Experimental Study for Measuring Density of slag melts by An Established Archimedean Double-bob Method

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Abstract. The apparatus of Archimedean double-bob method for practicing accurate was established for density measurements of slag melts. The accuracy of density measurements at room temperature to establish measurements was determined in the following ways. Firstly, the densities of water were measured at 25, 30, 35, and 40 °C. Secondly, the densities of silicone fluids with the viscosities 0.01, 0.999, 4.850, and 29.44 Pa·s were measured at 25 °C. The measured densities have good agreement with the data of water standards with a precision of 0.07% and silicone fluid standards with a precision of 0.16%. The densities of Na₂O–SiO₂ slag melts with 60, 70 and 80 mol % SiO₂ were measured in the temperature range from 1350 to 1500 °C. The density decreases with increasing temperature and increases with increasing SiO₂ contents for all compositions. The reproducibility of this work is within the error estimation of density measurements. The density results of Na₂O–SiO₂ melts with 60, 70 and 80 mol % at 1400 °C show that the measurements data are within 0.23 % of the density values.

Keyword: Archimedean double-bob, density, slag melt, temperature, composition

1. Introduction

Physical property data e.g., density, viscosity, surface tension for coal slags are required in the design, operation, and the development of gasifier in the IGCC (Integrated Gasification Combined Cycle) [1]. The density of slag melts is one of fundamental and important properties for IGCC process as shown in Figure 1 [2,3]. However, limited studies on reliable data of density have been reported for coal slag melts [4]. Furthermore, the chemical compositions of coal slag melts from different origin countries can vary significantly and consequently the density of these coal slags can show appreciable variability [5].

Density of melts is necessary for the calculation of other properties, such as molar volume and coefficient of volume expansion in order to discuss the molecular structure of slag melts [9–11]. The coefficient of volume expansion also is one of important physical properties to control the melting process of slag melts [9].

The density measurements at high temperatures have been mainly carried out using maximum bubble pressure, pycnometer and Archimedean single- or double-bob methods [10]. The Archimedean methods give reproducible data sets with better precision [11]. Therefore, the Archimedean double-bob method is selected in this work. This convenient technique was established presently, and temperature dependence of the density was examined. The objective of this research describes an established Archimedean double-bob method for measuring the melt density of water, silicone fluid and slag melts in silicate system containing Na₂O–SiO₂ (mol%).
2. Principle of Measurements

Density of melts were measured using the Archimedean double-bob method. The Principle of the Archimedean double-bob method is to measured buoyancies of two platinum bobs with different volume immersed in melts as shown in Figure 2. The buoyancy \( W \) against the volume \( V \) of the bob immersed in a glass melt is determined by the following equation [12].

\[
W = V \rho - 2\pi r y \cos \theta + A
\]

where:
- \( W \) is the buoyancy of the bob immersed in the melt \( (10^{-3} \text{ kg}) \)
- \( V \) is the volume of the bob immersed in the melt \( (10^{-6} \text{ kg}) \)
- \( r \) is the radius of the suspending wire \( (10^{-3} \text{ kg/m}) \)
- \( \rho \) is the density of the melt \( (10^{-3} \text{ kg}) \)
- \( y \) is the surface tension of the melt \( (10^{-3} \text{ N/m}) \)
- \( \theta \) is contact Angel between the suspending wire and the melt \( (^\circ) \)
- \( A \) is the constant that is related to the adhesion and convection of air \( (10^{-3} \text{ kg}) \)
The buoyancy \((W_1)\) against the volume \((V_1)\) of the first (large) bob and the buoyancy \((W_2)\) against the volume \((V_2)\) of the second ball (small) bob immersed in a glass melt are determined by Figure 3 and the same equation.

\[
W_1 = V_1 \rho - 2\pi r y \cos \theta \\
W_2 = V_2 \rho - 2\pi r y \cos \theta + A
\]

From Eq. 2 and 3, the density \(\rho\) of a glass melt can be expressed by the following equation.

