VISCOSITY AND ELECTRIC CONDUCTIVITY OF COPPER SLAG AT CONTROLLED OXYGEN POTENTIAL

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ABSTRACT

The measurement of viscosities and electric conductivities of synthetic slags of the system $FeO\text{-}SiO_2\text{-}CaO\text{-}MgO\text{-}Al_2O_3$*, in the range of temperatures 1200-1300°C, at oxygen partial pressures of* $10^{-8.5}$ *and* $10^{-7.0}$ *atm, has been carried out in a new experimental apparatus. The experimental setup enables the measurements to be undertaken at temperatures up to 1600°C at precisely controlled gas atmospheres. Another feature of the design is the ability to rapidly quench the sample to preserve liquid slag structure present at temperature; this structure can then be analyzed by X-ray microanalysis (EPMA).*

The synthetic slags investigated correspond to smelting slags from the Teniente Converter, for two Fe/SiO_2 *ratios, and the oxygen partial pressure reflecting the reduction conditions in the slag cleaning process in an electric furnace.*

The results obtained on viscosities and electric conductivities are in general agreement with the properties of the fayalite slags reported in the literature.

INTRODUCTION

Optimal control of the slag chemistry in the copper converting and smelting is one of the important issues influencing efficient and stable operation; and requires detailed knowledge of the slag properties. The slag properties, particularly slag viscosity and electric conductivity, play very important roles in copper concentrate smelting in the Teniente Converter and in slag cleaning in the electric furnace. Slag chemistry, phases present and temperature all have an effect on the slag properties that are of great importance in the effective and stable operation of both processes.

The high temperature measurements of physico–chemical properties of slags face a series of problems, which can lead to uncertainties and errors. Dissolution of crucible material in the slag, vaporization of some components, and crystallization of solid components are common problems. Various experimental setups have been used for the measurements of viscosity and electric conductivity; some of these are summarized in the literature [1, 2].

The technique used in the present study with Pt/Rh crucible, spindle and electrodes, a closed system with precise control of oxygen potential, and the ability to rapidly quench the slag samples solves the majority of these experimental problems.

The aim of the study is to determine the viscosities and electrical conductivities of synthetic slags in the FeO-SiO_2-CaO-MgO-Al_2O_3 system at fixed oxygen partial pressures, in the range of temperature corresponding to the operation of copper concentrate smelting and slag cleaning at the CODELCO NORTE smelter.

METHODOLOGY

Recently an experimental apparatus for high temperature viscosity and electrical conductivity measurements has been developed in the Pyrometallurgy Research Centre. This apparatus allows the slag viscosity and electrical conductivity measurements to be carried out in controlled or gas-tight atmospheres, and with a possibility of quenching the sample after the measurements have been completed. Detailed description of the experimental procedure for viscosity measurements has been presented in another paper by the authors [3]. A Brookfield DVIII+ rheometer with rotating spindle and crucible was used for the viscosity measurements. The rheometer was confined in a gas-tight chamber, the upper end of the furnace tube was connected with the chamber and the lower end of the furnace tube is closed by glass window. The furnace used for the viscosity measurement and the preparation procedure of the slags are similar to those described in the following sections.

The procedure for electrical conductivity measurement is similar to that described by Barati and Cooley [4], and presented as follows.

Description of the Experimental Apparatus for Electrical Conductivity

The four–terminal technique has been used in this study for measurement of the electrical conductivity. The slag impedance was measured by a PARSTAT 2273 potentiostat, which was supplied by Princeton Applied Research, USA. The apparatus used for electrical conductivity measurement in this research is shown in Figure 1. The major features of this apparatus are i) the sample is top–suspended and can be quenched into water after the measurement; ii) 3 platforms for crucible, plunger and electrodes are controlled by motors so that position of the crucible in furnace and electrodes in the slag can be changed any time; and iii) the electrodes and displacement meter are 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 oxygen partial pressure inside the system can be controlled by ratios of flowing CO/CO_2 gas.

