A Simple Test for the Measurement of Slag viscosities

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The inclined plane technique is a simple method in which 10.0 g of a slag sample is placed in a graphite crucible, heated to the required temperature and is then poured, quickly, onto a mild-steel, inclined plane. The length of the slag ribbon (L) formed has been found to be a function of the reciprocal viscosity (η^{-1}). Viscosities could be derived to ± 15% from measurements of L and the L-η^{-1} relationship for slags with viscosities in the range 1.5 to 6 dPas. Linear relations were identified between (i) log L and the reciprocal temperature (K^{-1}) and (ii) L and sin α, where α is the angle of inclination. The ribbon lengths were unaffected by the solidification temperature of (T_{sol}) of the slag providing the pouring temperature (T), was greater than (T_{sol} + 100 °C). A 'round robin' interlaboratory comparison programme was carried out on three reference materials of known viscosity. The results indicate that the method provides reliable results for slags in the range 1 to 10 dPas.

1. INTRODUCTION

The fluid flow in a process can have a decisive effect on process control and product quality. For instance, the infiltration of liquid slag into gap between steel strand and copper mould is the key process in the continuous casting of steel since failure to provide enough liquid lubrication can result in longitudinal cracking and sticker breakouts. For this reason the viscosity (η) of the slag is a key factor in the selection of a mould powder and empirical rules have been proposed such as ηV_c = 2.5 ± 1 dPas (m min^{-1}) where V_c is the casting speed[1]. Consequently, steel manufacturers carry out viscosity measurements to ensure that powder supplies are uniform. However, viscosity measurements are time-consuming and require considerable expertise. Consequently, there is a well-defined need for a simple test to provide viscosities (i) for quality assurance of supplies on a routine basis and (ii) viscosities to maintain good process control in high temperature processes such as steelmaking, non-ferrous metal production and coal gasification.

The inclined plane method is a simple test in which a weighed amount of material is placed in a graphite crucible and heated in a muffle furnace to a selected temperature and is then poured down an inclined plane[2]. The viscosity (η) of the melt can then be determined from a correlation of ribbon length (L) and reciprocal viscosity (η^{-1}). Alternatively, a known volume of liquid could be removed from the process vessel and then poured onto the inclined plane.

In order to check the potential of the inclined plane method for 'on plant' measurements of viscosities, the six laboratories, named at the beginning of this paper (which are denoted, randomly, I to VI below) carried out research and participated in an interlaboratory ('round robin') comparison project. This was funded by Standards Measurements and Testing Unit of the European Community. The principal objectives of this research programme were:

(i) to determine the factors affecting the relation between ribbon length and viscosity;

(ii) to determine the accuracy of the method and its limitations;

(iii) to provide a protocol for inclined plane measurements.

Consequently, in the preliminary phase of this project experiments were carried out to identify the principal factors affecting the reliability of the viscosity values obtained with the inclined plane method. Four laboratories (II, IV, V and VI) participated in this phase of the work. The knowledge obtained was subsequently used to establish a protocol for measurements. This was used in the second phase of the measurements in which all six laboratories determined the ribbon length under standard conditions for three reference materials covering a range of viscosities. Recommended values of ribbon length and viscosity were obtained for these three reference materials.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Preliminary studies - The preliminary experimental were carried out on a series of commercial mould powders covering a wide range of viscosity. Manufacturer's data for the chemical compositions and fluidity and solidification temperatures are given in Table 1, along with the viscosities determined in the present investigation. In order to see whether the inclined plane method could be applied to other types of slags, measurements were also made on a coal slag (S) a non-ferrous slag (P) a blast furnace slag (BF) and the reference material used in the interlaboratory comparison of viscosities[3,4].

