‘ROUND ROBIN’ PROJECT ON THE ESTIMATION OF SLAG VISCOSITIES

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ABSTRACT

A “round robin” project has been carried out to determine the accuracy and reliability of various models used to estimate the viscosities of industrial slags. The 21 participants were divided into measurement suppliers and modelling participants. Reference materials were issued to the measurement suppliers to check the validity of the viscosity data supplied. A data base of viscosity-temperature-composition data was established for eight different categories of slags. Chemical compositions were issued to the different modelling participants and the predicted viscosities were compared with calculated values. For mould fluxes the global % errors associated with the various models were: modified Iida (25), Riboud (30), Gupta (35), NPL (37). For non-fluoride slag systems, the Ling Zhang, KTH and modified Iida models all performed well.

1 INTRODUCTION

It was apparent at the 1996 Slags Conference in Sydney that there was a large effort being put into the mathematical modelling of the viscosities of slags from their chemical compositions. There were at least 10 models available and it was also apparent that each group pursued their own model and ignored the other extant models. Consequently, it is difficult for industrial laboratories to know which model to use for their needs without trying out each of the models and, even then, not knowing what is the probable uncertainty in the predicted values.

There is no doubt that there is industrial interest in accurate viscosity predictions. Viscosity is the physical property of most interest to the majority of industrial organisations; a recent questionnaire of British industries' requirements for physical property measurements on slags placed viscosity at the top of the list [1]. For instance, the viscosity of the mould slag is the key parameter determining the optimum casting conditions in continuous casting. The ability to predict slag viscosities accurately is of interest to a variety of industries viz (i) steel and (ii) non-ferrous metal producers, (iii) glassmaking, (iv) enamels, (v) coal combustion and gasification, (vi) waste disposal organisations.

Consequently a ‘round robin’ interlaboratory comparison project has been established to check the performances of various models and the uncertainties associated with these predictions. A key element in this project is the establishment of both traceability and the uncertainties of the viscosity-temperature-composition data used in checking the performances of the model. For instance, if viscosity data supplied by a certain laboratory are subject to a systematic error of +30%, then (a) any model based on these data will be in error by +30% or (b) the performance of other models when using these data may be subject to an uncertainty of -30%.

2 PROGRAMME RATIONALE

It was proposed that the performance of various models could be checked by comparing the results of predicted models with those obtained experimentally in a 'round-robin' exercise. It was suggested that this could be carried out by:

(i) Classifying slags into various groups, eg (a) synthetic slags, (b) coal slags, (c) mould slags etc.

(ii) Various laboratories would participate within these groups, these would be split into *measurement suppliers* providing measurements of viscosity-temperature and *modellers* ie those providing models to estimate viscosities.

(iii) A data base of traceable viscosities (± 10%) and chemical compositions of the slag would be established for each of these slag groups; traceability to be checked by issuing reference materials and comparing the results obtained with those obtained by other participants.

(iv) Each participating laboratory in the modelling group would be given the chemical compositions of the slags and asked to calculate the viscosity using their models and provide the coordinator with the results.

(v) The performance of each model would be evaluated and compared with the results obtained with other models by the coordinator.

3 PARTICIPANTS

There were 21 participants in the programme. Details of their participation are given in Table 1. The nature of their participation has been denoted using:

1 = Measurement of viscosity of reference materials

2 = Provision of viscosity-temperature-composition to the data base

3 = Prediction of viscosity from chemical composition using their models

The identity of the measurement participants has been masked but the identities of the modelling participants has not been masked since the purpose of the project was to compare the performances of the various published models.

4 RESULTS FOR REFERENCE MATERIALS

The objective of this exercise was to check the accuracy of the measurements by individual laboratories by issuing a reference material to the various participants supplying viscosity measurements. In this way any systematic errors in their results would be identified. A prefused mould flux was selected since:

(i) mould fluxes are not very aggressive towards crucible and bob materials
(ii) they are fluid at relatively low temperatures (> 1100 ^{o}C) and
(iii) in the prefused form they have a high degree of homogeneity.

