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Investigation on Viscosity of CaO-Al₂O₃ Based Mould Fluxes for the Continuous Casting of High-Al Steels [†]

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Abstract: In this study, the viscosity of CaO-Al₂O₃ based mould fluxes with the addition of B₂O₃ and the effects of increasing the lime/alumina ratio have been observed through IPT (Inclined Plate Test). Additionally, FactSage software, Riboud and Urbain models were used to calculate the viscosity of the mould fluxes. The experimental results show that the viscosity of the mould fluxes decreases dramatically with a change in the lime/alumina ratio from 1 to 1.5. They also show that with an increase in the lime/alumina ratio ranging from 1.5 to 2.5, the viscosity slightly decreases, then when the lime/alumina ratio is over 2.5, the viscosity becomes stable. However, the addition of B₂O₃ decreases the viscosity of the mould fluxes at a lime/alumina ratio of 1.2, 3.3 and 5.5.

Keywords: lime/alumina ratio; high-Al steels; mould fluxes; viscosity

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1. Introduction

It is understood that high amounts of dissolved Al in steel is likely to react with less stable oxides such as SiO₂ in CaO-SiO₂ based mould fluxes. As a consequence of this reaction, Si enters the liquid steel and Al₂O₃ enters the molten fluxes. The change in the mould flux composition generally leads to variations in the slag viscosity during the casting process and this change in viscosity deteriorates the casting process and declines the quality of the slab surface. Being one of the most consequential properties of metallurgical slags, viscosity is pertinent to the composition of the mould flux and the temperature. Thus, an investigation into the effects of compositional change on mould flux properties will be beneficial for the design of less reactive mould fluxes.

There has been much research done by scholars looking into the effect of the CaO/SiO₂ ratio and Al₂O₃/SiO₂ ratio on the properties of lime-silica based mould fluxes to inhibit the sudden change in viscosity. However, it is also widely agreed that it is not easy to stabilise the viscosity of lime-silica based mould fluxes because of the reaction between the molten steel and slag [1]. One suggestion has been that the determination of the optimal CaO/Al₂O₃ ratio holds a significant role in the design of mould fluxes for high-Al steel casting [2,3]. Yan et al. [4] systematically studied the consequence of the CaO/Al₂O₃ ratio on the viscosity of lime-alumina based mould fluxes by making use of the rotational cylinder method and suggesting that as the CaO/Al₂O₃ ratio ranged from 0.6 to 3.2, the viscosity first decreased and then increased below 1270 °C. In addition, Blazek et al. [5] revealed that the viscosity of the mould flux decreased with an increase in the CaO/Al₂O₃ ratio. A widely accepted approach for the development of lime-alumina based mould fluxes is that the CaO/Al₂O₃ ratio (C/A ratio) has an important effect on slag crystallisation. Therefore, it is important to determine the optimal C/A ratio by looking into the effects of compositional change on slag properties. There are several studies [4,6,7] that

have taken a closer look into the effects of the C/A ratio on the thermo-physical properties of lime-alumina based mould fluxes. These studies mainly fixate on the viscosity of the mould flux with small changes in the C/A ratio. Hence, it is necessary to investigate the effect of a broad range of C/A ratios on thermo-physical properties of lime-alumina based mould fluxes.

2. Materials and Methods

2.1. Materials

For this study, thirteen different types of mould flux were created to study the effect of the C/A ratio and B₂O₃ addition on the thermo-physical properties of lime-alumina based mould fluxes. Mould fluxes were produced from the pure chemical reagents CaO, Al₂O₃, SiO₂ and B₂O₃ (the purity of all chemicals was >99%) alongside Na₂CO₃ and Li₂CO₃ as the source of Na₂O and Li₂O. Their chemical compositions were selected with consideration to variations in the C/A ratio and B₂O₃ content, and are provided in Table 1.

Table 1. The chemical composition of the mould fluxes, CaO/Al₂O₃ ratio and B₂O₃ content (in weight percent).