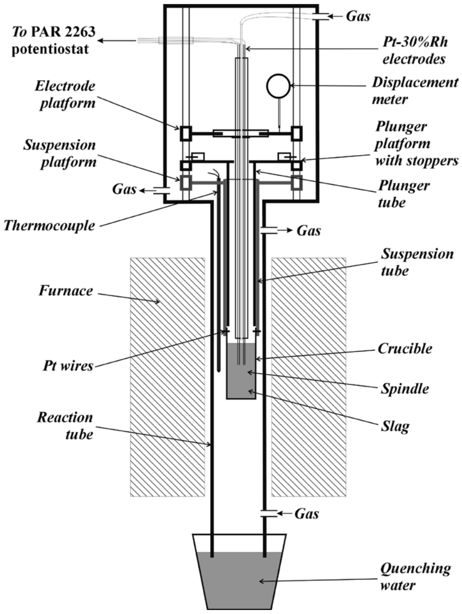

Figure 1: Experimental rig for electrical conductivity measurement

The 4 electrodes were made from 0.5 mm diameter Pt-30%Rh wire that were sheathed into two twin-bore alumina tubes in linear array. The two central electrodes were fixed 7 mm apart and the distance between the central and outside electrodes is 2 mm. The tubes were fixed into a 13 mm ID alumina support tube using alumina cement. The support tube was attached to a moveable platform. A digital displacement gauge with 50 mm stroke and 0.001 mm precision was attached to the platform to accurately determine the movement of the electrodes. The $CO-CO_2$ gas mixture was passed directly over the crucible through a 2 mm ID alumina tube co-centred with the support tube. The crucible is suspended using an alumina tube and Pt wires within the uniform hot zone of the Pyrox resistance furnace having lanthanum chromite heating elements. Temperature is monitored by the B–type thermocouple positioned next to the crucible. The temperature of the furnace is controlled within 2°C and overall uncertainty of the temperature is within 5°C. The crucible was made from Pt–30%Rh with 30 mm diameter and 90 mm height. Once the experiments have been completed the crucible is quenched using the plunger mechanism (alumina tube and stopper), which, 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.

Cell Calibration

The same electrodes and crucible used for measurement of slag electrical conductivity have been calibrated using standard aqueous KCl solutions at 25.0°C. The standard KCl solutions were provided by Alfa Aesar, and the concentrations and conductivities of the standard KCl solutions are given in Table 1.

Table 1: Concentrations and conductivities of the standard aqueous KCl solutions provided by Alfa Aesar

Solution	**1**	**2**	**3**
Concentration (mol/L)	0.0100	0.117	0.850
Conductivity, K, at 25°C ($S.cm^{-1}$)	0.001413	0.0150	0.100

Electrical conductivity is calculated from the resistance of the slag layer between the electrodes

$$k = G/R \tag{1}$$

Where k is electrical conductivity $S.cm^{-1}$, R is the resistance measured by the potentiostat, and G is cell constant relevant to the cell dimension. The G in Equation 1 is related to the length and cross–sectional area of the current path. In the setup used in the present study the length of the current path, i.e., the distance between the electrodes is constant. The cross–sectional area of the current path cannot be determined directly but related to the immersion depth of the electrodes. The standard KCl solutions listed in Table 1 were used to calibrate the potentiostat. It was found that the resistances of the standard KCl solutions are independent of frequency in the range from 5 to 100 kHz. The total resistance was measured as a function of the immersion depth the electrodes and was used to determine the cell constant G from Equation 1.

Sample Preparation

Approximately 100-110 grams of slag sample is required for each electrical conductivity measurement. To accurately determine the required height and composition of the slag, the sample has to be pre-melted separately. Before mixture preparation FactSage is used to calculate the anticipated FeO and Fe_2O_3 concentrations at 1300°C and Po_2 $10^{-8.5}$ atm. Then the pure powders of SiO_2, Al_2O_3, MgO, Fe_2O_3, Fe and CaO (calcined from $CaCO_3$) were mixed in an agate mortar with desired proportions and pelletised. It is not possible to fit all of the required powder mixture (100-110 g) into the crucible - the slag therefore was prepared in two melting stages. Under reducing conditions and high temperature some iron dissolves in the Pt crucible and the composition of the slag changes slightly. After the first melting stage the composition of the slag was measured by EPMA and additional iron oxide was added to adjust the slag composition to the desired values.