Table 1

Chemical composition and melting range of (a) powders and (b) alloy used in this investigation (mass %)

	$\%SiO_2$	%CaO	$\%Al_2O_3$	%MgO	$\%Na_2O + K_2O$	F	Fe_2O_3	$T_{fluidity}$ °C	T_{flow} °C	Viscosity dPas		
										1200 °C	1300 °C	1400 °C
A	39.6	37.5	6.4	0.56	9.7	6.5	0.8			8.0	3.7	1.8
B	41.4	33.1	5.4	1.3	11.1	7.3	2.2			7.8	3.7	2.2
C	32	32	4.5	-	12.3	6.5	< 1	1090	1130	3.4	2.3	1.4
D	27.5	27.5	13.5	-	3.3	6.3	5.0	1130	1290	24	8.8	4.0
E	28	36.5	4.8	-	10.3	3.5	1	1230	1260	4.7	2.2	1.2
F	32.5	25.5	8	1.0	5	4	1	1190	1220	22	12.1	7.5
G	31	34.5	3.5	0.5	12	7	2	1110	1150	2.1	0.83	0.36
H	42.3	29.6	11.5	1.4	6.9	2.6	3.5			5.1	2.64	1.48
J	39.6	37.1	6.5	-	9.7	6.7	-			7.3	3.4	1.78
K	34.9	38.7	8.9	-	8.6	8.05	-			5.1	2.45	1.6
L	34.3	38.7	4.3	-	11.8	8.8	-			1.9	1.08	0.66
N	33.1	35.2	3.6	3.6	14.0	10.2	0.6	1060	1120	1.2	0.68	0.42
SRM	63.6	0.1	14.9	-	0.4	Li_2O = 21.8		ca 1050		37.2	18.5	10
S	41.5	24.7	23.4	0.7	0.4	$\%TiO_2$ 1.7	5.6		1285	110	36	12.5
BF	32.4	35.4	15.4	11.5	0.95	$\%TiO_2$ 1.1	0.34				(1400) 5.3	(1500) 2.5

2.1.2 Reference materials - 25 kg batches of the reference materials R1, R2 and R3 were prepared by Metallurgica GmbH. The constituents were weighed and placed in a drum where they were ground and mixed for several hours to provide a homogeneous mixture. They were then transferred to a second vessel where they were mixed, bagged into 5 kg batches and distributed. Powder samples were removed periodically from the stream to carry out routine checks to detect any variations in (i) chemical composition and (ii) particle size distributions; no variations were detected.

The chemical compositions of reference materials are given in Table 2 along with the viscosities.

Table 2

Chemical compositions of reference materials, mass %

Sample	SiO_2	CaO	Al_2O_3	MgO	Na_2O	Li_2O	K_2O	Fe_2O_3	TiO_2	F	CO_2	T_{sol} °C	Viscosity dPas		
													1200 °C	1300 °C	1400 °C
R1 (a)	35.1	31.0	3.47	0.72	16.1	-	0.11	0.29	0.03	6.74	8.5	1109	2.6	1.5	0.87
(a)	(38.1)	(33.6)	(3.76)	(0.78)	(17.5)	(-)	(0.12)	(0.32)	(0.03)	(7.31)	(0)			[1.6] a	
(b)	35.1	30.7	3.3	0.61	15.1	-	0.09	0.36	-	6.89	-				
R2 (a)	39.3	34.4	5.01	1.47	8.95	-	0.13	0.52	0.22	7.01	5.1	1164	5.8	3.2	1.85
(a)	(41.3)	(36.2)	(5.26)	(1.55)	(9.40)	(-)	(0.14)	(0.56)	(0.23)	(7.38)	(0)			[3.2] a	
(b)	39.3	34.6	5.26	1.33	8.65	-	0.11	0.71	-	7.41	-				
R3 (a)	42.7	32.8	9.05	1.22	4.12	1.40	0.51	1.11	0.17	5.33	2.4	1099	14.2	6.6	3.2
(a)	(43.7)	(33.6)	(9.27)	(1.25)	(5.15)	(1.43)	(0.52)	(1.14)	(0.17)	(5.46)	(0)			[7.3] a	
(b)	42.1	32.3	8.69	0.88	3.62	-	0.44	1.3	-	5.32	-				