The aim was to distribute the reference material (RM) to all the participants. Unfortunately, it was not possible since:

(a) Carbo-ox, the powder producer, had switched from manufacturing pre-fused to spray-dried powders and only a limited amount of material was available
(b) the number of participating laboratories was much greater than expected
(c) some laboratories needed a large amount of material (1 kg).

Consequently, four reference materials were issued, PMF, R1, R3, and PAJ. In order to cross-check the viscosity values, some laboratories carried out measurements on more than one reference material.

4.1 Stability of the Reference Materials (RM)

Laboratory M carried out two runs on the RM (PMF) in which the experiment procedures were varied (i) 16h at 800 ^{o}C prior to measurement, (ii) 3h at 750 ^{o}C prior to measurement. It can be seen from Figure 1 that the viscosity in Run 1 is higher than in Run 2. Inspection of the pre- and post-measurement chemical compositions showed that there was a loss of 0.4% F in Run 1 compared with no loss of F in Run 2. Fluorine losses result in an increased viscosity. In addition, Laboratory G carried out pre- and post-measurement analyses on reference material R3 and found that there had been a loss of 2.5% F during the measurement experiments. However, the heat treatment in this case was much more extensive than that used by other laboratories.

Table 1 - Summary of participants and their activity within the programme

Organisation	Address[(a)]	Contact	Type	Participation		
				1	2	3
Agne-Gijutsu	Kitamura Bldg, Minato-ku, Tokyo, Japan	Prof Y Shiraishi	INS	✓		
Alabama Univ	Metall. Eng. Dept., Tuscaloosa, AL, USA	Prof R Reddy	EDU	✓	✓	✓
British Steel	Teesside Techn. Centre, Middlesbrough, UK	V Ludlow	STE	✓	✓	
Carbo-ox	Polo Industriale, Resende, RJ, Brazil	Dr O Afrange	MPM		✓	
CSIRO	Div. Coal Energy, N Ryde, Sydney, Australia	Dr H Hurst	RES		✓	
CSM	Via di Castel Romano, Rome, Italy	Dr A Di Donato	RES	✓	✓	
GKW/CRC/ CSIRO	CSIRO Minerals, Clayton, Vic., Australia	Dr L Zhang	RES	✓	✓	✓
EEUF MG	Metall. Eng. Dept., Bela Horizonte, Brazil	Prof Seshadri	EDU	✓	✓	✓
Hoogovens	Refract. Dept. Hoogovens, Ijmuiden, Netherlands	Dr M Franken	STE	✓		
HUT	Metall. Lab., Helsinki Univ. Tech., Espoo, Finland	Prof L Holappa	EDU	✓	✓	
Iscor	Steelworks, Vanderbijlpark, 1900, South Africa	Dr J Latusek	STE			✓
KTH	Dept. Theor. Metall., S-10044 Stockholm, Sweden	Prof S Seetharaman	EDU	✓	✓	✓
Kyushu Univ	Materials Science Dept., Fukaoka, Japan	Prof K Mori	EDU	✓	✓	
Metallurgica	Schiefferbank 6, 45472 Mulheim, Germany	Dr H Schmidt	MPM	✓	✓	
NPL	CMMT, NPL, Teddington, UK	Dr K C Mills Ms L Chapman	RES	✓	✓	✓
Osaka Univ	Dept. Material Science, Suita, Osaka, Japan	Dr Y Kita Prof T Iida	EDU	✓	✓	✓
Pretoria Univ	Dept Materials Science, Pretoria, South Africa	Dr C Pistorius	EDU	✓		
Prosimet	Via Rodijo, 24040 Filago, Italy	Dr R Carli	MPM	✓	✓	
SAIL	Steel Authority India, Ranch 834002, India	Dr V K Gupta	STE/ RES			✓
Shell	Res. And Technol. Centre, Amsterdam, Netherlands	Dr E Wesker	POW		✓	
SMI	Corp. R&D Labs., Hiraki, Kashima, Ibaraki, Japan	Dr M Kawamoto	STE/ MPM	✓		