\[
\rho = \frac{(W_1 - W_2)}{(V_1 - V_2)}
\]

where.
- \(W\) is the buoyancy of the bob immersed in the sample \((10^{-3} \text{ kg})\)
- \(V\) is the volume of the bob immersed in the sample \((10^{-6} \text{ kg})\)
- \(r\) is the radius of the suspending wire \((10^{-3} \text{ kg/m})\)
- \(\rho\) is the density of the sample \((10^{-3} \text{ kg})\)
- \(\theta\) is the acceleration of gravity \((\text{m/s}^2)\)

Because the same suspension wire is used for each buoyancy measurement, the effect of surface tension, adhesion and convention on the suspension wire are identical, and can be eliminated. The volume of each bob at the measuring temperature was calculated from the following equation.

\[
V'_1 = V_1 \times (1 + 3\alpha \Delta T) \\
V'_2 = V_2 \times (1 + 3\alpha \Delta T)
\]

where.
- \(V'\) is the volume of the bob at the measuring temperature \((10^{-6} \text{ kg})\)
- \(V\) is the volume of the bob at the room temperature \((10^{-6} \text{ kg})\)
- \(\alpha\) is the thermal expansion coefficient of bob \((1.0102 \times 10^{-5} \text{ K}^{-1}, 300-1273 \text{ K})\)
- \(\Delta T\) is the temperature difference between the measuring temperature and room temperature

The Volume of each bob at the room temperature was determined by measuring buoyancy of each bob in distilled water, of which the density is known, at the room temperature.

From Eq 1 and 2, the density \(\rho\) of a glass melt can be expressed by the following equation.

\[
\rho = \frac{(W_1 - W_2)}{(V_1 - V_2)} = \frac{(W_1 - W_2)}{(1 + 3\alpha \Delta T) \times V_1 - V_2}
\]

And then the final equation.

\[
V_1 - V_2 = \frac{W_1 - W_2}{\rho_w}
\]

where
- \(V_1, V_2\) are Volume of the large and small bobs immersed in the melt
- \(W_1, W_2\) are Buoyancy of the large and small bobs immersed in the melt
- \(\rho_w\) isDensity of purified water at room temperature
3. Materials and Methods

The samples of density measurements were Na$_2$O-SiO$_2$ slag melts with 60, 70 and 80 mol % SiO$_2$. The samples were prepared from a mixture of raw materials of Na$_2$CO$_3$ and SiO$_2$ powders with 99.99 % purity. The mixture was melted at 1400 ºC for 2 hours in a Pt crucible placed in a MoSi$_2$ box furnace. The slag melt was poured onto iron mold for cooling as a slag sample. The sample was crushed and then re-melted in the air for density measurements in the temperature range from 1350 to 1550 °C.

The sample of density measurements of water and silicone fluid were measured at room temperature 25 to 40 °C. The samples of silicone fluid provided by the Silicone viscosity standard fluids of Brookfield. The chosen sample similar with the viscosity of slag melts of 0.01, 0.999, 4.850, and 29.44 Pa·s.

The apparatus of Archimedean double-bob method used is similar to that[13], [8], [14] and is illustrated in Figure. 4. We have added some experimental techniques such us a computer interface to

**Figure. 4** Schematic apparatus for density measurements of slag melts: (a) whole diagram, (b) sample, and (c) large and small bobs.
see directly the graph buoyancy occurred in the monitor of PC and refractory under the electrical balances to avoid window blowing from the furnace.

The measuring temperatures were selected carefully that allows measure performed or until crystallization occurred in the sample based on fact sage data bank [15]. The buoyancies of the each bobs were measured by electrical balance with the addition a computer interface to connect of PC. The difference between two averages was entered into Eq. 9 to calculate melt density,

\[ \rho = \frac{W_1 - W_2}{V_1 - V_2} \]  \hspace{1cm} (9)

where \(W_1\) and \(W_2\) are the buoyancies and \(V_1\) and \(V_2\) are the submerged volumes of the large and small bobs, respectively. The thermal expansion of large and small bobs is corrected by Eq. 10, the data for thermal expansion of platinum (Waseda et.al., 1975) [6],

\[ V_1 - V_2 = (1 + 3\alpha \Delta T). (V_1' - V_2') \]  \hspace{1cm} (10)

where \(\alpha\) is the thermal expansion of Pt, \(\Delta T\) is temperature difference between measuring and room temperatures, and \(V_1\)' and \(V_2\)' are the volume of the large and small bobs at room temperature, respectively. Considering accuracy and reproducibility of the measurement were investigated density of water and silicone fluid as a standard sample measured in the room temperature.