Flux	C/A	SiO ₂	CaO	CaF ₂	Al ₂ O ₃	Li ₂ O	Na ₂ O	B ₂ O ₃
T1	1.2	10	33	10	27	5	10	5
T6	1.2	10	30	10	25	5	10	10
C1	1	10	30	-	30	5	10	15
C2	1.5	10	36	-	24	5	10	15
C3	2	10	40	-	20	5	10	15
C4	2.5	10	43	-	17	5	10	15
C5	3	10	45	-	15	5	10	15
P1	3.3	4	66	-	20	5	5	0
P2	3.3	0	65	-	20	5	5	5
P3	3.3	10	50	-	15	5	5	15
P4	5.5	5	71	-	13	5	5	0
P5	5.5	7	66	-	12	5	5	5
P6	5.5	4	60	-	11	5	5	15

2.2. Methods for Measuring Viscosity

For the purposes of this study, the Inclined Plane Test (IPT) and FactSage software, detailed below, were adapted to measure the viscosity of the mould fluxes. In addition to these techniques, the Riboud and Urbain models were also applied to the designed mould fluxes in an attempt to make an estimation of the viscosity.

2.2.1. Inclined Plane Test (IPT)

The inclined plane test is a straightforward method that can be used to measure the viscosity of mould fluxes at a temperature of 1300 °C. A V-shaped stainless-steel plate is arranged at 14° inclination with the aid of a supporting block. The experimental set-up is demonstrated in Figure 1.

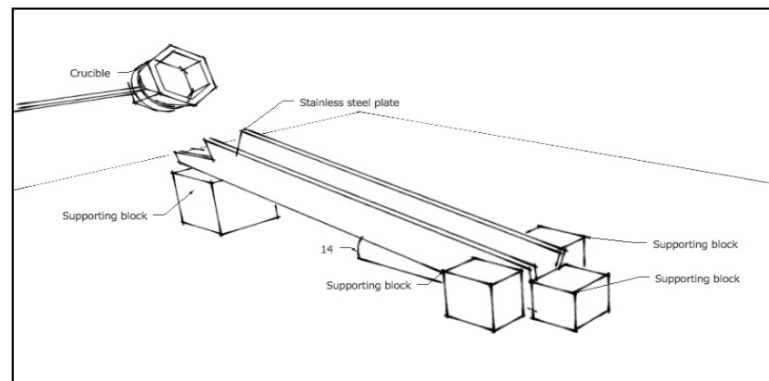


Figure 1. The experimental set-up of the Inclined Plane Test.

The mould fluxes were decarburised for 12 h at 700 °C. 15 g of decarburised mould flux was placed in a graphite crucible and held in a muffle furnace at 1300 °C. After a period of 10 min, the crucible was then removed from the furnace after which the molten slag was directly poured over the top of the inclined plane. In the next step, the molten slag flows down the inclined plane until it loses its fluidity. It forms as a ribbon on the inclined plane and the viscosity of the mould flux was then calculated at a temperature of 1300 °C from the length of the slag ribbon.

The relationship between the flux viscosity and ribbon length is reflected in the following equation:

$$\eta = C_1 \exp\left(\frac{C_2}{L_R}\right) \quad (1)$$

where η represents viscosity of the mould flux in dPa.s, L_R stands for the length of the ribbon and C_1 and C_2 are constants, which are determined as 0.2656 and 470 respectively [8].

2.2.2. FactSage

The FactSage software package was employed to calculate the viscosity of the designed mould fluxes at temperatures of 1300 °C, 1400 °C and 1500 °C from the chemical composition of these mould fluxes. For the calculations of FactSage, the database for melts was selected as this is valid for both supercooled and liquid slags. For the most part, this database generally corresponds to temperatures above 900 °C. Currently, the data entry for lithium oxide is unavailable on FactSage. Hence, the lithium oxide content of the mould flux was added to sodium oxide for the viscosity calculations.

