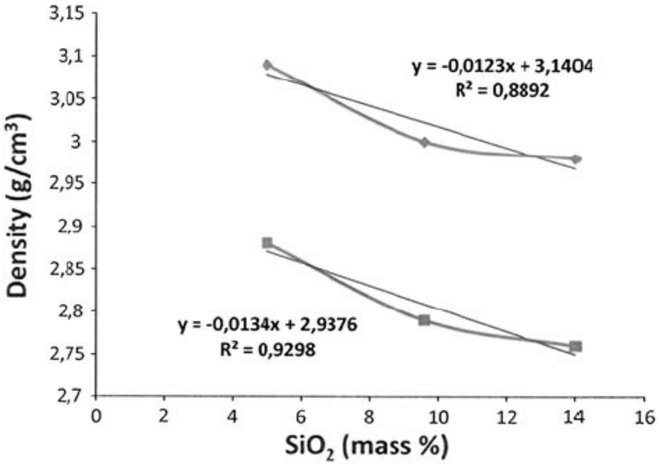

Figure 2: Linear fit to the ternary CaO- SiO_2-Al_2O_3 slag densities. The square symbol represents the density values at 1733 K and the diamond symbol indicated the density values at 1683 K.

Table IV shows the predicted binary slag density values using the linear fit equation. The model values were higher compared to the results from linear fit model, the reason for this deviation could be due to the uncertainties in the model predictions based upon uncertainties in the available literature data related to a) activity measurements b) estimation of molar volume of super cooled CaO. Another cause for the deviation would be the degree of linear fit due to lesser number of data points.

Table IV: Prediction of binary densities from ternary values and comparison with other references.

CaO (mass %)	SiO_2 (mass %)	Al_2O_3 (mass %)	ρ_{1683} from experimental results	ρ_{1733} from experimental results	ρ_{1683} Persson *et al.*	ρ_{1733} Persson *et al.*	ρ from literature
51.5	-	48.5	3.14	2.94	3.28	3.29	2.94 [13]
51.5	48.5	-	2.54	2.29	2.92	2.86	2.72 [18]

[13] Composition: 50.12% CaO- 49.88% Al_2O_3 , Temperature : 1723 K

[18] Composition: 50% CaO- 50% SiO_2 , Temperature : 1773 K

Comparison of the predicted density of CaO- Al_2O_3 slag at 1683 K was in very good agreement with the values of Zielinski and Sikora [13]. The reference value used for CaO-SiO_2 corresponds to a composition 50-50 wt% of both components taken at 1773 K.

Comparison with high silica systems

From the equation derived by the linear fitting of the density data points as explained in the previous section, it is possible to approximately estimate the densities of high silica compositions at 1733 K. Table V shows the density estimates and a comparison of the same with established research data. It was observed that there is good agreement with the density values obtained at the similar temperatures with high silica content.

Table V: Comparison of the densities derived from present measurements and those reported in the literature for high silica slag systems.

SiO_2 (mass %)	Density (Present work)	Density (Zielinski et al)[13]	Density (Bochorishvili et al)[12]	Density (Takayanagi et al)[7] T=1723 K

	T=1733 K	T=1723 K	T=1753 K	
0	2.92	2.94	-	-
1	2.91	2.94	-	-
3	2.89	2.87	-	-
5	2.87	2.81	2.90	-
10	2.82	2.75	2.75	-
15	2.77	2.75	2.70	-
20	2.71	2.68	2.70	-
25	2.66	-	2.75	-
30	2.61	-	2.65	-
39.5	2.52	-	-	2.72

Structural interpretations

Explanations for the decrease in density with increase in temperature can be traced to structural factors. In the case of ternary silicate melts, if the binary silicates are of equal silica mole fraction and if the cations are of similar size and valency, mixing could be considered ideal[19, 20]. However, in the present situation, the cations are of different valence states and size; hence non-ideal mixing would result. In the current slag compositions studies, the mole percent of SiO_2 was well-below 33% required for the orthosilicate composition. This would correspond to the existence of discrete SiO_4^{4-} tetrahedral units along with O^{2-} in the silicate melt and thus ruling out the possibility of the impact of silicate polymerization on the volumetric expansion at high temperatures. Hence, it is felt that the major focus should be given to the ionic bonding for the explanation of the decrease in melt densities with increase in temperature.