EDU = Educational Establishment INS = Instrument Maker MPM = Mould Powder Manufacturer
POW = Power Generation RES = Research Establishment STE = Steel producer
1 = Validation Study Phase 2 = Data Base Phase 3 = Modelling Phase

These observations indicated that some deviations in viscosity may result from volatilisation of F and possibly alkali metals (Na, K, Li) since NaF etc can be readily formed at temperature around 800 ^{o}C. Thus, some variation in the viscosity values might be expected to occur as a result of the procedures used in (i) filling the crucible and (ii) in heating the specimen during the measurement sequence.

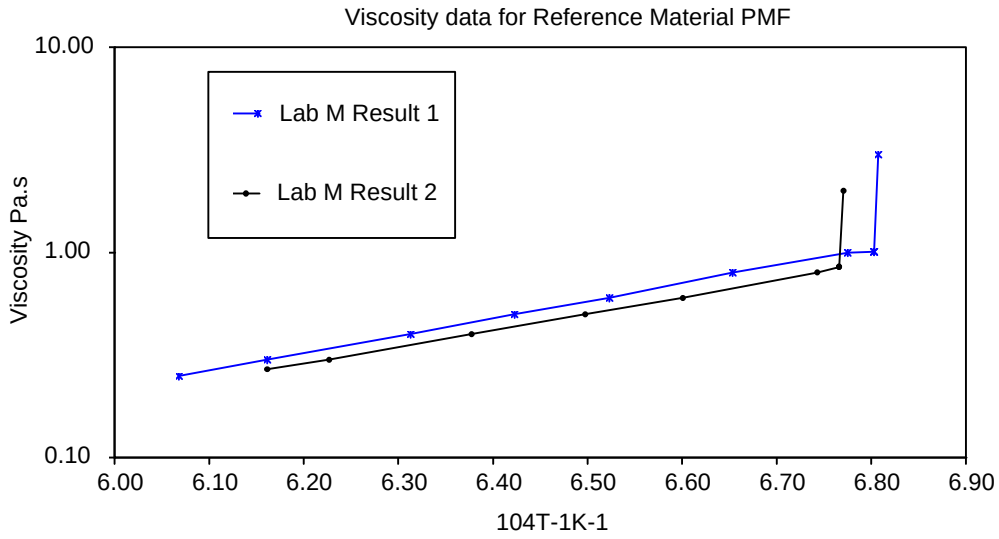

Figure 1 Viscosity (on a logarithmic scale) for PMF as a function of reciprocal temperature (K^{-1}), as reported by Laboratory M.

4.2 Viscosity of Reference Material - PMF

Viscosity results obtained by the various participating laboratories are shown in the form of an Arrhenius plot in Figure 2. The agreement in the results is quite remarkable, especially when it has been shown that differences in procedure in filling the crucible and in carrying out the measurements has been shown to affect the results. The overall spread of the data is about ± 10% around the mean.