In the first melting stage 60-70 grams mixture was placed in the Pt-30%Rh crucible to be used for the measurement and kept in Ar gas flow at 1000°C for 4 hours to sinter Fe_2O_3 and Fe. The temperature was then increased to 1300°C and CO/CO_2 gas mixture is introduced to obtain Po_2 $10^{-8.5}$ atm. After equilibration for 15-20 hours the crucible and sample were lowered into cold end of the furnace. As the slag was slow cooled in the furnace the liquid phase at temperature cannot be converted to homogenous glass for EPMA measurement. To prepare slag sample for EPMA measurement separate quenching experiments were carried out. Approximately 1.0 gram melted slag was placed in an iron-saturated Pt dish and equilibrated at 1300°C and Po_2 $10^{-8.5}$ atm. After equilibration the sample was quenched into water and mounted for EPMA analysis. Following EPMA measurement 30-40 g mixture (adjusted to compensate for Fe dissolved in Pt) was added into the crucible and the 2nd melting stage was performed using the same procedure as during the 1st melting stage.

Measurement of Electrical Conductivity at High Temperature

The Pt-10%Rh crucible containing 100-110 grams 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 tips of the electrodes were positioned initially about 15 mm above the surface of the slag. The furnace controller was sealed and the reaction tube was flushed with CO/CO_2/Ar gas mixture. The furnace was programmed so that the furnace temperature reaches 1300°C over a period of 4 hours with a linear heating rate and kept at this temperature. After 10-15 hours at 1300°C the electrodes were lowered very slowly until they touched the surface of the liquid slag. The first contact of the electrodes with liquid slag was noted by a sharp decrease in the resistance – this way the position of the slag surface was determined. From this position the electrodes were lowered further to the desired depth. Usually 4 immersion depths 2.5, 5, 10 and 15 mm were used. The constant readings of the resistance indicated the equilibrium within the slag has been achieved.

The slag resistance was measured using the same potentiostat as for the calibration. It was found that the resistance of the slag was independent of the frequency over the range of 1 to 20 kHz. All of the resistance data were therefore calculated at 10 kHz.

EPMA Measurement

After the separate viscosity and electrical conductivity measurements the samples were dropped into water. 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 were 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.

If the slag sample cooling rate is high then 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 the measurements all slag samples were sent to a commercial lab for XRF analysis.

RESULTS AND DISCUSSION

Results of Viscosity Measurements

Viscosity measurements have been carried out for two slag compositions at 1200, 1250 and 1300°C, and oxygen partial pressures of $10^{-8.5}$ and 10^{-7}.0 atm respectively.

The slag viscosities determined in present study are presented in Figure 2. For each measurement 5 rotation speeds were used to obtain approximately 30, 60, 70, 80 and 90% torque. It was found that the most stable and accurate measurements was determined to be at 70-100% of the maximum torque. The average of the viscosities measured at 70, 80 and 90% torque was adopted as the final value. The standard deviations are in the range from 0.3 to 2.5.

After the measurement at a given temperatures and Po_2 the temperature was changed and the CO/CO_2 ratio was also changed accordingly to maintain the same Po_2. The slag was quenched for each slag after the measurements at 3 temperatures and each temperature with Po_2 of $10^{-8.5}$ and $10^{-7.0}$ atm respectively. The bulk slag compositions have been measured by XRF after the viscosity measurements and are presented in Table 2. The principal difference between the two slags is Fe/SiO_2 weight ratio. Slag 2 has lower Fe/SiO_2 ratio, i.e., higher SiO_2 concentration. It can be seen from Figure 2 that at a given temperature the viscosity of slag 2 is always higher than that of slag 1 regardless Po_2.

