HIGH TEMPERATURE VISCOSITY MEASUREMENTS FOR SLAGS AT CONTROLLED OXYGEN POTENTIAL

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ABSTRACT

As process feedstocks to operations become more complex and variable, the control of viscosity of slags generated in various metallurgical and power generation processes is essential. To provide key data to enable this problem to be addressed a new high-temperature (up to 1600ºC) apparatus for viscosity measurements has been developed. The apparatus has several distinctive features to overcome some of experimental uncertainties. Viscosity measurements are based on the Couette-type (concentric cylinders) wide-gap technique suitable for both homo- and heterogeneous slag measurements. The whole apparatus is completely isolated from the external atmosphere, which enables measurements to be carried out in neutral or Po_2*-controlled atmospheres. A variety of sensor/container materials can be employed for viscosity experiments, depending on a particular slag system or temperature range. The apparatus has a system of quenching slag samples at any time during the experiment, which allows the slag phase assemblage and compositions existing at the temperature to be analysed with various techniques including electron probe X-ray microanalysis (EPMA).*

Examples of recent viscosity measurements relevant to different metallurgical and power generation slags are presented.

INTRODUCTION

The viscosity of metallurgical slags is an important physical property in optimisation of the processes. However, high temperature measurement of the slag systems is a complex, costly- and time-consuming procedure. A number of different experimental designs have been used to measure slag viscosities including the rotating cylinder (inner or outer) [1, 2, 3, 4, 5], falling body [6, 7], and oscillation [8] techniques.

In carrying out these high temperature measurements a number of experimental difficulties can be encountered that may lead to uncertainties in the absolute values of the viscosities of the materials under study. The principal sources of these uncertainties arise from: 1) changes in slag composition; 2) changes in atmosphere (particularly, in the oxygen partial pressure); 3) changes in oxidation state of species in the slag; and 4) partial crystallisation of the slag.

During high temperature viscosity measurements the slag composition can vary due to reaction of the slag with container or sensor materials and selective vaporisation of species from the condensed system. It is therefore important to measure the composition of the slag immediately after the viscosity measurement. The control of gas atmosphere is also important in high temperature measurements for slags containing transition metals that can be present in two or more oxidation states (e.g. Fe, Mn, Cr, Ti, etc).

When the viscosity measurement is undertaken at temperatures below the liquidus the behaviour of the slag will be different due to solids formation (the so-called slurry effect) and changes to the composition of the remaining liquid phase. In these situations it is essential that accurate characterisation of the phase assemblages at temperature is carried out.

An experimental apparatus for high temperature viscosity measurements has been developed by the authors. This apparatus allows the slag viscosity measurements to be carried out in controlled or gas-tight atmosphere, and with the possibility of quenching the sample after the measurements have been completed. The microstructures and compositions of the phases present in the quenched sample can be measured with electron probe X-ray microanalysis.

METHODOLOGY

Description of the Viscosity Apparatus

Figure 1 shows a schematic diagram of the experimental apparatus for high temperature viscosity measurements used in this study. The rotating cylinder technique has been adopted in the measurement. Brookfield DVIII+ rheometers (e.g. LV (low viscosities) or HB (high viscosities)) are used depending on the viscosity range to be investigated. The Brookfield DVIII+ rheometer located on the moving platform rotates the alumina driving shaft with the spindle immersed into the slag, which is placed into the crucible. The crucible is suspended using an alumina tube and held onto the tube with Pt wires. The crucible is positioned within the hot zone of the Pyrex tube furnace. Temperature is measured by the thermocouple next to the crucible. The temperature of the furnace is controlled within 2°C and overall uncertainty of the temperature is within 5°C. A range of different materials (e.g. Al_2O_3, MgO, Fe, Mo, Pt) each suitable for a particular slag system can be selected for the spindle and crucible set. After the experiments have been carried out the sample is quenched using the plunger mechanism (alumina tube and stopper), which, on being activated, pushes out the crucible by shearing platinum suspension wires so that the crucible falls down into the water bucket and is thereby quenched. To control the gas atmosphere during experiments the rheometer is confined in a gas-tight chamber, the upper end of the furnace tube is connected with the chamber and the lower end of the furnace tube is closed by glass window. The experimental set-up also has the option to use the traditional bottom crucible support method.