3. Result and Discussion

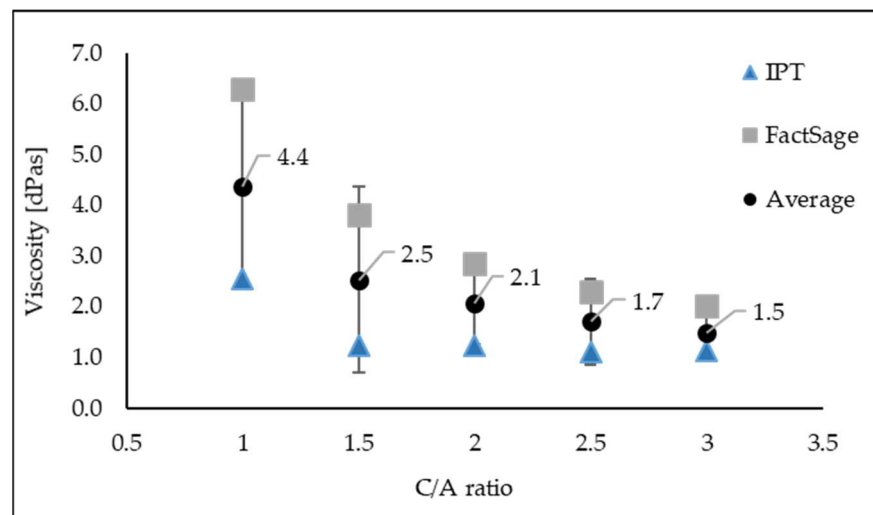
The Inclined Plane Test (IPT) and FactSage software were used to investigate the effect of B_2O_3 addition and C/A ratio on viscosity behaviour of the P, C and T series mould fluxes, as can be seen listed in Table 1. In Table 2, the results of the viscosity measurements derived by using both techniques for the P and T series lime-alumina based mould fluxes can be found. The Inclined Plane Test (IPT) could not be applied to the samples of P1, P2, P4 and P5 in the same way, as their viscosities are too high at 1300 °C, and so the test becomes invalid.

Table 2. The measured and estimated viscosity values of P and T series fluxes at 1300 °C.

Sample No	P1	P2	P3	P4	P5	P6	T1	T6
C/A ratio	3.3	3.3	3.3	5.5	5.5	5.5	1.2	1.2
wt.% B ₂ O ₃	0	5	15	0	5	15	5	10
viscosity (IPT) (d Pas)	-	-	0.70	-	-	0.72	3.18	1.06
viscosity (FactSage) (d Pas)	5.85	3.69	3.20	5.08	3.86	2.10	1.90	1.79

As can be seen from Table 2, the viscosity decreases from 3.18 to 1.06 poise with an increase in B₂O₃ at a fixed C/A ratio of 1.2. The calculated viscosities from the FactSage software for these two mould fluxes also present us with the same trend within the experimental results, however, the values are noticeably different. The reason behind this difference may be caused by the limited thermodynamic data references for the lime-alumina based slag system in the FactSage software package.

Upon close inspection of Figure 2, the change in the mould flux viscosity as a function of the C/A ratio at 1300 °C is clearly demonstrated. Figure 2 clearly shows that the viscosity of the mould fluxes decreases rapidly when the C/A ratio is changed from 1 to 1.5. The viscosity of the C-series mould fluxes clearly demonstrates that with an increase in the C/A ratio ranging from 1.5 to 2.5, the viscosity slightly decreases, although when the C/A ratio surpasses 2.5, the viscosity nearly levels off. Figure 2 also brings to light the comparison of the experimental data acquired by the IPT with the estimations of the viscosities by FactSage. The viscosity of C-series mould fluxes acquired by these particular methods presents the same bearing. Additionally, both the measured and estimated viscosities decrease with an increase in the C/A ratio. The methods of measurement for viscosity used in this study were credible when the experimental uncertainties associated with the viscosity determination tests were considered. Nonetheless, a good correlation between the measured and the calculated viscosities was observed.