It is widely understood that any ion with an ion-oxygen parameter, (defined by the Coulumbic force between the cation and oxygen anion) in the range of 0.7 -1.7 could behave either as a network former or modifier depending on the melt environment [21]. The melt system would consist of Ca^{2+}, AlO_4^{-5}, SiO_4^{4-}, O^{2-} and O^- ions. The high CaO and Al_2O_3 contents in the slag suggest that the predominant bonding would be between the two. Some CaO would behave as a network modifier hence creating more non-bridging oxygen in the melt. As the ion-oxygen parameter also represents the Coulombic interaction between the oxygen ion and cation, Al^{3+} being in the higher side (1.66) along with Si^{4+} (2.45) as compared to Ca^{2+} (0.7), the predominant ionic expansion should be that contributed by the Ca-O bonding.

Figure 3 shows the volumetric expansion coefficient plotted against the molar fraction of alumina content in the slag. The CaO - SiO_2 and CaO - Al_2O_3 binaries are at the left and right extremes respectively. It could be observed that the melt expansivity decreases with increase in alumina content. The region corresponding to the present work is that between 0.25 - 0.3 mole fractions of Al_2O_3. In this region, the variation in the CaO content was 0.53-0.64, it could be concluded that the decrease in expansivity as seen in Figure 3 was due to the reduction in silica content and increase in the Ca-O bonds which resulted in more ionic bonds hence reducing volumetric expansion. Further, as the mole fraction of CaO was greater than that of Al_2O_3, the melt expansivity would be expected to be predominantly due to the ionic expansion of the Ca-O bonds.

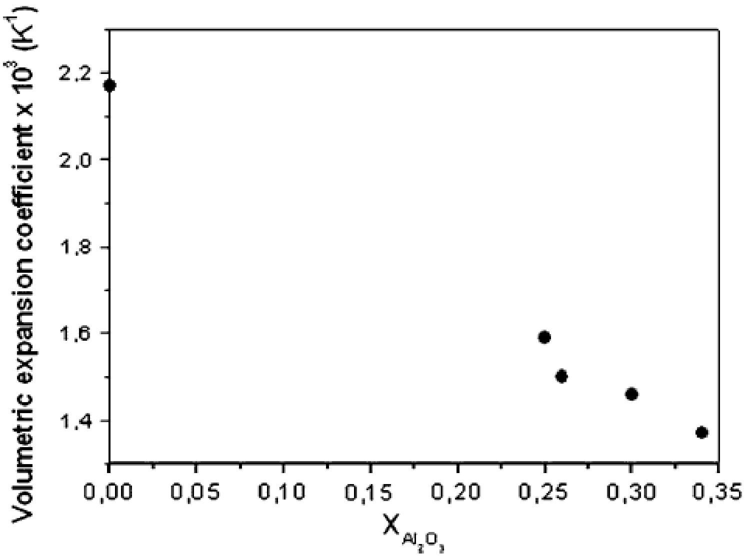

Figure 3: Expansivity variation with alumina content. Left extreme indicates 51.5% CaO- 48.5% SiO_2 binary region and the right extreme indicates the 51.5% CaO- 48.5% Al_2O_3 binary.

The decrease in the melt expansivity towards the CaO- Al_2O_3 binary suggests that a stable structure with respect to Ca-Al-O bonds seems to be taking place which could lead to microsegregation. In other words, the drooping melt expansivity curve could indicate that the inherent ionic bond expansivity is being counteracted by the thermal relaxation caused by microsgeregation. This was earlier explained by Lee and Gaskel [4] in FeO-SiO_2 and CaO-SiO_2 melt systems. As the mole fraction of CaO was greater than that of Al_2O_3, the melt expansivity could predominantly be due to the ionic expansion of the Ca-O bonds.