(a) Supplied by Metallurgica (b) supplied by British Steel
( ) denotes values for the composition after the loss of CO_2 on heating

2.2 Measurements

2.2.1 Viscosity measurements - The viscosities were measured by NPL using the rotating cylinder method using a Brookfield viscometer head and molybdenum crucibles, rotors and suspension rods[5]. Some measurements were also carried out by Metallurgica using the same technique and Platinum alloy components. An atmosphere of argon was maintained in the furnace. Temperatures were measured by a thermocouple sited adjacent to the mid height of the crucible. Small corrections were made to the recorded temperature to allow for temperature differences between the melt and the measurement thermocouple; these corrections had been determined in preliminary experiments. All temperatures were measured with calibrated thermocouples traceable to national standards. The viscometer was calibrated at ambient temperature using 6 reference oils of known viscosity supplied by PTB Braunschweig and at ambient temperatures with two reference materials of known viscosity. The values obtained with the reference material SRM were within ± 5% of the recommended values[3,4].

2.2.2 Melting range - The melting range was determined by the Leitz microscope test, which is widely used to measure the melting ranges of mould powders[6].

2.2.3 Inclined plane tests - 10.0g of the sample was transferred to a graphite crucible (25 mm id and 50 mm high) and placed in a preheated muffle furnace at the selected temperature. The temperature of the crucible was determined from a calibrated Pt/Pt13Rh (Type R) thermocouple placed adjacent to the crucible. When the sample attained thermal equilibrium it was heated for a further 15 minutes, removed from the furnace and poured (within 6 seconds) onto the inclined plane. The inclined plane was formed from mild-steel sheet which was pressed into a V-shape. It was abraded with emery paper and cleaned with acetone before each run. The length of the slag ribbon formed on the plane was measured and recorded. It is recommended that at least 5 tests should be carried out on each sample.

A temperature of 1300 °C and an inclination of 9 ± 0.5^{o} were employed as the standard conditions but a higher angle (23^{o}) was used for more viscous slags to obtain a reasonable ribbon length.

2.3 Statistical evaluation

The following procedures were carried out on the results recorded for the reference materials R1 and R2:

(i) Ribbon length data for each laboratory were used to produce scatter plots.

(ii) A multiple t test was carried to compare the means of each laboratory with that of each other laboratory.

(iii) A one-way anova test was carried out on the means of each laboratory's results.

The purpose of these two tests was to determine whether data from each laboratory (for a specific sample) were from the same population ie that they could be pooled.

(iv) A Cochran test was used to identify outlying variances.

(v) A Grubb test was carried out to identify outlying data set averages.

(vi) Kolmogorov-Smirnov-Lilliefors, skewness and kurtosis tests were applied to assess whether the pooled population of all individual values were normally distributed.

(vii) The mean value, within laboratory standard variance, between laboratory variance, repeatability standard deviation and reproducibility standard deviation were calculated.

(viii) An F test was carried out to see if between *data sets standard deviation* was significantly different from zero, if not, the data were pooled.

3. RESULTS AND DISCUSSION

3.1 Operator effect

In the test it is necessary that the operator (i) opens the furnace (ii) grasps the graphite crucible in tongs (iii) transfers the crucible to the inclined plane and (iv) pours the molten slag onto the plane. Typically this procedure takes 4 to 6 seconds. One laboratory carried out trials with four operators and found that initially there was some variability in the ribbon lengths (L) recorded, but these differences rarely exceeded 10% and more reproducible lengths were recorded after some practice. Table 3 indicates the results obtained with a practiced operator. Variability was found to increase more at (i) high temperatures, and (ii) when pouring more fluid melts.

One laboratory (IV) did obtain variable results when using an inexperienced operator, and it was noted that the maximum ribbon length (L_{max}) was in good agreement with the mean values recorded by other laboratories. This suggests that when using high temperatures or very fluid slags there is a case for using L_{max} since this represents the conditions of minimum heat loss during the pouring operation.

