STANDARD REFERENCE MATERIAL (SRM) FOR HIGH TEMPERATURE VISCOSITY MEASUREMENTS

C.P. Broadbent*, M. Franken**, D.Gould***, K.C. Mills****
*Billiton Research B.V., The Netherlands, **Hoogovens B.V., The Netherlands,
***Bureau Communautaire de Reference (BCR), Belgium, ****National Physical Laboratory, The United Kingdom

SYNOPSIS

Viscosity has a decisive influence on the fluid flow in many industrial processes. Error limits of ±25% are quoted frequently for the viscosity of molten slags and it is suspected that variations in values reported by different laboratories is greater. Calibration of the various viscometers with an SRM would provide one method of improving this unsatisfactory situation. BCR coordinated a round robin test with the aims of providing a comparison of all principal types of viscometer and to develop an SRM slag. Results from both phases showed considerable scatter around the mean (±80K and ±55K). Data from labs using the concentric cylinder method with Mo parts gave a scatter of K. The following temperature-viscosity relationship is recommended for the SRM:

$$\text{Log 10 (Pas)}\ \mu = -4.504 + 7461\ T^{-1}$$

1. INTRODUCTION

There is considerable demand for reliable viscosity measurement for molten materials involved in high temperature processes since this property has a decisive influence on fluid flow in many industrial processes. A typical example is the continuous casting of steel. It has been shown that good lubrication is achieved only when the molten casting powder satisfies the empirical relationship:

$$\mu Vc = 3\text{-}6\ \text{mPam}^{-1} \qquad (1)$$

Where μ = viscosity (Pas) and Vc = casting speed of steel.

Error limits of ±25%are quoted often in the literature for values of the viscosity of molten slag. Many workers have the impression that the variations in values reported by different laboratories would be even greater than these quoted error limits. Calibration of the different viscometers with a suitable standard reference material (SRM) would be one method of reducing these uncertainty limits. Currently, standard glasses are available from the National Bureau of Standards in America (now known as NIST) but the three SRM's for high temperature viscosity measurements (NBS 710, 711 & 717) exhibit viscosities at least an order of magnitude higher than the majority of metallurgical slags. In addition the recommended data relate to oxidising conditions only and many determinations relevant to industrial processes require reducing atmospheres. Consequently, the European Economic Community Bureau of Reference (BCR) convened a meeting which led to the manufacture of a potential SRM by Hoogovens. The target composition for this slag was (19.46% Li_2O, 14.06% Al_2O_3, 63.8% SiO_2) and the full composition of the material which was distributed to participants in the round robin test programme is shown in Table 1. The following objectives were set:

a) To determine the viscosity of the SRM and provide recommended data;
b) To determine the effects of different contact materials on the measured viscosity;
c) To determine the viscosity of the SRM in a wide variety of viscometers in order to establish systematic errors specific to particular types;
d) To determine the thermal stability of the SRM;
e) To monitor changes in chemical composition occurring during the measurements and relate these to variations in viscosity measurements.

Table 1 Chemical composition of "as produced" SRM slag.
(Wt.% - Means of 5 separate determinations)

Compound	Mean %	σ	Compound	Mean %	σ
Li_2O(b)	20.3	0.1	SiO_2(a)	63.8	0.1
Al_2O_3(a)	15.0	0.1	C(c)	0.15	0.3
Mo	<0.1	<0.1	Na_2O(b)	0.3	
MgO(a)	<0.1		P_2O_5(a)	<0.1	
K_2O(b)	0.13		CaO(a)	0.1	
TiO_2(a)	<0.1		MnO(a)	<0.1	
Fe_2O_3(a)	0.2		LOI(d)	0.4	0.1

(a) Determined by XRF
(b) Determined by flame spectrometry
(c) Determined by heating sample to 1200 °C in oxidising conditions
(d) Determined by wieght loss after 12h at 1000 °C

2. PARTICIPANTS IN THE ROUND ROBIN TESTING

The participants and the viscosity measurement techniques employed in the round robin testing are summarised in Table 2. Viscosity measurements were obtained using rotating cylinder (including Brookfield, Haake and "own design" measurement heads), rotating crucible, oscillating plate, falling sphere and inclined plane techniques.