Lee and Gaskel [4] have mentioned that the inherent expansivities of the bond types and the degree of polymerization are two major factors influencing the expansivity of a binary silicate melt; this observation could be true for ternary melts as well. As Ca^{2+} is the predominant cation in the melt, the change in the volume which resulted in the decrease in density of the melt could be attributed to the bond expansivities in the order,

Al^{3+}- O^{2-} < Ca^{2+} - O^{2-} < Ca^{2+} - O^{-}

The slag structure variations in the metasilicate composition were studied in terms of sulfide capacity measurements. CaO-Cr_2O_3-SiO_2 slag was studied with silica content ranging from 43 – 61 % [14]. The sulfide capacity values were plotted against $X_{CrO}/X_{CrO1.5}$. It was observed that the sulphide capacity decreased with increase in $X_{CrO}/X_{CrO1.5}$ at constant basicity. The trend was observed to be consistent in three different basicity ratios. In addition, the slag basicity had a strong influence on the ratio $X_{CrO}/X_{CrO1.5}$ [14].The Cr^{2+}/ Cr^{3+} ratio decreased with an increasing basicity. This behavior was analogous to that of the variation of (Fe^{2+}/Fe^{3+}) ratio in silicate slags [22]. With the addition of CrO to the CaO-SiO_2 system, the Ca^{2+} was gradually replaced by less basic Cr^{2+} and, consequently, one would expect a decrease in the sulfide capacities. At silica concentrations above the orthosilicate composition, Richardson[23] suggested that polymerization of the silicate network would provide the necessary oxygen ions for the exchange reaction with sulfur. The polymerization reaction may be represented as follows:

$$2(\vdots\ \ Si-O^{-})\leftrightarrow(\vdots\ \ Si-O-Si\ \ \vdots)+O^{2-}$$

Lee and Gaskell [4] reported that, for the system 1.273 (FeO, CaO) SiO_2, the experimental thermal expansivity showed a minimum at about 0.4 mole fraction of CaO at 1773 K. Lee and Gaskell attributed this behavior to the inherent expansivities of the cation-anion bond types as well as to the degree of polymerization—apart from the temperature dependence on the degree of polymerization. Lee and Gaskell demonstrated that calcium silicate melts were less polymerized than the corresponding iron silicates. It is reasonable to assume that the behavior of Cr^{2+} would be somewhat similar to that of Fe^{2+}, even though the chemistry of CrO-containing melts is not well known. Thus, it is reasonable that, beyond the minimum point, the polymerization reaction may favor an increase in the sulfide capacities.

5. Conclusions

Measurements of densities of low silica $CaO\text{-}SiO_2\text{-}Al_2O_3$ systems was made using Archimedes principle and the results obtained were in good agreement with those obtained from the model earlier developed in the present group by Persson *et al.*[3] as well as with works of Zielinski and Sikora [14]. A suitable value for the densities of $CaO\text{-}Al_2O_3$ and CaO- SiO_2 binaries were obtained by extrapolating the ternary densities. Higher silica systems were also assessed and the experimental values showed good agreement. As the current slag composition had mole percent of SiO_2 well below 33% required for the orthosilicate composition, discrete SiO_4^{4-} tetrahedral units would exist along with free O^{2-} ions. Thus, the impact of silicate polymerization for volumetric expansion at high temperatures would be negligible. It was hence concluded that the change in expansivity was due to the ionic expansion contributed predominantly by the Ca^{2+} - O^{2-} , Ca^{2+} - O^{-} bonds present in the melt. The impact of polymerization on the sulfide capacities was studied in the metasilicate composition using $CaO\text{-}Cr_2O_3\text{-}SiO_2$ slag. It could be concluded that beyond a minimum CrO composition, the polymerization reaction may favor an increase in the sulfide capacities.

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