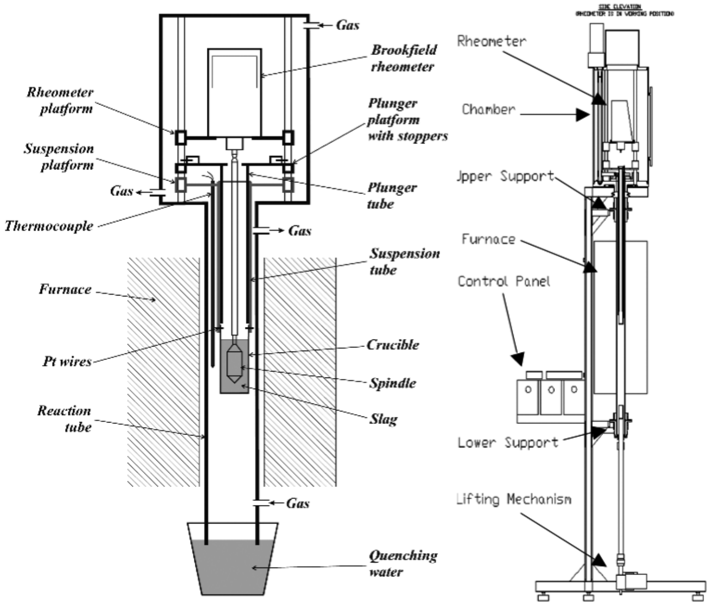

Figure 1: Schematic diagram of the Pyrosearch high-temperature viscosity apparatus

The features of this experimental set-up are:

Experiments can be performed in a gas-tight atmosphere

The atmosphere inside the viscosity apparatus can be controlled using mixtures of pure gases. For example, the CO + CO_2 gas mixture can be used at fixed CO/CO_2 ratio so that accurate oxygen partial pressure is controlled through the reaction $CO(g) + 0.5O_2(g) = CO_2(g)$.

The slag can be quenched after the experiment

The ability to quench the slag samples after the viscosity experiments is important since this enables the microstructure of the slag and compositions of the phases present in the slag at the temperature to be measured accurately after the viscosity measurement. In this way the uncertainty associated with the changes of the slag composition during the measurement can be minimised. In addition, presence of crystals, if any, during the experiment can be identified.

The geometries of bob and crucible used in this study are shown in Figure 2. The volume of the melted slag is usually kept constant. As the density of the slag varies the weight of the slag is adjusted for different slag systems.

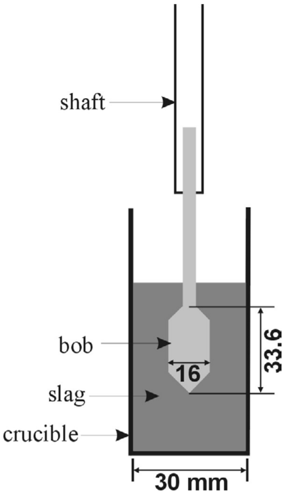

Figure 2: Illustration of the bob and crucible geometry for viscosity measurement

Calibration of the Rheometer

The viscosity of the fluid can be determined as follows:

$$\eta = K \frac{Ms}{\Omega} \tag{1}$$

where η is viscosity of a Newtonian fluid, K is the instrument constant, Ms [N m^{-1}] is the measured torque at a given rotation speed Ω. The instrument constant K depends only on spindle/crucible geometry and can be evaluated from calibration of the apparatus with fluids of known viscosity. In the present study spindle/crucible set has been calibrated at 25.0°C with the standard viscosity fluids supplied by Brookfield Engineering Ltd. for a range of viscosities (0.049 – 200.2 Pa·s). During calibration with the standard fluids the range of the most stable and accurate measurements was determined to be at 70-100 per cent of the maximal torque. This range was used for all experiments.