**Figure 2.** Comparison of the measured and estimated viscosity of C-series mould fluxes at 1300 °C.

It is general knowledge that Al₂O₃ is an amphoteric oxide and has an exceptional effect on the viscosity of mould fluxes. It behaves as a basic oxide (network modifier) or an acidic oxide (network former) depending on the basicity of the slag. The literature extensively details the nature of alumina in the melt. In the lime-alumina melts, Al-O complexes present 4-, 5- and 6-fold coordinations and form as AlO₄, AlO₅ and AlO₆ units [9,10].

Additionally, at higher temperatures, more alumina is needed in the formation of the aluminate structure with a decrease in the C/A ratio. This causes an increase in the degree of polymerisation as well as an increase in the viscosity of the melt. Be that it may, with an increase in the C/A ratio, more O²⁻ ions are able to depolymerise the aluminate network

and ergo reduce the viscosity of the melt [4,11,12]. At lower temperatures, particles with higher melting temperatures begin to precipitate in the melt and these solid particles start to control the viscosity. Consequently, the viscosity of the mould flux increases.

The mole fraction of basic oxides (CaO and Na₂O) exceeds the mole fraction of Al₂O₃ for the fluxes used in this part of the study. Consequently, alumina operates as an acidic oxide and has the capacity to promote [AlO₄]⁵⁻ ions when an adequate charge balance is available by basic oxides. Any remaining excess Ca²⁺ cations in the CaO-Al₂O₃ melt depolymerise AlO₄ structural units and lessen the viscosity. Thus, in the C-series mould fluxes, whilst the viscosity decreases, the C/A ratio increases. As reflected in Figure 2, the viscosity abruptly decreases followed by it gradually becoming stable with an increase in the C/A ratio. This is because the further increase in the C/A ratio supplies an excess of free O²⁻ ions, and hence the viscosity ultimately becomes stable.

Figure 3 demonstrates the variation in viscosity of the investigated mould fluxes with the addition of B₂O₃ at a temperature of 1300 °C using the FactSage software—where the B₂O₃ content was 0, 5, 10 and 15 wt.% at each C/A ratio of 1.2, 3.3 and 5.5. The viscosity of the mould fluxes is reduced with the addition of B₂O₃ at all three of the studied C/A ratios. However, it is also particularly noticeable that the measured viscosity decreases when B₂O₃ is added regardless of the C/A ratio at a temperature of 1300 °C. This is seen to be consistent with the reported results [12–15]. Huang et al. [13] looked into the effect of adding 0, 3, 6 and 9 wt.% B₂O₃ on the viscosity of mould fluxes containing a low silica content. It was pointed out that the viscosity decreased with an increasing B₂O₃ content. The results of this study suggest that adding B₂O₃ substantially decreases the melting temperature of the slag, and therefore increases the degree of superheat in the melt. Under higher degrees of superheat, the mobility of the particles in the melt rises and thus the viscosity decreases. The authors also bring to attention that boron is usually 3- or 4- coordinated with oxygen and that the addition of CaO or Na₂O, may cause configuration changes in the melt [11,13]. Since the mould flux in the work of Kim et al [12] contains more than 50% network modifiers, the BO₃ is dominant in these melts. Additionally, according to Fourier Transform Infra-Red (FTIR) spectroscopy results carried out in this work, the amount of 3-coordinated boron is higher than 4- coordinated boron in the slag samples. This tells us that when adding B₂O₃, charge compensating cations break the B-O bonds and BO₃⁻ units form in the melt with additional non-bridging oxygen. Therefore, the structure becomes simpler and thus the viscosity decreases.