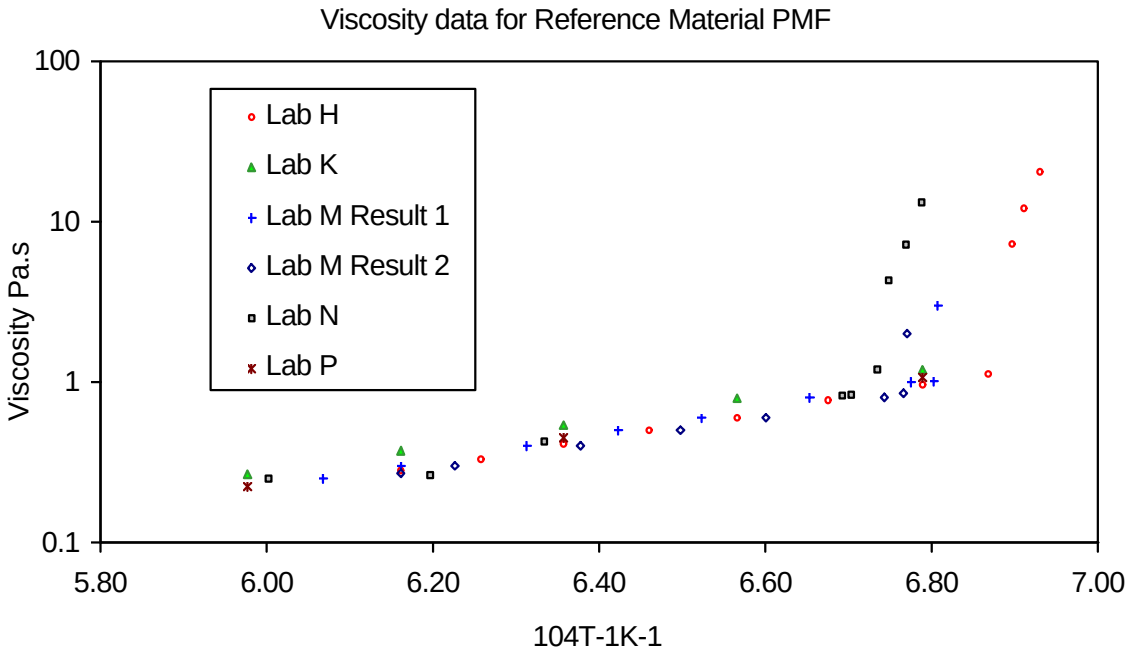

Figure 2 Viscosity (on a logarithmic scale) of PMF as a function of reciprocal temperature (K^{-1})

4.3 Viscosity of Reference Material - R3

The viscosity results for RM-R3 reported by various investigators are plotted in Figure 3 and it can be seen that there is good agreement between the results obtained by Labs G, F, N and R. The results recorded by Lab G are approximately 25% higher but it is noticeable that the first measurement recorded was in good agreement with the results obtained by Labs F, N and R. The values for 1400 ^{o}C recorded by Lab Q are about 20% lower than those due to Labs F, N and R but are in good agreement (< 10%) for temperatures below 1400 ^{o}C.