Slag Preparation

Approximately 35 ml of melted slag is required for each viscosity measurement. To accurately determine the height of the slag and obtain homogenous composition the slag has to be pre-melted before the viscosity measurement. Pure powders of chemicals such as SiO_2, Al_2O_3, MgO, Fe_2O_3, Fe, K_2O, PbO and CaO (calcined from $CaCO_3$) were mixed in an agate mortar with desired proportions and pelletised. It is usually not possible to fit all of the required mixture into the crucible in the first time - the slag therefore was prepared in two melting stages. On high temperature heating the composition of the slag may change. For example, K_2O and PbO can vaporise at high temperature. Under reducing conditions and high temperature iron dissolves in the Pt crucible and the composition of the slag changes. After the first melting stage the composition of the slag was measured by EPMA and additional K_2O, PbO or iron oxide was added to adjust the slag composition. The conditions used for high temperature melting of the slag, i.e. temperature and oxygen partial pressure, are the same as in the viscosity measurement. After equilibration the crucible and sample were rapidly lowered into cold end of the furnace.

Viscosity Measurement

The crucible containing fused slag was attached to the suspension tube by 0.5 mm diameter Pt wire. A B-type thermocouple (Pt-6%Rh/Pt-30%Rh) was attached to the suspension tube next to the crucible. The crucible was placed into the hot zone of the furnace. The plunger tube and rheometer were set up to the proper positions. The bob attached to an alumina shaft was suspended on the rheometer. When it is necessary the furnace was sealed and the reaction tube was flushed with $CO/CO_2/Ar$ gas mixture. The furnace was programmed so that the required temperature was reached over 4–6 hours with a linear heating rate and kept at this temperature. After equilibration at required temperature the bob attached to the rheometer was lowered slowly with rotation speed 30 rpm. When the bob touched the surface of the slag the readings of the rheometer showed a torque higher than 0 – this way the exact position of the liquid slag surface was identified. From this position the bob was lowered further 31 mm (note that the height of the slag changes when the bob is submerged into the slag) so that whole bob was submerged into the slag.

Once the bob is submerged in the slag the torque readings were taken at a fixed rotation speed. The constant torque reading at a given rotation speed indicates the slag has attained chemical equilibrium. It usually takes 2-24 hours before the equilibrium is achieved depending on the viscosity of the slag.

At a fixed rotation speed 60 torque readings (5 seconds for each reading) were taken. The first 10 readings were ignored since the rotation speed was not stable and the average of the rest 50 readings was taken as the final value. For a given temperature 3-5 rotation speeds were used. The viscosity was calculated by use of Equation (1).

When the viscosity measurements had been completed at a given temperature the temperature was changed for the next measurement. The measurements were usually carried out in the order from high temperature to low temperature. The CO/CO_2 ratios were also changed accordingly to achieve required Po_2. Constant torque reading at a new temperature indicates that the equilibrium has been achieved. Figure 3 shows two examples of torque reading for a given slag as a function of time at a given rotation speed. The reading started just after the temperature was decreased by 50 degrees. It can be seen that the stable torque reading is obtained after 12 minutes in case A and 15 minutes in case B. In actual measurements the waiting time was much longer to ensure that equilibrium has been achieved. If gas/slag equilibrium is involved the stable torque reading only indicates a local equilibrium surrounding the bob is attained. In this case the spindle was usually raised and lowed many times to ensure a uniform slag composition is achieved within the slag. The torque readings at different positions of the slag are measured to confirm the uniformity of the slag.