Table 3

Ribbon lengths recorded by various laboratories for reference materials (α = 9°, T = 1300 °C); σ = standard deviation

Sample	Laboratory	Ribbon length, L (mm)	Mean L (mm)	L_{max} (mm)	σ
R1	Lab I	194; 193; 191; 197; 195; 196; 197; 196; 194; 194	195	198	2.2
η = 1.5 dPas	Lab II	195; 200; 197; 196; 193; 192; 190; 197	195	200	3.2
$1/\eta$ = 0.667	Lab III	202; 201; 204; 212; 194; 190	200.5	212	7.7
	Lab IV	160; 157; 160; 167; 165; 166	162.5	167	4.0
	Lab V	192; 201; 199; 198; 203	198.6	203	4.2
	Lab VI	182; 175; 172; 179; 182; 183; 170; 181; 178	178	183	4.7
R2	Lab I	152; 153; 153; 149; 151; 149; 150; 154; 147; 147	150.5	154	6.3
$1/\eta$ = 0.312	Lab II	126; 137; 134; 135; 136; 136; 130; 130; 130	132.7	137	3.8
η = 3.2 dPas	Lab III	137; 129; 142; 132; 130; 135	134.2	142	4.9
	Lab IV	114; 97; 120; 118; 137; 135	120.2	137	14.7
	Lab V	139; 138; 132; 133; 132; 132; 129	133.6	144	3.6
	Lab VI	139; 138; 133; 133; 132; 129; 126; 124; 140	132.7	139	5.7
R3	Lab I	113; 115; 113; 110; 113; 117; 109; 113; 113;	112.6	117	5.8
η = 6.6 dPas	Lab II	105; 104; 98; 104; 108; 105; 101; 100; 101; 99	102.5	108	3.2
$1/\eta$ = 0.153	Lab III	94; 98; 90; 94; 90; 92	93	98	3.0
	Lab IV	87; 98; 95; 99; 95; 100	95.7	100	4.7
	Lab V	90; 94; 93; 99; 90	93.2	99	3.7
	Lab VI	95; 95; 98; 95; 96; 92; 96; 96	95.4	98	2.8

3.2 Relation between melt fluidity and ribbon length

3.2.1 Preliminary tests - NPL measured the viscosities of the various samples given in Table 1. Inclined plane tests were then carried out on each of the samples. The ribbon lengths (L) are plotted as a function of the fluidity (ie the reciprocal viscosity, $(1/\eta)$) in Figure 1. It can be seen that:

(i) for melts with viscosities in the range 1.5 to 6 dPas the uncertainties in the calculated viscosities are of the order 10 to 15%;

(ii) there seems to more scatter from the results obtained for the more fluid melts which could be due to either or both (a) sensitivity of ribbon lengths to small differences in heat losses during the pouring and (b) uncertainties in viscosity values which tend to be larger for low viscosity melts;

(iii) although the scatter was low for more viscous slags (6 dPas) the calculated viscosities tend to be more sensitive to small deviations from the curve and in this viscosity range there may be a case for using a higher angle of inclination.

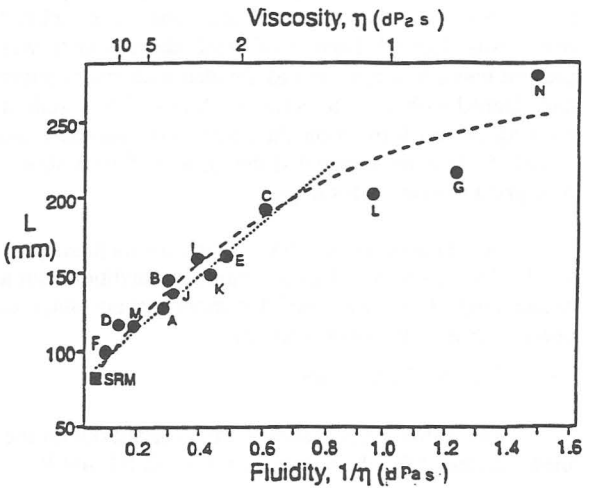

Figure 1 Ribbon length as a function of fluidity (reciprocal viscosity, η^{-1})