4. Results and Discussion

4.1. Error Estimation

The error estimation of the above method was taken as the deviations in the determination of buoyancy, temperature, and electrical balance reading. The errors caused by temperature, viscosity and inhomogeneity of the sample in density measurements. The error range was depended on composition in slag melts [16]. The average value of error was 0.15% for all measured densities.

In order to confirm the reproducibility of density values, the standard sample was measured in the following ways. Firstly, the densities of water were measured 25, 30, 35, and 40 °C. Fig. 5 shows the densities of water were measured to be 0.9966, 0.9945, 0.9939, and 0.9912 at 25, 30, 35, and 40 °C, respectively. The measured densities have good agreement with data of previous study [17] with a precision of 0.07%.

![Figure 5](image_url)

**Figure 5** Variation of the density as a function of temperature in water. The dashed lines represent average linear fit of this study and previous study.
Secondly, the density of silicone fluids with the viscosities 0.01, 0.999, 4.850, and 29.44 Pa·s were measured at 25 °C. Fig. 6 shows that the densities of silicone fluids were tested to be 0.941, 0.972, 0.973, and 0.974 g/cm³, respectively. The measured densities have good agreement with the data of silicone fluid standards with a precision of 0.16%.

![Figure 6](image)

**Figure 6** Variations of density with viscosity of silicone fluids. The dashed lines represent average linear fit of this study and previous study.

The results show that the precision density measurements of water and silicone fluid were 0.07 and 0.16 % of the density values, respectively. The accuracy and reproducibility of this work is within the error estimation of density measurements. Furthermore, the density of water and silicone fluid values are good agreement with previously reported values [18] within a deviation with the mean differences of 0.10%. The accuracy and reproducibility of density for water and silicone fluids support the reasonable results of density measurements in this work for measuring slag melts at high temperature.

### 4.2. Density of Na₂O-SiO₂

The difficulties of measuring density at high temperature are the consistency buoyancies of the bobs [12]. Data on the temperature dependence of the buoyancy of the Pt-wire and bobs immersed in the slag melts are shown in Fig. 7.

![Figure 7](image)

**Figure 7** Relation between buoyancy (g) and time (s) for (a) small and (b) Pt bobs in 20Na₂O-80SiO₂ slag melt. The dashed lines represent average linear fit of the buoyancy.
The buoyancy data became stable within 30 min after the immersion into the slag melts. The average of buoyancy during the last 30 min was used in density calculation.

Fig. 8 shows the temperature dependences of density for Na$_2$O-SiO$_2$ slag melts with 60, 70 and 80 mol % SiO$_2$. There are linear relationships between density and temperature for all Na$_2$O -SiO$_2$ slag melts between 1350 and 1500 °C. The densities of the NaO-SiO$_2$ slag melts decrease linearly with increasing temperature. The density varied from 2.213 to 2.238 g/cm$^3$. The density of Na$_2$O -SiO$_2$ slag melts decreases almost monotonically with increasing SiO$_2$ content.

![Figure 8](image_url)

**Figure 8.** Variations of density with temperature for NaO-SiO$_2$ slag melts with 60, 70 and 80 mol % SiO$_2$. The dashed lines are least square fit of this study

![Figure 9](image_url)

**Figure 9** Experimental data of previous and this study and model fit for the binary system Na$_2$O – SiO$_2$ at 1400 °C
The apparatus of Archimedean double-bob method was established for density measurements of slag melts. The densities of water and silicone fluid were measured and have good agreement with the data of Bockris [13,19,20] and this study and the model fit [21] for the binary system Na₂O–SiO₂ at 1400°C. It can be seen that the experimental data by Shartsis et al. [19] and Bockris et al. [13] are different. It is possible that Bockris in 1955 used the experimental data by Shartsis et al. from 1951 for calibration. The measured densities data of this study have good agreement with the data of Bockris data with a precision of 0.23%.