EPMA Measurement

After the viscosity measurements have been completed the sample was dropped into water so that phase assemblages at temperature can be retained. The quenched samples were sectioned, mounted and polished for EPMA measurement. The polished samples were coated with carbon using a JEOL (Japan Electron Optics Ltd) Carbon Coater for electron microscopic examination. A JXA 8200 Electron Probe Microanalyser with Wavelength Dispersive Detectors was used for microstructure and composition analyses. The analysis was conducted at an accelerating voltage of 15 kV and a probe current of 15 nA. The ZAF correction procedure supplied with the electron probe was applied. The average accuracy of the EPMA measurements is within 1 wt %. Under reducing conditions both Fe^{2+} and Fe^{3+} are present in the samples. However, only the metal cation ratios can be measured using the EPMA; the phase compositions are usually recalculated to oxides on the assumption that all iron is present as Fe^{2+}. The standards used for analysis were provided by Charles M Taylor Co., Stanford, California, USA.

When the slag and crucible are dropped into water if the cooling rate is high enough on quenching the liquid is converted to a glass phase. If no solid phase is present in the sample the composition of the glass phase will be the bulk composition of the slag. If solid phase is present in the slag at temperature the compositions of the liquid and solid phases can be measured by EPMA but the bulk composition of the slag has to be determined by other methods. After viscosity measurement all slag samples were sent to a commercial lab for bulk analysis using XRF.

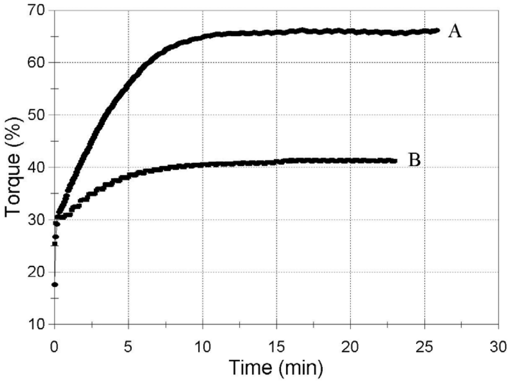

Figure 3: Plot of the torque reading as a function of time at a given rotation speed

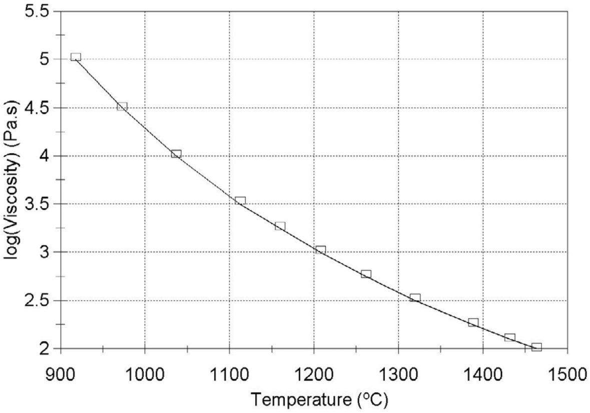

Figure 4: Results of viscosity measurements with the NIST SRM 710a in air solid line: viscosities given by NIST symbols: measurements in this study

RESULTS AND DISCUSSION

Viscosities have been experimentally determined for a number of different slag systems. Examples of the results are summarised in the following sections.

Soda-Lime-Silica Glass

A Standard Reference Material (SRM) 710a (soda-lime-silica glass) provided by the National Institute of Standards and Technology (NIST), USA was used to evaluate the reliability and accuracy of the viscosity apparatus. The measurements were carried out in air using the platinum crucible and spindle in the temperature range 918 to 1464°C. The sample was quenched immediately after viscosity measurements were completed. EPMA shows that only glass phase is present in the sample quenched from 918°C. The compositions of the sample have been measured before and after the viscosity measurement using EPMA and XRF. The compositions of SRM 710a are given in Table 1. It can be seen that the compositions of the samples did not change after the viscosity measurements. The compositions are little different by different measurement methods. The results of the viscosity measurements are given in Figure 4. The solid line in the figure represents viscosities given by NIST and symbols represent results in this study. It can be seen that the measured viscosity values are in very good agreement with those given by NIST. The difference is within 10% in the temperature range measured.