Table 2 Participants and techniques used in round - robin test programme

Oraganisation	Country	Technique	Measuring Head	Contact Material(s)
Billiton Research	Nl	RCyl	Brookfield	Mo
British Gas	UK	RCyl	Haake	Graphite / Mo
CIREP	Fr	RCyl	Own Design	Pt/Pt20%Rh
CNRS	Fr	Rcr	Own Design	Mo
Haake (1)	D	RCyl	Haake	Graphite
Hoogovens	Nl	RCyl	Haake	Graphite
Hoesch Stahl	D	RCyl	Own Design	Graphite
Metallurgica	D	RCyl	Haake	Graphite/Pt
NPL	UK	RCyl	Haake	Graphite/Mo/Pt
KSR (1)	UK	IPl	-	-
Imperial College(2)	UK	FS	-	Mo
Osaka Univ. (2)	Jap	Opl	-	Al_2O_3 / Pt
Tohoku Univ.(2)	Jap	RCr	Own Design	Graphite

Notes:
(1) Results from phase 1 only
(2) Results from phase 2 only
RCyl Rotating cylinder
RCr Rotating crucible
IPL Inclined plane viscometer FS Falling sphere
OPL Oscillating plate viscometer

2.1Concentric cylinder methods

This is the most widely used technique for viscosity measurement at high temperatures and both the rotating crucible (RCr) and rotating cylinder (RCyl) methods are based on this principle. In both cases a fluid is contained in an annular gap between two concentric cylinders, one of which, either the bob (RCyl) or crucible (RCr), is rotated at constant speed, causing the fluid to rotate,transmitting a torque to the bob (inner cylinder). Viscosities are calculated from the measured torsional resistance, for example, according to:

$$\mu = G * S/n \qquad (2)$$

Where, μ = viscosity, G = cell constant, S = scale deflection and n= speed of rotation.

Both Hakke and Brookfield make commercially available measurement heads. It can be seen from equation 2 that this technique (in common with others used in high temperature measurements) is not an absolute method for determining viscosity. It is customary to determine an apparatus constant (G) by calibration at ambient temperature with oils of known viscosity. Hence, the reason for standards for use in calibration at high temperature.

2.2Oscillating plate method

If a plate undergoing linear oscillations is immersed in a fluid it will experience a retarding force which is proportional to the viscosity of the fluid. If the density of the liquid is determined independently the viscosity can be calculated according to:

$$\mu\rho = G\left(\frac{\phi a}{\phi}\right)^{N} \qquad (3)$$

Where μ = viscosity, ρ = density, G = cell constant, ϕa amplitude in air, ϕ = amplitude in liquid and N = constant with a value close to 2.

2.3Falling sphere method

There are several types of falling body viscometers, in the version used in this investigation a sphere is dragged through the melt and the viscous drag force exerted on the sphere determined by monitoring the apparent mass of the sphere and the viscosity of the liquid derived from the Stokes equation:

$$Fd = 3\pi\mu d \qquad (4)$$

Where Fd = viscous drag force, μ = viscosity and d = diameter of sphere

2.4Inclined plane method

In this technique the sample is placed in a crucible, heated to the required temperature and the liquid poured onto an inclined plane. The viscosity is then derived by assuming that it is proportional to the length of the cooled ribbon of slag formed on the plane. This method is used frequently in industry to provide quick and approximate values (especially for comparative purposes) of viscosity.

3. RESULTS

3.1Phase 1

The viscosity measurements reported by the laboratories participating in phase 1 of this investigation are summarised in Figure 1. It can be seen that there is appreciable scatter in the results (±80K around the mean) and these results more than justify the need for development of a suitable SRM. A full description of the viscometers used in this study and discussion of all the results has been provided by Mills [1]. These data appear to confirm that the contact materials used in the viscometer have a significant effect on the results. The higher viscosity values were (mostly) derived from experiments in which graphite components were used. At a meeting of all the phase 1 members in Brussels it was agreed that viscosity measurements should be repeated on the SRM according to a strict protocol in an attempt to reduce the scatter shown by the results. This recommended that the sample should be dried overnight at 110°C before onset of measurements; molybdenum (or platinum) components in the viscometer were preferable to graphite; a neutral (N_2 or Ar) or reducing (Ar + 10% H_2) atmosphere should be provided during measurements; samples should not be heated above 1400°C; all thermocouples should be checked against calibrated thermocouples; the difference between Tmelt and Tmeasured should be determined; nature of the isothermal hot zone should be well known and before measurements on the SRM slag the viscometer should be calibrated with at least two oils in the 0.1 - 1.0 Pas range as well as NBS710 glass at high temperature. Furthermore, each participant was to make three separate determinations and all post measurement samples were to be returned to Hoogovens for chemical analysis.