3.2.2 Reference material tests - The ribbon lengths recorded for standard conditions of $\alpha = 9^{o}$ and T = 1300 °C for reference materials R1, R2 and R3 are given in Figures 2a to 2c, respectively and Table 3. It should be noted that Lab IV used an inexperienced operator and that Labs I and IV were unable to place a thermocouple adjacent to the specimen.

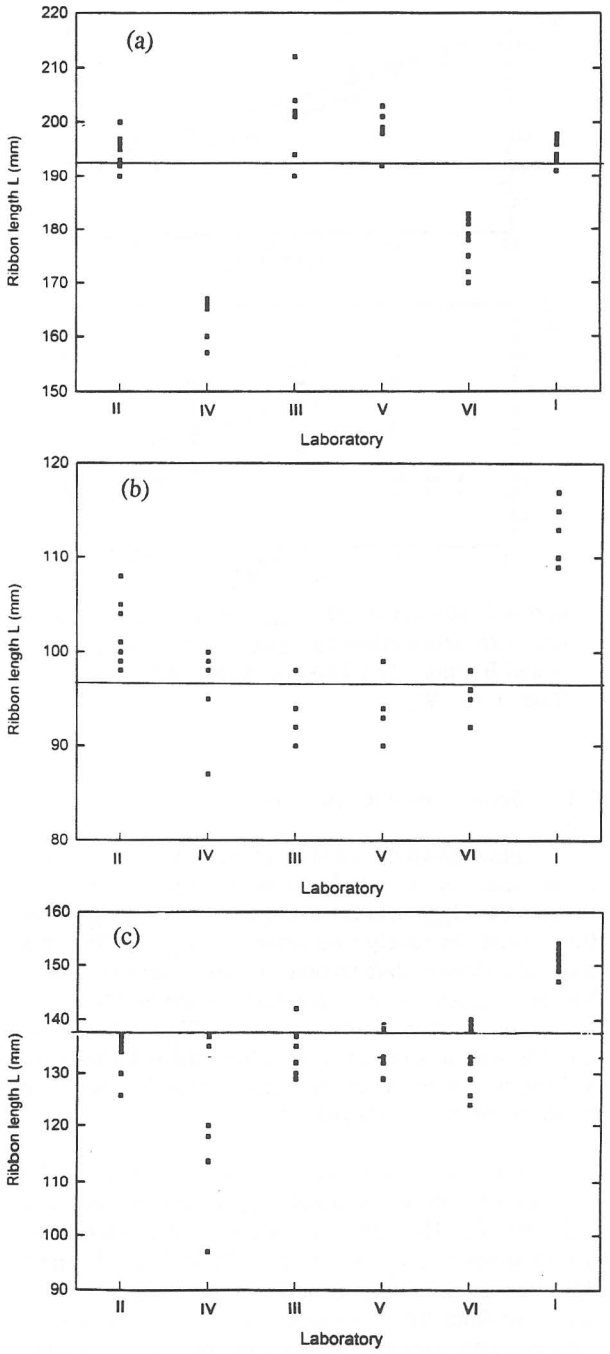

Figure 2 Ribbon length reported by various laboratories for reference materials (a) R1, ——, certified value (excluding Lab IV), (b) R2 (excluding Lab IV) and (c) R3 (excluding Lab I).

Statistical evaluations of the results indicated that the values reported by Lab IV for R1 and R2 and Lab I for R3 were from a different population. Consequently the statistical procedure outlined in Section 2.3 was repeated excluding these results. The following mean lengths were obtained for R1, R2 and R3, respectively, for angle of inclination of 9^{o} and a temperature of 1300 °C, 192.3 ± 9.1 mm, 137.4 ± 8.2 mm and 96.7 ± 4.0 mm.