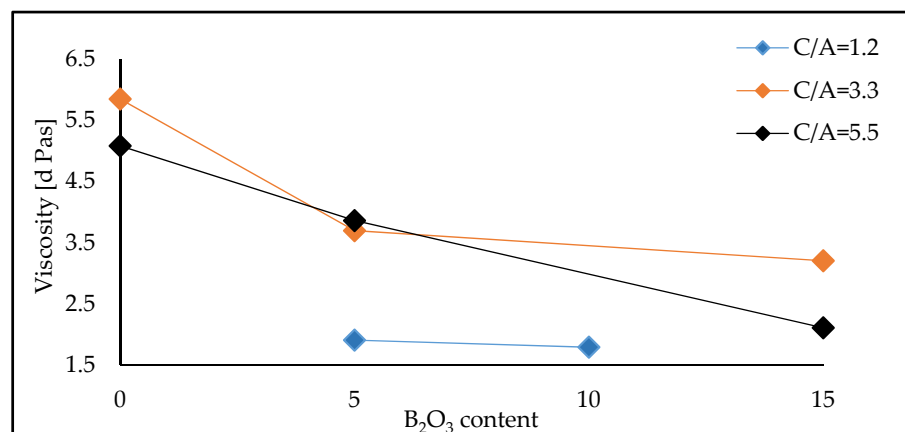


Figure 3. Effect of B₂O₃ addition on the estimated viscosity of mould fluxes with different C/A ratios at 1300 °C.

The measured viscosity of the mould fluxes with a constant amount of 15 wt.% B₂O₃ is more or less stable when the C/A ratio increases from 3.3 to 5.5. The FactSage viscosity calculations for P3 and P6 demonstrate a decreasing trend that holds no similarities to the experimental results as the absolute values are higher than the experimental results.

Lately, some researchers have suggested [4,12,15] that adding B_2O_3 has a somewhat minor effect on the slag viscosity when the mould flux has a high C/A ratio. Research done by Kim and Sohn [12] brought to light that increasing the C/A ratio for mould fluxes containing 18 wt.% B_2O_3 beyond a C/A ratio of 1 had a minor effect on viscosity. A likely explanation derived from the authors' work suggested that the existing B_2O_3 and Na_2O modified the slag structure and caused the disappearance of large complex structures in the melt. For this reason, increasing the C/A ratio will supply free oxygen ions to the melt and so the viscosity will stabilise.

5 wt.% Li_2O and B_2O_3 at various percentages were added to the P-series mould fluxes. Yu et al. [15] researched the viscosity of mould fluxes for the casting of high-Al TRIP steels and made the suggestion that adding Li_2O and B_2O_3 to mould fluxes could have a synergistic effect in stabilising the acidity as well as stabilising the amphoteric characteristics of Al_2O_3 and that, as a result, the viscosity should level out. This also correlates with the research done by Omoto et al. [16].

The effect that temperature has on the viscosity of the lime-alumina based mould fluxes with different C/A ratios and B_2O_3 contents are shown in Figure 4, where the viscosity is seen to be decreasing with an increasing temperature at all C/A ratios, as expected. The calculated viscosity decreases with an increasing B_2O_3 content at C/A ratios of 1.2, 3.3 and 5.5 at varying temperatures. Nonetheless, at temperatures of 1300 °C, 1400 °C and 1500 °C, the viscosity of the C-series mould fluxes decreases with an increase in the C/A ratio.