Table 1: Compositions (wt%) of the NIST SRM 710a before and after viscosity measurement

Sample	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	ZnO	TiO_2	As_2O_3	Sb_2O_3
Provided by NIST	67.55	2.1	8.05	9.3	8.5	3.6	0.4	0.05	0.2
EPMA before	68.2	2.1	7.1	9.9	7.8	3.5	0.4	0.2	0.8
EPMA after	67.8	2.1	7.3	10.0	7.9	3.5	0.4	0.2	0.8
XRF before	67.1	2.2	9.6	9.1	8.4	2.9	0.4	0.1	0.2
XRF after	67.3	2.2	9.5	9.0	8.3	2.9	0.4	0.1	0.2

Viscosities in the K_2O-CaO-SiO_2 System Relevant to Biomass Slags

The major components of the biomass slags are K_2O, CaO and SiO_2. It is difficult to measure the viscosity of the K_2O–containing system since K_2O vaporises at high temperature. With the present technique the composition of the slag is measured after the viscosity measurement so that effect of changes of the composition during the measurement on the final results is minimised. A synthetic slag with 41.8 wt% K_2O, 13.4 wt% CaO and 44.8 wt% SiO_2 has been used to determine the viscosities in the temperature range 1100 to 1400°C. The measurements were conducted using Mo crucible and bob under gas flow of ultra high purity argon. It can be seen from Figure 5 that the viscosity of this slag increases from 0.28 to 3.9 Pa.s when the temperature decreases from 1400 to 1100°C.

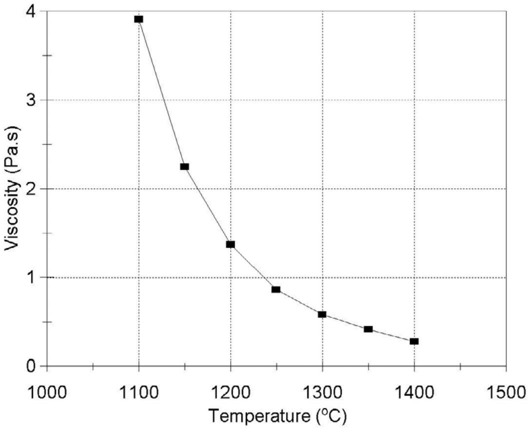

Figure 5: Experimentally determined viscosities of K_2O–CaO–SiO_2 slag

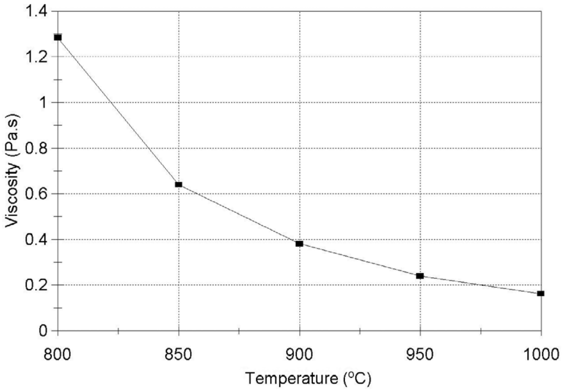

Figure 6: Experimentally determined viscosities of PbO-ZnO-Fe_2O_3-CaO-SiO_2 slag in air

Viscosities in the PbO-ZnO-FeO-Fe_2O_3-CaO-SiO_2 System Relevant to Lead Smelting Slag

The major components of the lead smelting slags are PbO, ZnO, FeO, Fe_2O_3, CaO and SiO_2. Since PbO vaporises at high temperature the composition of the sample has to be measured after the viscosity measurement. The bulk composition of the synthetic slag is 74.6 wt%, PbO, 2.9 wt% ZnO, 5.6 wt% Fe_2O_3, 1.5 wt% CaO and 14.8 wt% SiO_2. The viscosities were measured in air in the temperature range 1100 to 1400°C. The measurements were conducted using Pt crucible and alumina bob. 0.6 wt% Al_2O_3 was found to be present in the quenched slag indicating that there was interaction between the slag and bob. It can be seen from Figure 6 that the viscosities of this slag increase from 0.16 to 1.28 Pa.s when the temperature decreases from 1000 to 800°C.