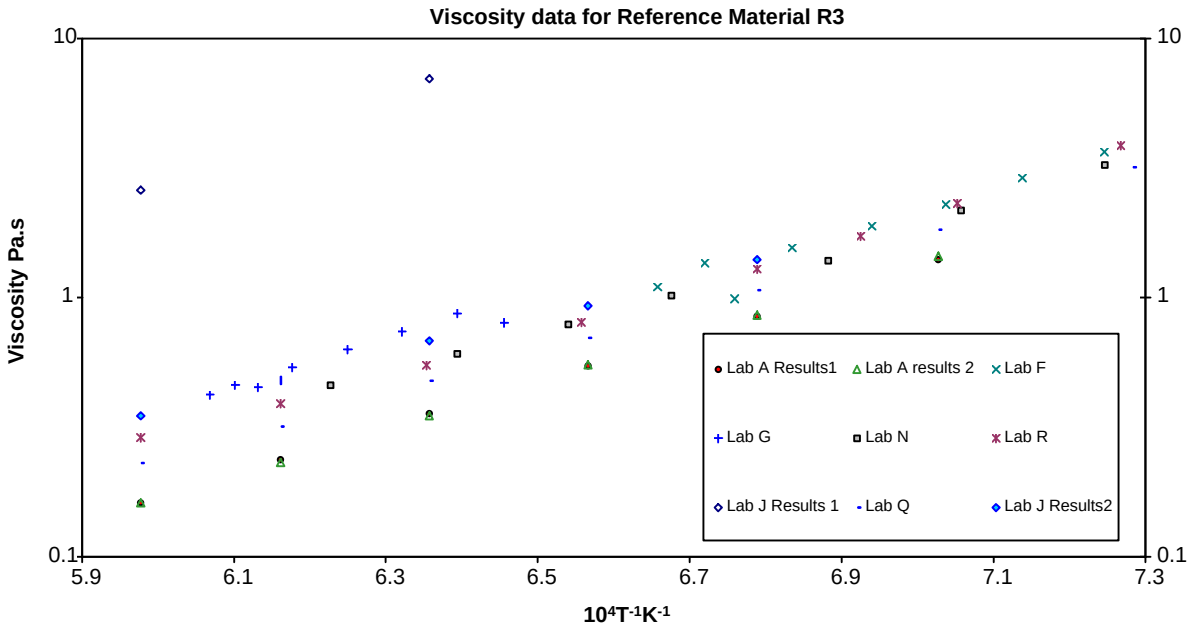

Figure 3 Viscosity (on a logarithmic scale) of RM-R3 as a function of reciprocal temperature (K^{-1})

Lab J used a novel experimental arrangement consisting of two round ended Al_2O_3 tubes as cylinders and calibrated out the friction created by the 2 tubes being in contact. The results obtained vary by an order of magnitude from the other results. The most likely explanation for the deviation in the results is the pick-up of Al_2O_3 by the reference material which could be up to 30% (no analysis provided). Lab J subsequently repeated the measurements using a Pt/4%Rh crucible and as can be seen from Figure 3 the results although showing some scatter were in good agreement with values reported by Labs G, N and R. The values obtained by Lab A are about 50% lower than values recorded by Labs N, R and Q. It is possible that this may be a result of sample contamination resulting from the distribution and storage (e.g. the

effects of moisture). However, it is more probably a result of using graphite components where non-wetting conditions could result in '*slip*' and a low torque measurement.

4.4 Viscosity of Reference Material - PAJ

The viscosity results obtained by the various participants are plotted in Figure 4. The results show that there is appreciable scatter, the results obtained by Lab S with the oscillating plate method are significantly lower than (i) those reported by Lab O using the same technique and (ii) other laboratories using the rotating cylinder method. However, it must be pointed out that Laboratory N found the values showed some variation with rotation speed which suggests the sample was not very satisfactory as a reference material.