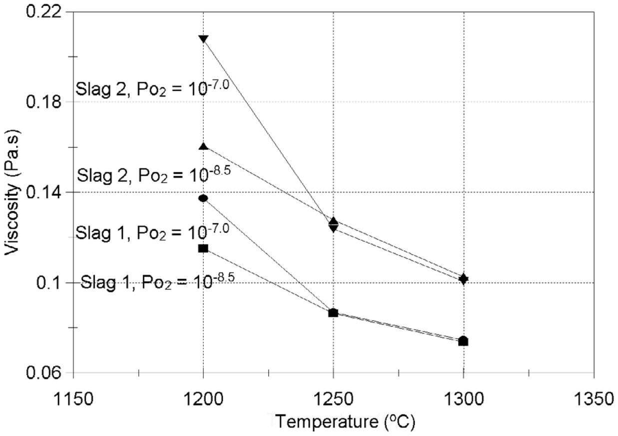

Figure 2: Experimentally determined viscosities for copper slags 1 and 2

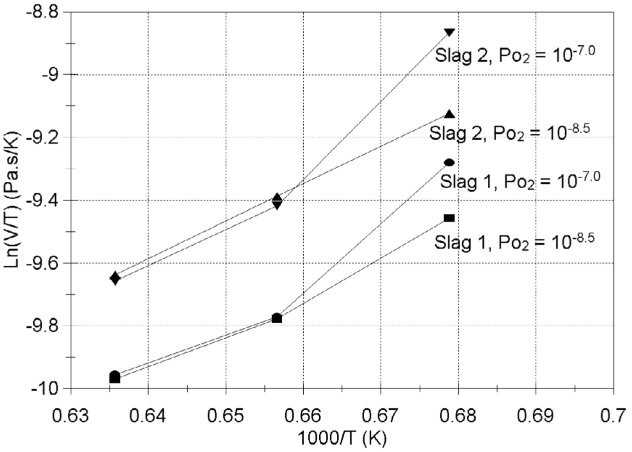

Figure 3: Relationship between ln(viscosity/T) and (1000/T)

Table 2: Bulk compositions of the slag 1 and 2 after viscosity measurements determined by XRF

Sample	**Composition after viscosity measurement (wt%)**					
	FeO	**SiO_2**	**CaO**	**MgO**	**Al_2O_3**	**Fe/SiO_2**
Slag 1	64.1	29.8	2.0	0.5	3.6	1.67
Slag 2	61.8	31.7	2.0	0.4	4.0	1.51

Kaiura *et al.* [5] investigated viscosities of fayalite slag in the system $FeO–SiO_2$ under controlled Po_2. At 1300°C and Po_2 $10^{-7.0}$ atm the viscosities were reported to be 0.052 and 0.049 Pa.s respectively for the slags with 31.2 and 30.0 wt% SiO_2, that are close to the SiO_2 concentrations in the slags used in the present research. These viscosities are lower than the data given in Figure 2 for Slag 1 (0.073 Pa.s) and Slag 2 (0.10 Pa.s). It has been pointed out by Kucharski *et al.* [6] that at the same SiO_2 concentration replacement of FeO by CaO and MgO will increase viscosity since the FeO is a stronger modifier for silicate slag. It is expected that replacement of FeO by Al_2O_3 will also increase viscosity as Al_2O_3 is a much weaker modifier comparing to CaO and MgO. Recent research [10] on the $FeO–Al_2O_3–SiO_2$ system at iron saturation has shown that viscosity increases with increasing $Al_2O_3/(Al_2O_3+FeO)$ ratio at fixed SiO_2 concentration. These measurements support the hypotheses that the *charge composition effect*, associated with the occupancy of tetrahedrally coordinated sites by Al^{3+} ions and the composition of the excess negative charge by alkali or alkali earth, may be responsible for the increases in viscosity observed in some Al_2O_3–containing slags. Kaiura *et al.* [5] used Mo crucible and bob for the viscosity measurements. The slag compositions were not measured after the viscosity measurements. Dissolution of small amount of MoO_3 in the slag will result in decrease of the slag viscosity.

It can be seen from Figure 2 that in the temperature range 1250 to 1300°C the viscosity of the same slag is almost independent of Po_2. The slight difference of the viscosity in this temperature range may be reflection of the difference in their bulk composition. However, it can be seen that at 1200°C the viscosity of the same slag is significantly different and is always higher at $Po_2 = 10^{-7.0}$ than that of $10^{-8.5}$.

If slag is fully liquid the relationship between viscosity and temperature can be expressed as Weymann-Frenkel equation [7]

$$\mu = AT\exp(1000B/T) \tag{2}$$

or

$$\ln(\mu/T) = 1000B/T + \ln(A) \tag{3}$$

Where μ is the viscosity in Pa.s and T is the temperature in K.

Equation 3 shows that ln(μ/T) has linear relationship with 1000/T if slag is fully liquid. Figure 3 plots ln(μ/T) versus reciprocal temperature (1000/T) for slags 1 and 2. It can be seen that in the temperature and Po2 range investigated the linear relationship is present only for Slag 2 at $Po_2 = 10^{-8.5}$. This indicates that for all other conditions at low temperature solid phase was most likely present during viscosity measurement.