From Fig. 9, it can be estimated that the error of repeated density measurements at 1400°C considering several investigators is approximately 0.007 g/cm³. The error of repeated density measurements of one investigator using one experimental technique is approximately 0.001 to 0.01 g/cm³ (4) for Na₂O–SiO₂ slag melts. The difference between the error of one investigator compared to the overall error of several investigators is caused by small systematic errors. Furthermore, the accuracy and reproducibility of density for Na₂O–SiO₂ (mol%) slag melts support the reasonable results of density measurements for gasified coal and synthesized slag melts in our previous study [4].

5. Conclusion
The apparatus of Archimedean double-bob method was established for density measurements of slag melts. The densities of water and silicone fluid were measured and have good agreement with the data of water standards with a precision of 0.07% and silicone fluid standards with a precision of 0.16%.

The temperature dependences of density for Na₂O–SiO₂ slag melts with 60, 70 and 80 mol % SiO₂. There are linear relationships between density and temperature for all Na₂O–SiO₂ slag melts between 1350 and 1500 °C. The densities of the Na₂O–SiO₂ slag melts decrease linearly with increasing temperature. The density varied from 2.213 to 2.238 g/cm³. The density of NaO₂–SiO₂ slag melts decreases almost monotonically with increasing SiO₂ content.

The accuracy and reproducibility of density measurements for Na₂O–SiO₂ (mol%) slag melts support the reasonable results of density measurements for measuring gasified coal and synthesized slag melts

6. References
[1] Arman, Tsuruda A, Arma LH, Takebe H. Viscosity measurement and prediction of gasified and synthesized coal slag melts. Fuel 2017;200:521–8. doi:10.1016/j.fuel.2017.03.094.
[2] Aineto M, Acosta A, Rincon J, Romero M. Thermal expansion of slag and fly ash from coal gasification in IGCC power plant. Fuel 2006;85:2352–8. doi:10.1016/j.fuel.2006.05.015.
[3] Mondol JD, McIlveen-Wright D, Rezvani S, Huang Y, Hewitt N. Techno-economic evaluation of advanced IGCC lignite coal fuelled power plants with CO2 capture. Fuel 2009;88:2495–506. doi:10.1016/j.fuel.2009.04.019.
[4] Arman, Okada A, Takebe H. Density measurements of gasified coal and synthesized slag melts for next-generation IGCC. Fuel 2016;182:304–13. doi:10.1016/j.fuel.2016.05.117.
[5] Hsieh PY, Kwong KS, Bennett J. Correlation between the critical viscosity and ash fusion temperatures of coal gasifier ashes. Fuel Process Technol 2016;142:13–26. doi:10.1016/j.fuproc.2015.09.019.
[6] Mysen BO, Virgo D, Seifert FA. The structure of silicate melts: Implications for chemical and physical properties of natural magma. Rev Geophys Sp Phys 1982;20:353–83. doi:10.1029/RG020i003p00353.
[7] Mills KC. Estimation of physicochemical properties of coal slag and ashes. Miner Mater Ash Coal, Am Chem Soc Washington, DC 1986;301:195–214. doi:10.1021/bk-1986-0301.ch015.
[8] Hwang C, Fujino S, Morinaga K. Density of Bi₂O₃–B₂O₃ binary melts. J Am Ceram Soc 2004;87:1677–82. doi:10.1111/j.1551-2916.2004.01677.x.
[9] Kuromitsu Y, Yoshida H, Takebe H, Morinaga K. Interaction between alumina and binary glasses. J Am Ceram Soc 1997;80 (6):1583–7. doi:10.1111/j.1151-2916.1997.tb03020.x.
[10] Sugawara T, Katsuki J, Shiono T, Yoshida S, Matsuoka J, Minami K, et al. High-temperature heat capacity and density of simulated high-level waste glass. J Nucl Mater 2014;454:298–307. doi:10.1016/j.jnuclmat.2014.07.055.
[11] Linard Y, Nonnet H, Advocat T. Physicochemical model for predicting molten glass density. J
Acknowledgments
This research is supported by New Energy and Industrial Technology Development Organization (NEDO) of Japan and Directorate General of Human Resource for Science, Technology and Higher Education (DIKTI) of Indonesia.