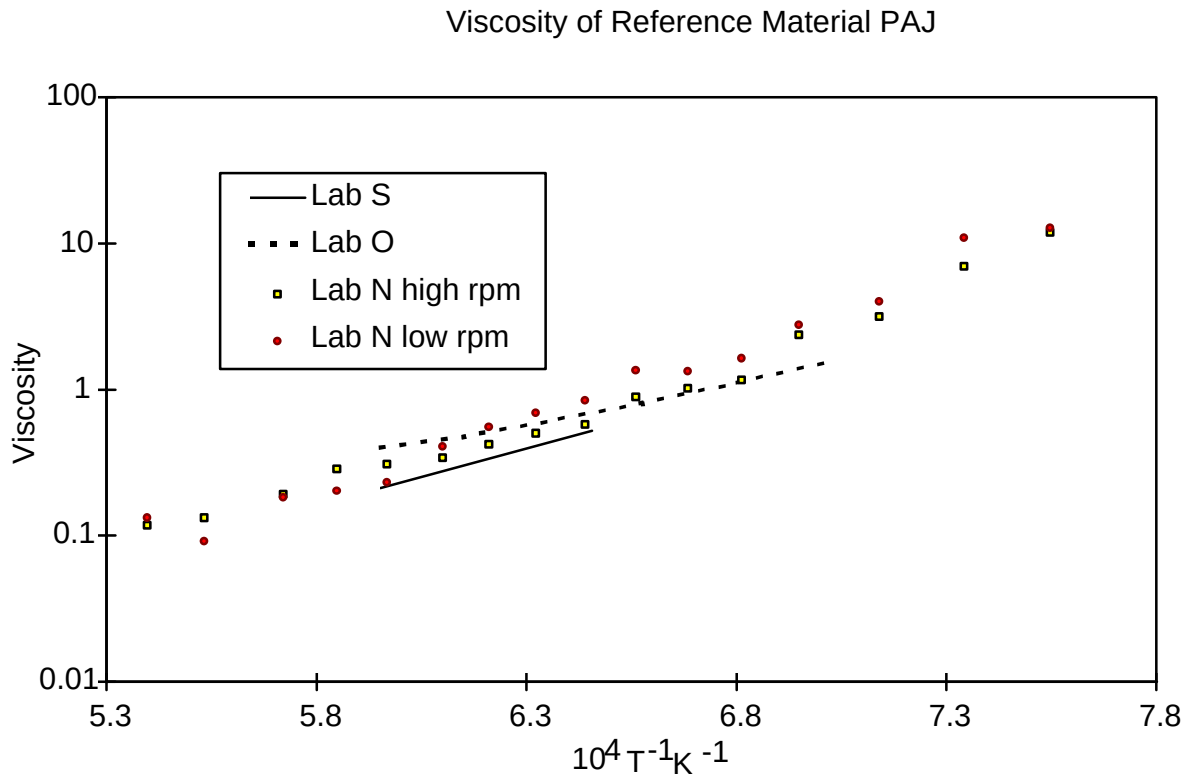

Figure 4 Viscosity (Pa.s) (on a logarithmic scale) for reference material, PAJ, as a function of reciprocal viscosity (K^{-1})

5 ESTABLISHMENT OF A DATA BASE

Data for the composition and viscosity-temperature results for the slags were submitted by various participating laboratories. These data were sub-divided into slag-types namely:

- mould fluxes
- blast furnace (BF) slags
- ladle slags
- F containing slags
- synthetic slags
- coal slags
- borates
- boro-silicates.

The contents of the data base are summarised in Table 2.

Table 2 - Contents of data base according to slag type showing the number of composition-viscosity data for slags submitted by individual laboratories

Mould fluxes	BF slags	Ladle slags	F-containing slags	Synthetic slags	Coal slags	Borates	Boro-silicates
B (12)	E (116)	N (1)	E (15)	E (57)	F (66)		A (15)
C (11)	W (2)		K (8)	I (6)	L (11)	K (11)	K (116)
D (58)			R (22)	K (29)	T (6)		
M (50)				R (35)			
N (6)							
O (19)							
P (7)							
R (3)							

The compositional data were issued to various participants who had developed models e.g. University of Alabama, GKW/CRC/CSIRO, EEUFMG, Osaka University, KTH and SAIL. In addition, software was developed by Dr S Sridhar and Mr A B Fox (Imperial College) to calculate viscosities using various published models (e.g. Riboud, Iida etc).

6 WEIGHTING OF THE DATA

It is necessary to weight the data in order to give more weight to the more reliable measurements. The viscosity-temperature data were weighted according to the performance of the laboratory in the validation phase. Equal weighting was given to all data produced by laboratories which fell within the bounds of ± 10% around the accepted values for the various reference materials since some of this variation could be due to F-losses.

With regard to compositional information the highest weighting was given to the data where chemical analysis was carried out on the post-measurement sample. The weighting accorded was in the hierarchy: post measurement > pre-measurement > batch > typical analysis and target compositions. The weighting applied to the results submitted by various participants is shown in Table 3.

Viscosity measurements from mean
- ± 10% = 1
- ± 10-20% = 2
- ± 20-35% = 3
- > ± 35% = 4

No reference
- material measurements = 5

Chemical composition
- Post measurement = 1
- Pre-measurement composition = 2
- Batch analysis = 3
- Typical analysis, target composition = 4

Table 3 - Summary of weighting applied to databases supplied by different laboratories

Laboratory	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**	**M**	**N**	**O**	**P**	**R**
Measurements	1	1	5	5	1	1	1	5	1-2	1	1	1	1	1-2	1	1
Composition	3	3	2	-		-	-		-	4?		1	3	?	2	1

7 MATHEMATICAL MODELLING OF VISCOSITY-TEMPERATURE RELATIONS

The performances of the following models shown in Table 4 have been examined. These were checked in two ways:

(i) by creating software describing different models (referred to as Central Software) and

(ii) by sending composition data to the modellers and comparing the calculated values with experimental values.

Since the size of the data base was so large, only the results obtained for mould flux are described in detail here.