Chemical analyses carried out on the slag ribbons indicated that any variation in composition lay within the bounds of uncertainty associated with the chemical analysis of the slag sample. Weight losses of 0.9, 0.5 and 0.3%, for R1, R2 and R3, respectively were consistent with weight losses due to loss of CO_2 on heating.

These values are plotted as functions of reciprocal viscosity in Figure 3 and it can be seen that the values are in excellent agreement with the L_{mean} - η^{-1} relations recorded in the preliminary experiments on the test materials. These results show that for viscosity values between 1.5 and 6 dPas, the viscosity can be determined to within 15%. This compares well with the results of an interlaboratory comparison project which indicated that the viscosities obtained by different laboratories for a reference material varied by about ± 50% around the mean, but for laboratories using Mo and Pt components in the viscometers, these variations were reduced to ± 10%[3,4].

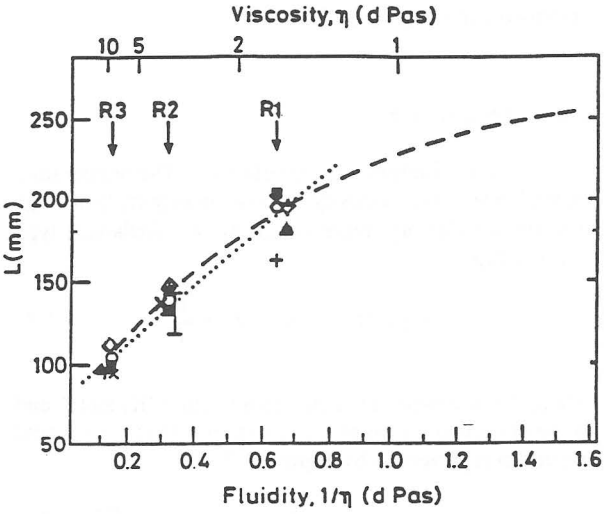

Figure 3 Ribbon length L_{mean} as a function of reciprocal viscosity for reference materials R1, R2, R3, - - -, • • • •, L_{mean} - η^{-1} curves from Figure 4; ◊, Lab I; O, Lab II; ■, Lab III; +,I, Lab IV; x, Lab V; ▲, Lab VI.

3.3 Inclination of the inclined plane.

The ribbon length (L) would be expected to be a function of sin α. The relation between L and sin α for melts A and B are shown in Figure 4 and it can be seen that a linear relation exists.

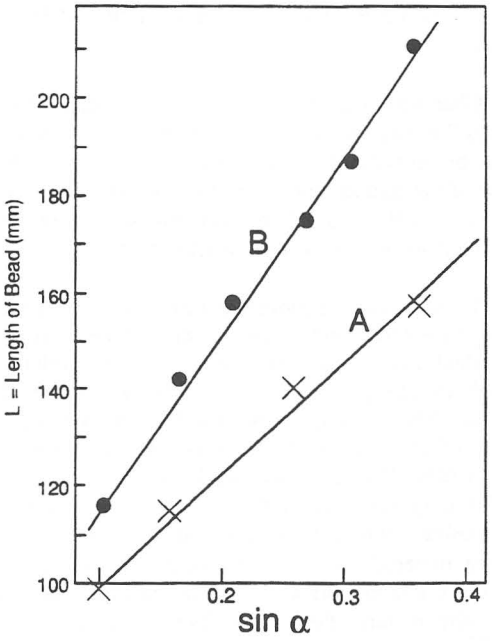

Figure 4 Ribbon length as a function of sin α, results reported for 1300 °C by Lab VI.