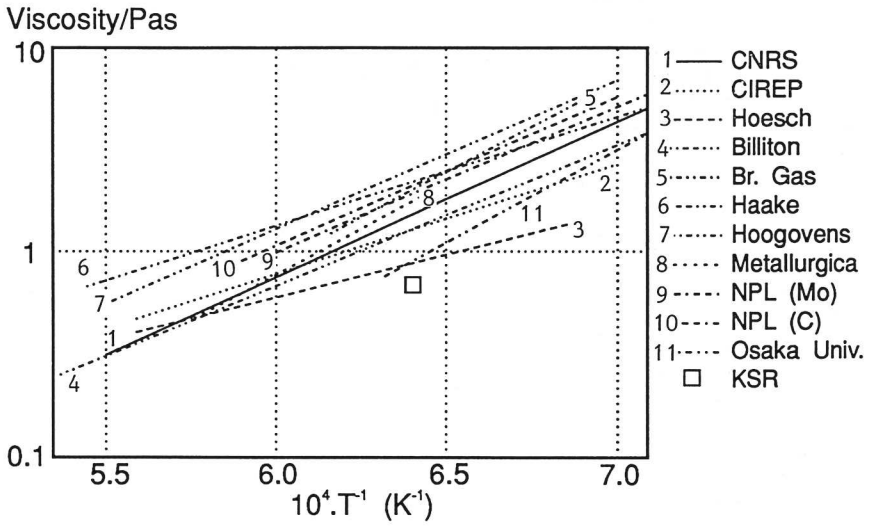

Fig. 1. Viscosity measurements reported by labs participating in phase I

3.2Phase 2

The viscosity measurements reported by the various labs involved in phase 2 are presented in Figure 2. Although the scatter is less than in phase 1 it is still appreciable at ±55K around the mean. In order to determine to what extent the values were influenced by the nature of the contact materials within the viscometer Mills and Machingawuta [2] separated the data into sets corresponding to Mo, C or Pt/Rh components. Data obtained from equipment containing graphite in contact with the slag (NPL, Metallurgica, Hoogovens, Hoesch, British Gas, and Tohoku Univ.) showed

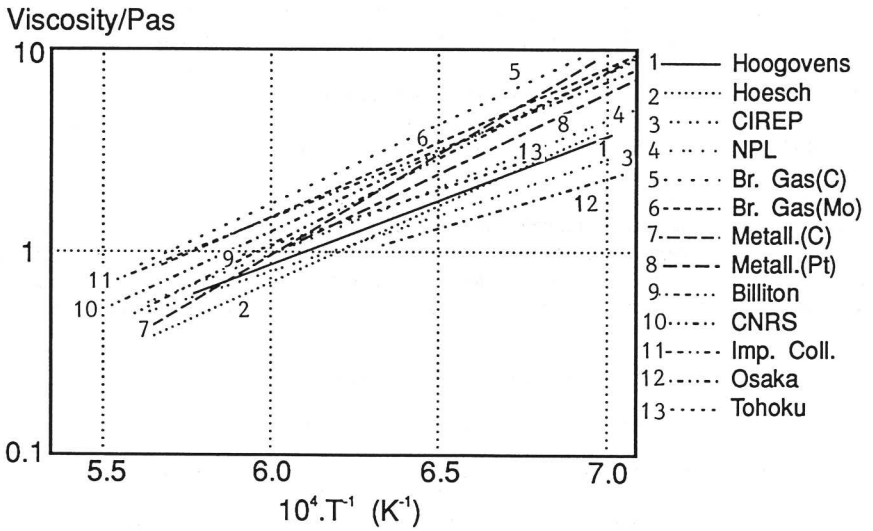

Fig. 2. Viscosity measurements reported by labs participating in phase II

considerable scatter, and generally, the highest viscosity values. It has been postulated [3] that this lack of consistency was due to chemical reactions occurring between the SRM and graphite (some evidence of the evolution of a white plume of smoke reported) and additional work by Green [4] suggested evidence for a structural change in the slag. An alternative explanation for the (apparent) high viscosities may be due to the presence of (solid) carbon particles in the liquid slag. In any case the calibration of viscometers with the SRM can not be recommended for viscometers containing graphite components.

Figure 3 shows the data obtained by those labs where molybdenum components are used. There is good agreement between the data obtained by Billiton Research, British Gas, CNRS and NPL. The scatter band covered by these measurements is <20K. Data provided by the falling sphere method is included in this diagram though there is good justification for treating the result separately as a) the difference between Tmelt and Tmeasured was significantly higher than that found in any other apparatus (70K) and the technique is not regarded as being as accurate as the concentric cylinder methods.