Table 4 - Models applied to different slag systems

Model	Mould flux	Synthetic	BF	Ladle	F-slags	Borates, Borosilicates	Coal slags
Riboud [2]	✓	✓	✓	✓	✓		✓
Koyama [3]	✓						

Kim [4]	✓						
NPL [5]	✓	✓	✓	✓	✓		
Iida (Osaka) [6,7]	✓						
Utigard [8]	✓				✓		
Gupta [9,10]	✓						
Seshadri [11]	✓						
Urbain [12]		✓	✓	✓			✓
KTH [13]		✓	✓	✓			✓
Ling Zhang [14]		✓					✓
Reddy [15]						✓	

The performance of the model was evaluated by determining relative differences between the calculated and measured viscosities. The following parameter δ_n due to Iida [6] has been employed

$$d_n = \frac{(h_n)_{cal} - (h_n)_{mea}}{(h_n)_{mea}} \times 100 \qquad (1)$$

where $(\delta_n)_{cal}$ and $(\delta_n)_{mea}$ are the calculated and measured viscosities for a multicomponent industrial flux n, respectively

$$\Delta = \frac{1}{N} \sum |d_n| \qquad (\%) \qquad (2)$$

where N is the number of samples. The parameters δ_n and Δ imply the relative difference between calculated and measured viscosities [6].

In large data bases, errors other than experimental ones are likely, these mainly include typing and compositional errors. To correct these errors unusually large δ_n values were identified and the composition and spreadsheet equations checked or other explanations sought.

7.1 Results obtained with Central Software

Software was written for most of the models used for mould fluxes (see Table 4 columns 1 and 2) with the exception of the Seshadri and Gupta models. In order to avoid giving excessive weight to the results of these participants supplying large data bases about 12 to 20 compositions were selected randomly. The results obtained are shown in Table 5. It can be seen that the Riboud, Iida and NPL models all performed reasonably well for the whole data set with Δ values around 30%. When the data for laboratories with the highest weighting (Laboratories M, R and P) are considered, the Riboud model performed astonishingly well for Lab M data but less well for Labs P and R. In contrast, the Iida and NPL models were more uniform in performance with these data sets.

Table 5 - Values of Δ (defined in Equn 3) for the mould flux viscosity data submitted by the various participating laboratories. The weighting is shown in parenthesis eg (1:3) { } [ ] < > represent 1200, 1300 & 1400 ^{o}C respectively

Model	Δ% for data supplied by various Laboratories							Global
	B (1:3)	C (1:3)	D (5:2)	N (1:3)	M (1:1)	P (1:2)	R (1:1)	Δ%
Riboud	{27.5} [18.6] <28.1>	{29.3} [28.9] <28.5>	{57.4} [52.6] <52.7>	{29.4} [28.9] <28.3>	{4.4} [3.5] <3.3>	{46.8} [48.4] <46.8>	{35.2} [28.8] <29.7>	{31.8} [28.8] <30.6>
Koyama	{48.3} [51.1] <56.8>	{89.3} [77.2] <61>	{50.2} [52.7] <54.8>	{55.4} [49.0] <45.0>	{169} [141] <121>	{73.1} [66.1] <57.6>	{57.2} [49.7] <35.3>	{84.1} [76] <69.6>
Kim	{26.1} [33] <52.3>	{20} [22.8] <33.6>	{53.8} [53.3] <59>	{25.5} [41.1] <54.3>	{62.9} [50.9] <48.5>	{ } [ ] < >	{ } [ ] < >	{39.1} [41.1] <49.9>
NPL	{47.3} [37.5] <44.8>	{25.2} [20.4] <23.4>	{56.6} [45.4] <41.4>	{51.4} [42.6] <32.1>	{42.9} [36.7] <33.2>	{42.5} [33.1] <29.8>	{36.2} [21] <13.7>	{43.1} [34.5] <32.4>
Iida	{40.3} [34] <42.3>	{28.5} [23.1] <19.8>	{34.7} [30.6] <30>	{46.3} [43.1] <40.5>	{32.2} [29.4] <27.4>	{41.9} [37] <31.8>	{45.8} [42.8] <50.8>	{36.7} [32.2] <32.4>