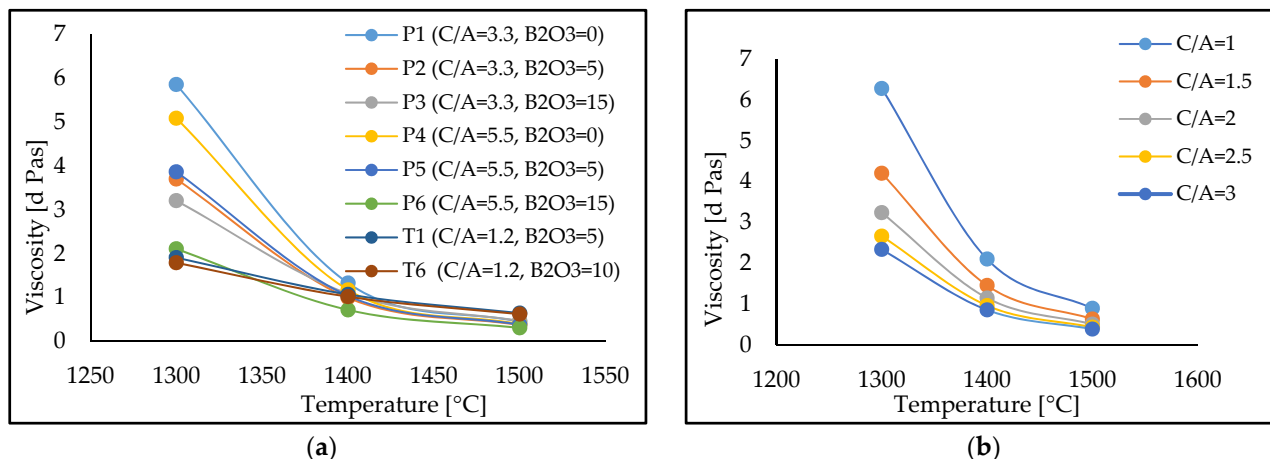


Figure 4. Viscosity-temperature curves of mould fluxes calculated by FactSage software (a) P-series, T1 and T6 (b) C-series.

Figure 5 demonstrates the comparison of experimental data obtained by the IPT (Inclined Plane Test) with the viscosities estimated by the FactSage software. As reflected in Figure 5, the agreements between the calculated viscosities from FactSage and the measured values are unreasonable even though the calculated viscosities display the same trend as the measured viscosities for an increase in B_2O_3 content.

The calculations regarding the viscosities of P-series, T1 and T6 lime-alumina based mould fluxes have also been made using the Riboud and Urbain models. Figure 6 displays a comparison of the measured viscosities and data calculated from the Urbain and Riboud models. The correspondence between the estimated viscosities from the Urbain model and experimental results are reasonably good at the C/A ratio of 1.2. At the fixed C/A ratios of 3.3 and 5.5, there is a considerable deviation between the experimental data and calculated viscosities from both the Urbain and Riboud models. As reported by the viscosities estimated by FactSage, the viscosity of the P-series mould fluxes is seen to decrease with additions of B_2O_3 . The estimated viscosities from both the Urbain and Riboud

models present opposite trends to the viscosities estimated by the FactSage software, when regarding the effect of B_2O_3 addition.

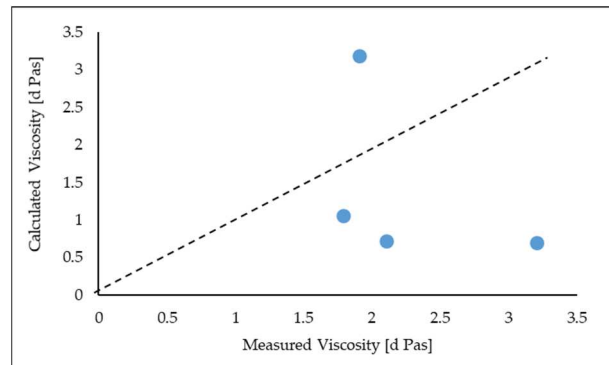


Figure 5. Comparison of the measured and estimated viscosity of P-series, T1 and T6 mould fluxes at 1300 °C and of those obtained by IPT and FactSage.

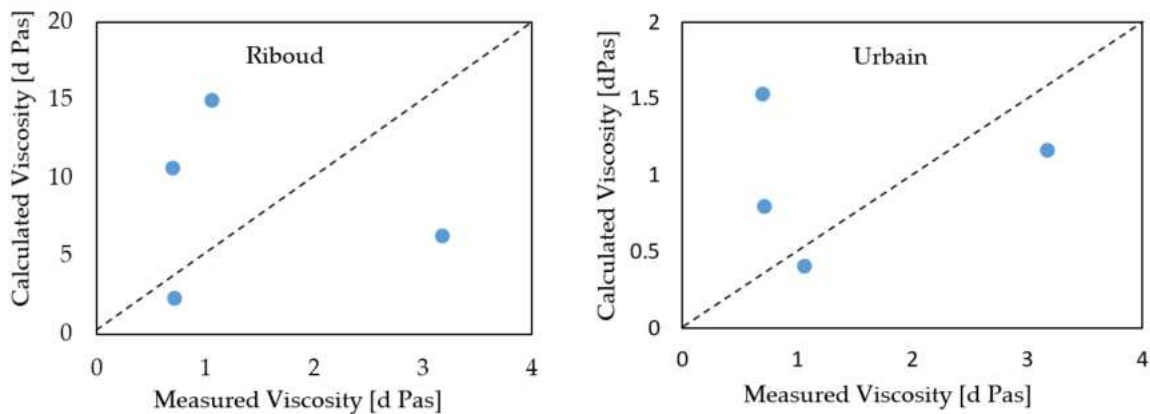


Figure 6. Comparison between the measured (Inclined Plane Test) and calculated viscosities (Riboud and Urbain models) of P-series, T1 and T6 lime-alumina based mould fluxes.