Viscosities in the Al_2O_3-MgO-FeO-Fe_2O_3-CaO-SiO_2 System Relevant to Copper Smelting Slags

Recently it has been found that the concentrate feed-stocks at Kennecott Utah Copper Corporation (KUCC) occasionally contain higher than desired levels of SiO_2 and MgO. Increased levels of SiO_2 and MgO may influence the operability and integrity of the Flash Smelting Furnace. Viscosities have been measured to provide information to support KUCC in treatment of these high SiO_2– and MgO–containing concentrate. Examples of viscosity measurement are presented here for 2 synthetic copper smelting slags at controlled oxygen partial pressures. The bulk compositions of the slags presented in Table 2 were measured by XRF after the viscosity measurements. The viscosity measurements were conducted using Pt–10%Rh crucible and bob. The oxygen partial pressures were controlled at $10^{-8.0}$ atm by $CO/CO_2/Ar$ gas mixture. Iron was found to be dissolved into the crucible and bob during premelting. Extra iron oxide was added to obtain the required slag composition. It usually takes 6-24 hours to achieve equilibrium of slag/gas/metal. Figure 7 shows viscosities of the slags at temperatures 1300 to 1330°C and Po_2 $10^{-8.0}$ atm.

Table 2: Slag bulk compositions measured by XRF and phase compositions measured by EPMA for copper smelting slags

Sample	Phase	Composition (wt%)					
		FeO	SiO_2	CaO	MgO	Al_2O_3	Fe/SiO_2
Slag 1	bulk	51.6	39.4	3.4	2.2	3.5	1.0
Slag 2	bulk	57.4	29.1	3.2	6.9	3.3	1.5
Slag 2 quenched from 1300°C after viscosity measurement	glass	57.0	29.3	3.4	6.8	3.5	1.5
	olivine-primary	39.5	35.0	0.3	25.2	0.1	
	olivine-secondary	52.1	32.6	1.1	13.5	0.7	

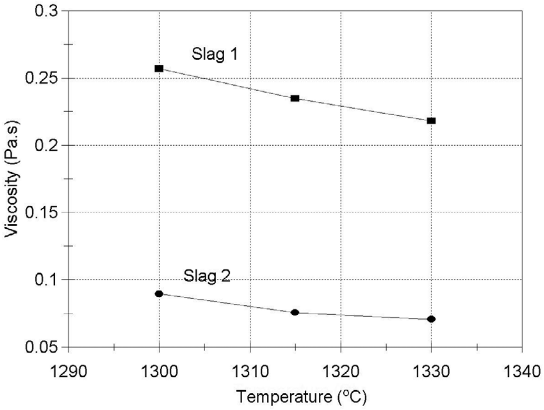

Figure 7: Experimentally determined viscosities of Al_2O_3-MgO-FeO-CaO-SiO_2 slag at $Po_2 = 10^{-8.0}$ atm

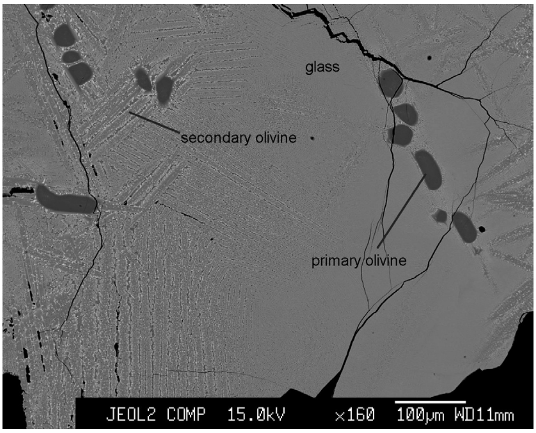

Figure 8: Microstructure of the copper slag 2 quenched from 1300°C and $Po_2 = 10^{-8.0}$ atm after viscosity measurement