7.2 Results obtained by Modelling Participants

7.2.1 Gupta model

Inspection of the global Δ values obtained from the data supplied by SAIL using the Gupta model indicate that:

(i) it gives Δ% values: Lab B (40), Lab C (35), Lab D (42), Lab M (28), Lab N (30)

(ii) it tends to underestimate the viscosity

Thus its performance is similar to that of the Riboud, Iida and NPL models.

7.2.2 Iida model

The calculated viscosity values submitted by Iida and Kita indicated that in some cases there were some differences with the viscosity values calculated with the Central Software. It transpired that these differences arose from recent improvements in the model to account for the behaviour of Al_2O_3 [7]. Inspection of the results derived by Iida and Kita indicated:

(i) the Δ values for the following data sets were Lab B (26) Lab C (23) Lab M (25) Lab N (26) Lab P (34) with the Global Δ at ca 25;

(ii) these results are slightly better than the values calculated with the original Iida Model in the Central Software and suggests that the correction for Al_2O_3 in the modified model does improve the reliability of the predictions;

(iii) values calculated by Iida with the Riboud model provided a much poorer fit than those calculated with the Central Software.

In summary the Iida model performs well with Global Δ of 25.

7.3 Summary of Other Results for Categories of Slags

Excellent results were obtained on other slag systems using the Ling Zhang [14] and KTH [13] models. These models can not be applied to mould flux since they do not include CaF_2 at the present time. Using the Ling Zhang model a global Δ value of 22% was obtained for the large coal slag data base. This is remarkable given the difficulties associated with the viscosity measurements on coal slags. The KTH model was applied to the synthetic slags and Δ of 15% was obtained, showing the model is capable of very reliable estimates of the viscosity.

The modified Iida model [7] performed well with blast furnace and coal slags giving a global Δ values of 27 and 19%, respectively.

8 DISCUSSION

The performance of the models, as expressed by the global Δ, value should be judged against the size of experimental errors in the viscosity measurements. There are differences of $\pm$10% in values reported by various laboratories. These probably arise from:

(i) not correcting for temperature differences between the measurement thermocouple and the actual temperature of the melt;

(ii) varying fluorine (and other elements) losses which occur if held either for long times at temperatures >800 ^{o}C or at temperatures above 1500 ^{o}C.

In addition, few laboratories carry out full chemical analyses on their post-measurement samples and losses of fluorine etc could give rise to changes in viscosity of a further $\pm$10%.

Consequently most of the viscosity-temperature-composition data are subject to uncertainties of $\pm$20%. Given this it would be remarkable if the models predicted values with global Δ values below 20 %. For mould fluxes the Δ values obtained with the Riboud, modified Iida, Gupta and NPL models ranged between 25 and 35%, which should be considered to be very reasonable when compared with experimental uncertainties of $\pm$20%.

For non-fluoride systems, the Ling Zhang, KTH and modified Iida models worked extremely well with Δ values of around 20%. This may be a result of (a) the good performance of the model and (b) the slags being more stable.

On the basis of this study, it is recommended that in any future "round robin" project, the data base should be based solely for systems where there were chemical analyses for the post-measurement samples.

CONCLUSIONS

1) The bulk of the experimental viscosity-temperature-composition data held in the data base are probably subject to uncertainties of $\pm$20%.
2) The estimated viscosities for mould fluxes obtained with the various models (in terms of the global Δ values) are modified Iida (25%), Riboud (30%), Gupta (35%), NPL (37%).
3) The Ling Zhang, KTH and modified Iida models all performed well ($\Delta \sim$20%) for slag systems with no fluorides present.
4) If viscosity models are to be improved it will be necessary to use a data base containing results based solely on post-measurement chemical analysis since existing models are currently making predictions with uncertainties close to the experimental uncertainties (for both viscosity determination and chemical composition).

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