Riboud and Urbain models have also been used to calculate the viscosities of the C-series lime-alumina based mould fluxes. Figure 7 displays the comparison of the viscosities measured as well as the data calculated by the Urbain and Riboud models. Although both models present a similar trend (ie. the viscosity of the mould flux decreases with an increase in C/A ratio) with the viscosities measured by the inclined plane test, the calculated viscosities using the Riboud model are considerably higher in contrast to the measured results. Nonetheless, the Urbain viscosity prediction model presents a relatively better estimation. The cause behind this large discrepancy in the Riboud model can be explained due to B_2O_3 being classified as a basic oxide in the Riboud model while it was treated as an amphoteric oxide in the Urbain model.

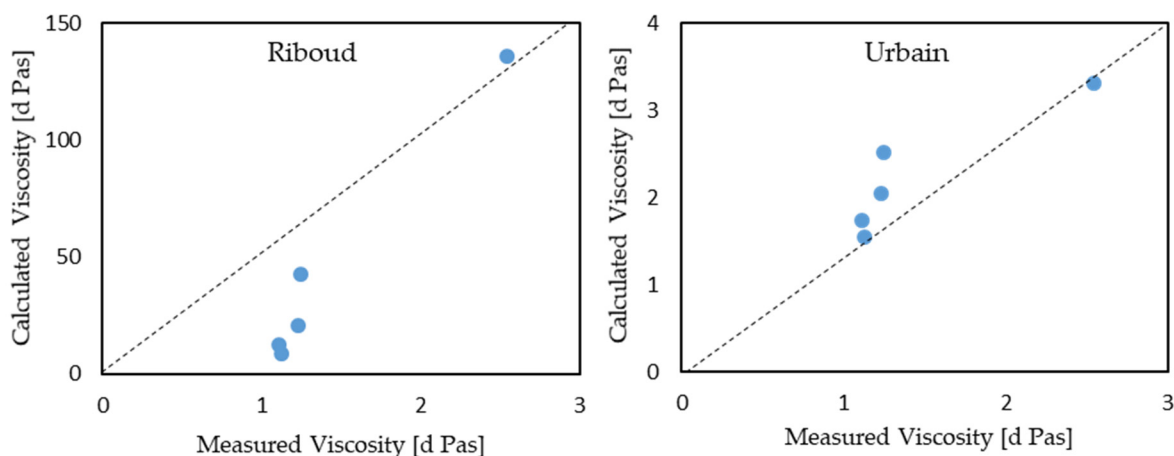


Figure 7. Comparison between the measured (Inclined Plane Test) and calculated viscosities (Riboud and Urbain models) of C-series mould fluxes.

4. Conclusions

In this study, IPT (Inclined Plate Test) experiments have been used to observe the viscosity of lime-alumina-based mould fluxes with the addition of B_2O_3 and with an increasing CaO/Al_2O_3 ratio. In addition to this, FactSage software and empirical models were employed to calculate the viscosity of these fluxes. To summarise, the following conclusions can be drawn:

1. Viscosity measurements using the IPT technique demonstrate that the viscosity suddenly decreases and then gradually stabilises with an increase in the C/A ratio.
2. The addition of B_2O_3 decreased the viscosity of the mould fluxes at all C/A ratios.
3. A good correlation was observed between the measured and the calculated viscosities (FactSage) for the C-series mould fluxes.
4. The Urbain viscosity prediction model offers us a better estimation than the Riboud model for the C, P and T series mould fluxes.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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