3.4 Temperature

3.4.1 Preliminary experiments - The temperature dependence of the viscosity (η) and fluidity (η^{-1}) of slags can be satisfactory represented by an Arrhenius-type relationship

$$\log_{10} \eta = \log_{10} A + \frac{B}{T} \qquad (1)$$

where T is the thermodynamic temperature (K) and A and B are constants. Thus if L is a function of η^{-1} we would expect to represent L by Equation 2

$$\log_{10} L = f(\log_{10} \eta^{-1}) = \log_{10} A* + \frac{B*}{T} \qquad (2)$$

The temperature dependencies of the ribbon lengths obtained for samples A and B are shown to be linear in Figure 5(a).

Results obtained by Lab V indicate that the ribbon length values show the characteristic '*dogs-leg*' form of viscosity temperature relations as a consequence of the solidification of the melt.

3.4.2 Reference materials - The linear relationship between $\log_{10}$ L and reciprocal temperature is shown in Figure 5b; L_{max} has been used since results of Lab IV showed some variability as consequence of using an inexperienced operator.

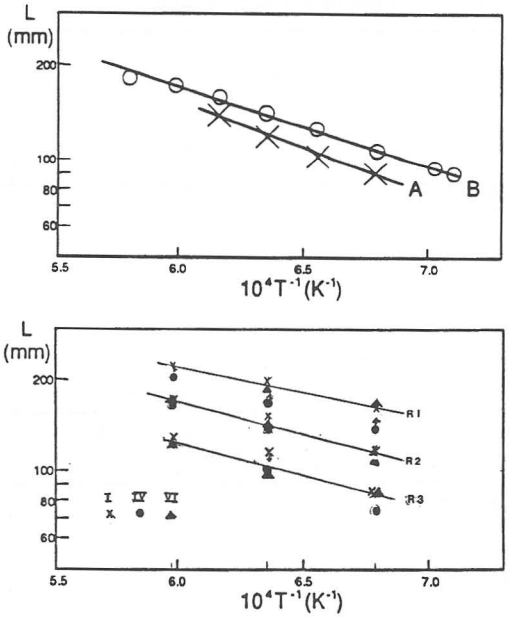

Figure 5 Ribbon length ($\log_{10}$ L) as a function of reciprocal temperature for results on (a) samples A and B reported by Lab VI, (b) R1, R2 and R3 (Labs I, IV, VI).

3.5 Solidification temperature

Flow down the inclined plane would be expected to be less for a sample with a high solidification temperature (T_{sol}) than for a sample with a low T_{sol} since flow would effectively stop when $T < T_{sol}$. In this case the fluidity temperature recorded in Leitz microscope tests has been taken to be a measure of the solidification temperature. The results shown in Figure 6 are for samples with a wide range of solidification temperature and the low level of scatter suggests that T_{sol} has little effect on the L-η^{-1} relationship.

Lab II carried out a series of tests on 13 commercial samples in which T_{sol} varied between 952 and 1285 °C. The ribbon lengths, estimated viscosities[7] and fluidities and T_{sol} are given in Table 4 and Figure 6 Although the use of estimated viscosities leads to a small departure from the experimental L-η^{-1} curve, it can be seen that only sample 9 shows a marked departure from this curve and this sample had the highest T_{sol} of 1285 °C, just below the pouring temperature of 1300 °C. These results indicate that reasonable values can be obtained, providing the pouring temperature is more than 100 °C above T_{sol}.

Table 4

The effect of solidification temperature on ribbon length obtained by Lab II

Powder	1	2	3	4	5	6	7	8	9	10	11	12	13
T_{sol} °C	1178	1142	1079	1061	952	1198	1120	1078	1285	1150	1150	1150	1150
η(dPas)	1.4	1.2	1.5	1.8	1.2	0.7	3.3	1.3	1.4	1.2	1.2	1.2	1.2
η^{-1} $(dPas)^{-1}$	.714	.833	.667	.556	.833	1.43	.303	.769	.714	.833	.833	.833	.833
L (mm)	165	150	156	190	179	197	123	165	96	169	172	170	175