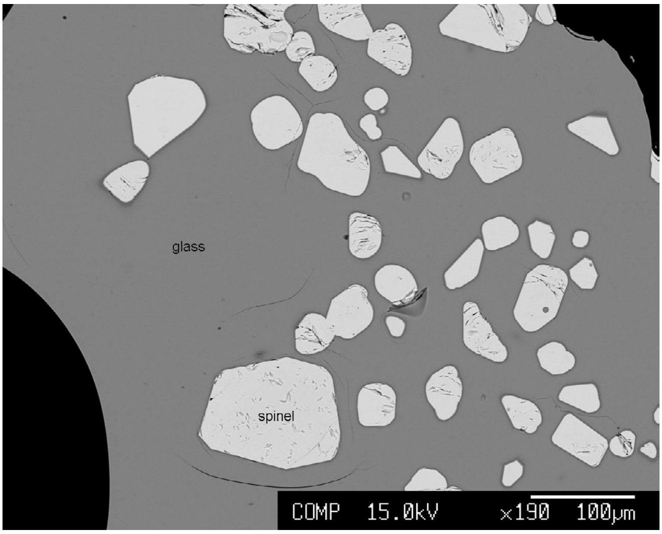

Figure 4: Typical microstructure of slag 2 quenched from 1200°C and $Po_2 = 10^{-7.0}$ atm

With the new technique used in this research it is possible to quench the sample after the viscosity measurement. Inspection of quenched samples after the viscosity measurement it was found that spinel $(Fe^{2+},Mg^{2+})O\cdot(Fe^{3+},Al^{3+})_2O_3$ is present in all samples quenched from 1200°C. A typical microstructure of slag 2 quenched from 1200°C and $Po_2 = 10^{-7.0}$ is shown in Figure 4. Spinel phase is also present in Slag 2 quenched from 1200°C and $Po_2 = 10^{-8.5}$ but the proportion of the crystals is small and consequently the linear relationship between ln(μ/T) and 1000/T was not significantly affected.

The formation of solids in the slags under study here can have two effects on the slag viscosity a) the presence of solids leads to a so–called *slurry effect*, increasing the effective viscosity of the mixture even under conditions when it behaves as a Newtonian fluid [11]. b) The formation of magnetite will result in a decrease in the Fe, Mg and Al concentrations in the remaining liquid, that is, the silica concentration in the remaining liquid will increase. An increase in silica concentration in the liquid phase will also lead to an increase in viscosity.

Results of Electrical Conductivity Measurement

Electrical conductivity measurements have been carried out for two slag compositions at 1200, 1250 and 1300°C and oxygen partial pressures of $10^{-8.5}$ and $10^{-7.0}$ atm respectively. The results of the electrical conductivity measurements are presented in Figure 5. The bulk slag compositions have been measured by XRF after the electrical conductivity measurement and are presented in Table 3.

It can be seen from Figure 5 that at high temperature 1300°C, where the solid phase was not present, the electrical conductivity of slag 1 is higher than that of slag 2. This can be explained by higher Fe/SiO_2 ratio in slag 1. At 1300°C the electrical conductivities of both slag 1 and 2 are higher at $Po_2 = 10^{-7.0}$ than those at $Po_2 = 10^{-8.5}$. These trends should be retained if no solid phase is formed. However, it was found, from separate quenching experiments, that significant amount of spinel crystals were present in the slag 2 quenched from 1250 and 1200°C at $Po_2 = 10^{-7.0}$. As a result, the electrical conductivities are significantly decreased.

Fontana *et al.* [8] measured electrical conductivities of $FeO–SiO_2$ and $FeO–CaO–SiO_2$ slags at 1350°C and $Po_2 = 10^{-7.0}$ atm. They used Pt–20%Rh crucible and Pt–40%Rh electrodes. A slag containing 56.5 wt% *FeO*, 12.8 wt% CaO and 30.7 wt% SiO_2, which is close to the slags used in this research, has electrical conductivity of 3.38 $S.cm^{-1}$ at 1350°C and $Po_2 = 10^{-7.0}$ atm. From Figure 5 it is estimated, assuming linear relationship between the electrical conductivity and temperature, the electrical conductivities of slags 1 and 2 are 4.46 and 3.85 $S.cm^{-1}$ respectively. According to Jiao and Themelis [9] FeO, CaO and MgO have major contributions to the electrical conductivity of the silicate slag. The slags used in this research have higher *(FeO+CaO+MgO)* concentration than that slag used by Fontana *et al.* [8]. This explains the higher electrical conductivities obtained in the present research.