A wide discrepancy exists in the data provided by labs using platinum or platinum/rhodium components. NPl and Metallurgica presented values which are in fairly good agreement with the results reported by labs using molybdenum contact materials, whereas Osaka and CIREP show considerable differences. The reason for these discrepancies can not be accounted for.

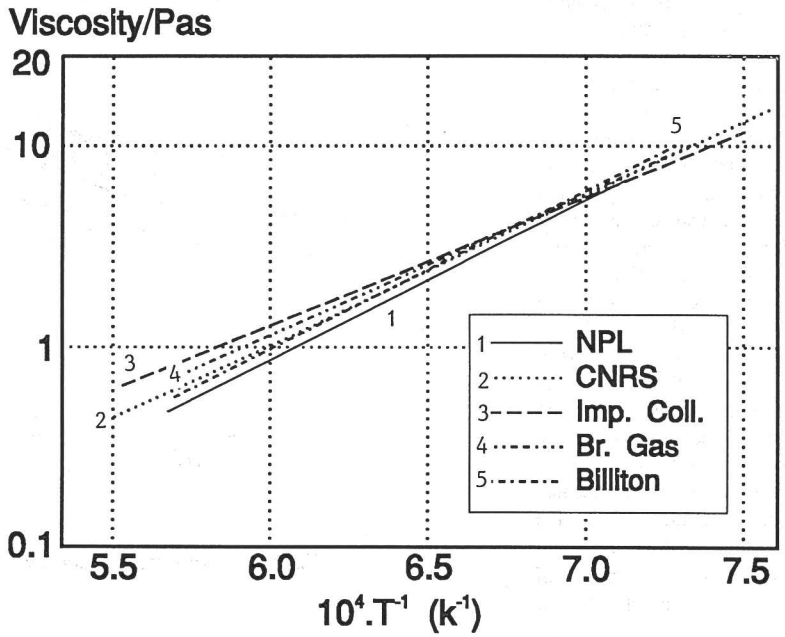

Fig. 3. Viscosity measurements reported in phase II by labs using Mo components

4. CONCLUSIONS

This investigation represents one of the few round robin studies in which high temperature viscosity measurements of the same material have been made using a variety of techniques and at a wide number of different institutions. The considerable scatter displayed by the results have highlighted the need for such an SRM. Furthermore, they have shown that accurate viscosity values can only be obtained if great time and care are taken with the measurements, preferably performed according to a strict protocol and have indicated the effect contact materials can have on the results. The development of an SRM slag and associated protocol would aid calibration of viscometers and could lead to an improvement in the accuracy of reported values.

A statistical analysis of the viscosity data sets [3] indicates that the data obtained with concentric cylinder viscometers using molybdenum components could provide a recommended viscosity - temperature relationship for an SRM based on a lithia-aluminium silicate slag. This relationship could take the form of a "best fit" relationship using all data reported by Billiton Research, British Gas, CNRS and NPL plus results obtained from Metallurgica using platinum crucibles. The final regression equations for the Arrhenius and Weymann equations respectively, derived from the collected data presented in this work are considered to provide the "best fits" for the experimental data:

$$\log 10\ \mu\ (\text{Pas}) = -4.504\ (\pm 0.019) + 7461\ (\pm 30)\ T^{-1} \qquad (5)$$

$$\log 10\ \mu\ (\text{Pas}) = -8.125\ (\pm 0.019) + \log T + 8127 T^{-1} \qquad (6)$$

These recommended viscosity values are subject to experimental uncertainties of ±10%.

It is hoped that following this study an SRM for high temperature viscometry, applicable to the study of metallurgical slags, will be produced shortly and be available commercially from BCR.

ACKNOWLEDGEMENTS

This project was partially funded by the European Economic Community (BCR). The authors would like to express their gratitude to all participants in the project, including P. Green (British Gas), J.N. Pontoire (CIREP), G. Urbain (CNRS), R. Bauer (Haakke), R. Scheel (Hoesch Stahl), Metallurgica Gmbh, T. Iida (Osaka), J. Kinder (KSR International), P. Rogers (imperial College), N.Machingawuta (NPL), Tohoku Univ.

REFERENCES

1) K.C.Mills: NPL Report DMA(A)175 1989.

2) K.C.Mills & N.Machingawuta: NPL Report DMM(A)29 1990.

3) K.C.Mills: NPL Report DMM(A)30 1990.

4) P. Green: Private communication.