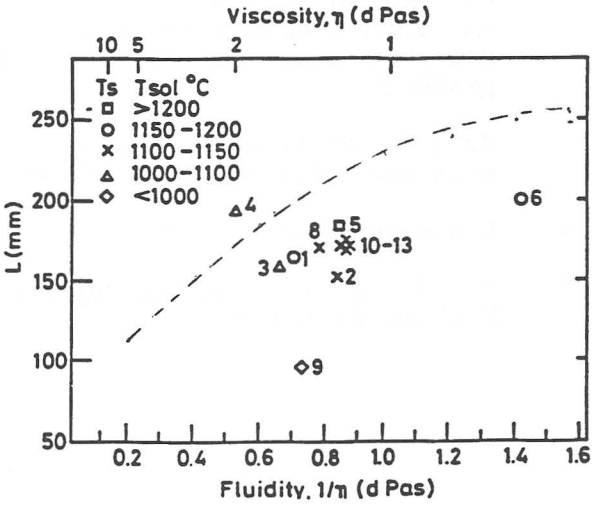

Figure 6 Ribbon length as a function of reciprocal viscosity for samples with various solidification temperatures, reported by Lab II.

Lab VI ran inclined plane tests at 1500 °C on the three samples with higher melting temperatures (P, S and BF). It was found that the ribbon lengths were small when using an angle of inclination of 9°, so the angle was increased to 23°. The results shown in Table 5 show considerable variability. This is due to the fact that radiative heat losses at 1500 °C are 60% higher than those at 1300 °C; since viscosity is a sensitive function of temperature any variations in heat loss during pouring will have a marked effect on ribbon length. Furthermore, even at 1300 °C, it was noted that use of old crucibles tended to lead to shorter ribbon lengths due to higher heat losses through the thinner walls. Consequently, when ribbon lengths are variable there is a case for using the maximum ribbon length (L_{max}) since this represents the minimum heat loss during pouring. There is also a case for using crucibles with thicker walls when carrying out measurements at high temperatures.

The viscosities of slags S and BF at 1500 °C were calculated by converting L_{max} values obtained at $\alpha = 23^{o}$ to $\alpha = 9^{o}$ using Figure 4. ($L^{23^{o}}_{max}/L^{90^{o}}_{max} = 1.56$) and Figure 2; the calculated viscosity values of 1.8 and 0.29 Pas for slags S and BF are slightly higher than the measured values of 1.25 and 0.25 Pas, respectively. Given the approximations used, the agreement can be considered to be reasonable but in order to improve reliability of the viscosity values obtained a L_{max}-$(1/\eta)$ relationship should be established for $\alpha = 23^{o}$. However, it is also possible that Na_2O and F may have been lost from the sample on heating to 1500 °C which could result in an increase in viscosity.

Table 5

Ribbon lengths for non-ferrous slag (P) and coal slag (S) obtained by Lab VI, T = 1500 °C, $\alpha = 23^{o}$

Sample	L (mm)	L_{mean}	L_{max}
BF	196, 221, 177, 170, 174, 179, 170, 197, 184	178	221
S	97, 80		97
P	96		

CONCLUSIONS

1. Viscosity values, in the range 1.5 to 6 dPas, derived from inclined plane measurements lie within ± 15% of experimental values.

2. There is more scatter in the predicted ribbon length values for more fluid slags (η < 6 dPas) but the viscosity is less sensitive to ribbon length uncertainties in this range. More work needs to be done with more fluid slags.

3. For more viscous slags (η > 0.6 Pas) the ribbon lengths (L) tend to be shorter and viscosities tend to be more sensitive to small changes in L; it is recommended that a higher angle of inclination should be used to obtain longer ribbon lengths.

4. Ribbon lengths tend to be more variable when carried out at 1500 °C due to larger variations in heat losses whilst pouring. For this reason it may be advantageous to use thicker-walled crucibles for tests at 1500 °C.

5. In tests where ribbon lengths show significant variability, a good case can be made for using the maximum length in preference to the mean ribbon value.

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