It can be seen from Table 2 that the SiO_2 concentration in the slag 2 is lower than that in slag 1. It is well known that the viscosity of the silicate liquid is dependent on SiO_2 concentration. As a result, the viscosities of slag 1 are significantly higher than those of slag 2 in the conditions investigated. It was found that solid olivine phase $(Fe,Mg)_2SiO_4$ was present in the slag 2 quenched from 1300°C and $Po_2 = 10^{-8.0}$ atm after viscosity measurement as shown in Figure 8. It can be seen that primary olivine was present at temperature and secondary olivine was formed on cooling. It can be seen from Table 2 that primary olivine contains higher MgO than the secondary olivine.

Fit of Experimental Data with Weymann-Frenkel Equation

Weymann-Frenkel Equation [9] can be expressed in the following form for viscosity temperature dependence:

$$\mu = AT\exp(1000B/T) \qquad (2)$$

Where μ is the viscosity in Pa.s and T is the temperature in K. A and B are parameters characteristic of the slag.

From Equation (1) it is obtained

$$\ln(\mu/T) = 1000B/T + \ln(A) \qquad (3)$$

Equation (3) shows that $\ln(\mu/T)$ has linear relationship with 1000/T. Figure 9 presents correlation of $\ln(\mu/T)$ versus reciprocal temperature (1000/T) for the KCS slag, Pb slag and Cu slags. The solid lines in Figure 9 are the best fit using Equation (1) in Pa.s and the symbols are the experimentally determined results.

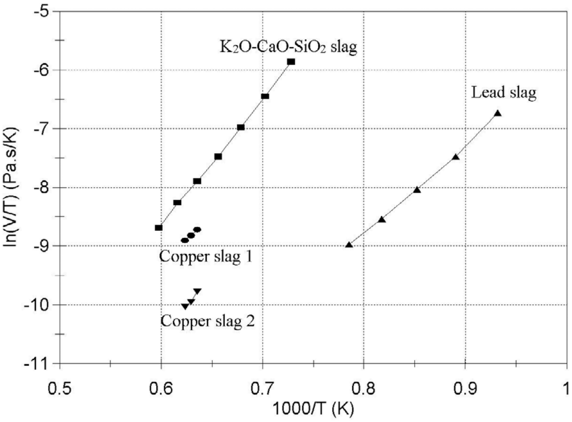

Figure 9: Relationships between ln(viscosity/T) and (1000/T) for KCS, lead and copper slags

The constants *A* and *B* in Equation (1) are presented in Table 3 for the KCS slag, Pb slag and Cu slag. *R* in Table 3 represents the linear correlation between ln(μ/T) and (1000/T). It can be seen that R^2 is close to 1 for KCS slag, Pb slag and copper slag 1 and only 0.956 for copper slag 2 indicating the presence of solid phase in the copper slag 2 at low temperature.

Table 3: Constants A and B in Equation (2)

Sample	A (Pa.s/K)	B	R^2
KCS slag	4.565E-10	21.434	0.999
Pb slag	7.769E-10	15.227	0.997
Cu slag 1	8.989E-9	15.424	0.998
Cu slag 2	6.284E-11	21.551	0.956

CONCLUSIONS

A new experimental apparatus has been developed to measure slag viscosities at high temperatures. The apparatus is completely isolated from the external atmosphere, which enables measurements to be carried out in neutral or Po_2-controlled atmospheres. A variety of sensor/container materials have been employed for viscosity experiments of various slag systems and over a wide temperature range. The apparatus has a top–suspension arrangement that allows quenching slag samples at any time during the experiment, so that the slag phase assemblage and compositions existing at the temperature to be analysed with various techniques including electron probe X-ray microanalysis (EPMA).

A Standard Viscosity Reference Material 710a has been used to evaluate the accuracy of the technique. It was found that the differences between the present results and standard data are within 10%. Examples of recent viscosity measurements for biomass slag, lead smelting slag and copper smelting slag are presented.

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