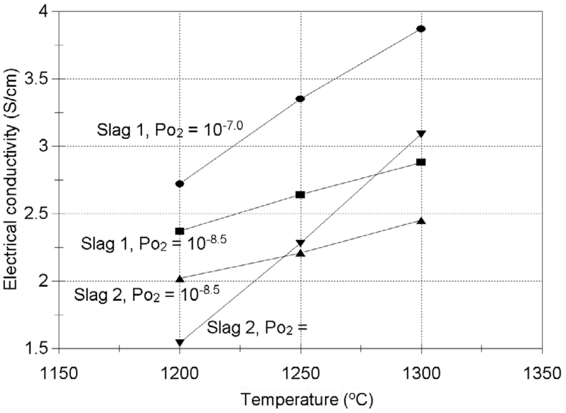

Figure 5: Experimentally determined electrical conductivity for copper slags 1 and 2

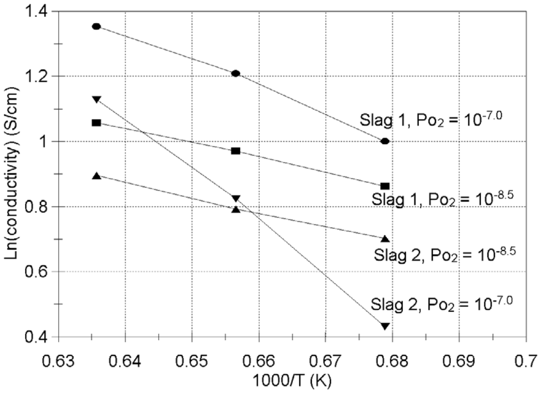

Figure 6: Relationship between Ln (electrical conductivity) and (1000/T)

Table 3: Bulk compositions of the slag 1 and 2 after electrical conductivity measurements determined by XRF

Sample	Composition after viscosity measurement (wt%)					
	FeO	SiO_2	CaO	MgO	Al_2O_3	Fe/SiO_2
Slag 1	61.9	31.1	2.6	0.7	3.8	1.55
Slag 2	59.4	33.3	2.7	0.7	3.9	1.39

The temperature dependence of the electrical conductivity can be expressed by the Arrhenius relationship [2] shown in Equations 4 and 5.

$$k = A_k \exp(-E_k/RT) \quad (4)$$

$$\ln(k) = \ln(A_k) - E_k/RT \quad (5)$$

Where k is the electrical conductivity, Ak the constant, Ek the apparent activation energy, R the gas constant and T the temperature (K). Figure 6 shows plots of ln(k) against 1/T for slag 1 and 2. It can be seen that near linear relationship is observed for both slags at different Po_2. The apparent activation energy can be derived from Figure 6 and given in Table 4. It can be seen that the apparent activation energy of the electrical conductivity is the same for slag 1 and 2 at $Po_2 = 10^{-8.5}$ and it is in good agreement with the value reported by Fontana *et al.* [8] for the same slag system. Higher activation energies of slag 1 and 2 at $Po_2 = 10^{-7.0}$ may indicate the presence of solid phase at low temperatures.

Table 4: The apparent activation energy of the electrical conductivity calculated from the experimental results (kJ/mol)

Sample	Slag 1	Slag 1	Slag 2	Slag 2
Po_2 (atm.)	$10^{-8.5}$	$10^{-7.0}$	$10^{-8.5}$	$10^{-7.0}$
activation energy	38	68	37	134

CONCLUSIONS

Using a new high-temperature apparatus developed by the authors experimental measurement of the viscosities and electrical conductivities of synthetic slags in the $FeO-SiO_2-CaO-MgO-Al_2O_3$ system has been conducted at oxygen partial pressures of $10^{-8.5}$ and $10^{-7.0}$ atm in the range of compositions and temperatures directly relevant to the Codelco electric furnace operation.

It was found that the viscosities of the slags are in the range of 0.07 to 0.21 Pa.s and the electrical conductivities are is in the range of 1.5 to 4 S/cm. The formation of solid phase in the slag can significantly increase viscosities and decrease electrical conductivities of these slags, thereby influencing plant operations.

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