Development of a Quasi-chemical Viscosity Model for Fully Liquid Slags in the Al_2O_3 – CaO –‘ FeO ’– MgO – SiO_2 System. Part 3. Summary of the Model Predictions for the Al_2O_3 – CaO – MgO – SiO_2 System and Its Sub-systems

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A structurally-based quasi-chemical viscosity model for fully liquid slags in the Al_2O_3 – CaO –‘ FeO ’– MgO – SiO_2 system has been developed. The focus of the work described in the present paper is the analysis of the experimental data and viscosity models in the quaternary system Al_2O_3 – CaO – MgO – SiO_2 and its sub-systems.

A review of the experimental data, viscometry methods used and viscosity models available in the Al_2O_3 – CaO – MgO – SiO_2 and its sub-systems is reported. The quasi-chemical viscosity model is shown to provide good agreement between experimental data and predictions over the whole compositional range.

KEY WORDS: slag viscosity; viscosity model; Al_2O_3 – CaO – MgO – SiO_2 .

1. Introduction

The quaternary system Al_2O_3 – CaO – MgO – SiO_2 is a key slag system for a number of industrial processes in iron-making and ferroalloys production. The present paper, which is the third in a series, describes development of the quasi-chemical viscosity model^{1–3)} for fully liquid slags in the quaternary Al_2O_3 – CaO – MgO – SiO_2 system.

The first step in the model development has been the assessment of the available information on liquid slag viscosities in the Al_2O_3 – CaO – MgO – SiO_2 system. A summary of the systematic and critical review of the experimental data obtained for the Al_2O_3 – CaO – MgO – SiO_2 system and its sub-systems has been provided. Phase equilibrium analysis has been carried out to ensure that only data from fully liquid slags are used in the model development. The model is then used to predict the viscosities of slags as a function of temperature and slag composition. Comparisons between experimental data and the model predictions have been provided and the behaviour of the model parameters systematically analysed.

A comparison of different viscosity models with the experimental data for the Al_2O_3 – CaO – MgO – SiO_2 system and its sub-systems is given in the last section of the paper.

2. Summary of Experimental Viscosity Data in the Al_2O_3 – CaO – MgO – SiO_2 System

Experimental measurements of slag viscosities at high temperatures are difficult to undertake and are subject to a number of error sources. A careful and systematic analysis of the experimental results is therefore important to reject inaccurate and erroneous measurements before the model optimisation. A summary of the experimental viscosity data

available in the literature for the Al_2O_3 – CaO – MgO – SiO_2 system and its MgO -containing sub-systems is given in Table 1.

The column “Technique” in Table 1 identifies the method used for viscosity determination, atmosphere and temperature measurements. Some authors reported viscometry methods using names different from those commonly used; the exact names are cited in Table 1 instead of standard abbreviations in these cases. The column “Error” indicates the experimental error reported by researchers, in most cases this does not exceed 10%. The column “Accepted” indicates number of the experimental points used in the optimisation of the viscosity model in the present study. More detailed discussions on the reasons for acceptance of the results are given below in comparison with the experimental data. Blank or partially filled cells (*e.g.* Ermolaeva,⁹⁾ Prihod’ko³⁸⁾) in Table 1 indicate that corresponding information (*i.e.* error, atmosphere *etc.*) was not reported by investigators.

The viscosity measurements in the MgO – SiO_2 , Al_2O_3 – MgO – SiO_2 , Al_2O_3 – CaO – MgO and CaO – MgO – SiO_2 systems have been discussed in the previous papers of this series.^{2,3)} An analysis of the experimental data in the Al_2O_3 – CaO – MgO – SiO_2 system, followed by a general discussion on the results, methods and procedures used to determine viscosities in the Al_2O_3 – CaO – MgO – SiO_2 system and its sub-systems is given below.

Since the system Al_2O_3 – CaO – MgO – SiO_2 forms the basis of slags used in iron- and steel-making, there are a lot of experimental studies^{10,12,21,22,24,29–44)} for this system available in the literature. More than 20 papers summarised in Table 1 were critically analysed, and the experimental points were selected or rejected for use in model optimisation.

Table 1. Summary of experimental viscosity measurements in the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ system.

System	Source	Technique	PE A	Material of			Number of temp. points	Temperature range [K]	Error %	Accepted
				crucible (cup)	bob (sphere)	compo sitions				
1. MgO	Leu ⁹⁾	Calculations								
2. MgO- SiO ₂	Bockris ⁴⁾	RC; Air; p/m	+	Mo	Mo	5	25	1823 - 2073	±7	25
	Hofmaier ⁵⁾	RC; ; p/m	+	Mo	Mo	1	15	1899 - 2358	±2.6	15
	Licko ⁶⁾	OB; ; t/c	-	Pu/30Rh	Pu/40Rh	1	4	1673 - 1973		0
	Urbain ⁷⁾	RC; Ar; p/m	+	Mo	Mo	3	28	1987 - 2461	±2	28
3. Al ₂ O ₃ - MgO- SiO ₂	Ermolaeva ⁸⁾	Torsional	-			8	84	1598 - 1933	±2.5	0
	Hofmaier ⁵⁾	RC; p/m	+	Mo	Mo	3	46	1771 - 2400	±2.6	46
	Johannsen ⁹⁾	RB; t/c	+	Pu/20Rh	Pu/20Rh	2	8	1573 - 1723	±2.3	8
	Lyutikov ¹⁰⁾	RB; N ₂ ; t/c	+	Mo	Mo	50	336	1673 - 2073	±10	336
	Machin ¹¹⁾	OB; Air; t/c	-	Pt	Pt	7	28	1523 - 1773		28
	Mizoguchi ¹²⁾	RC; Air; t/c	-	Pt	Pu/Rh	10	40	1773 - 1848		40
	Riebling ¹³⁾	CBS; t/c	+	Pu/40Rh	Pu/40Rh	11	90	1773 - 1993		90
	Toptis ¹⁴⁾ - melt	RB; Air; t/c	+	Pu/20Rh	Pu/20Rh	22	105	1673 - 1913	±5	105
	- glass	MP or UAC; Ar				7	30	1094 - 1147		0
	Urbain ⁷⁾	RC; Ar; p/m	+	Mo	Mo	3	29	1803 - 2388	±2	29
	Zhilo ¹⁵⁾	RB; Ar; t/c	-	Mo	Mo	9	46	1873 - 2173	±13	46
	Zhilo ¹⁶⁾	RB; N ₂ ; t/c	-	Mo	Mo	40	302	1673 - 1973		296
4. Al ₂ O ₃ - CaO- MgO	Bakhvalov ¹⁷⁾	Vibrational	-			9	146	1554 - 1874	±5	146
	Shalimov ¹⁸⁾	RB; Ar; t/c	-	Mo	Mo	5	52	1706 - 1964		52
5. CaO- MgO- SiO ₂		Rotational; N ₂ ; t/c	-	C		20	89	1573 - 1823		63
	Gul'tyai ²⁰⁾									
	Kawai ²¹⁾	RB; t/c	-	C	C	15	29	1773 - 1873		0
	Kozu ²²⁾	RB				1	3	1673 - 1698		0
	Licko ⁶⁾	OB; t/c	-	Pu/30Rh	Pu/40Rh	13	52	1673 - 1973	±3	52
	Machin ¹¹⁾	OB; Air; t/c	-	Pt	Pt	6	20	1623 - 1773		20
	Machin ²³⁾	OB; Air; t/c	-	Pt	Pt	10	27	1623 - 1773		27
	Scarfe ²⁴⁾	RB; t/c	+	Pt	Pu/10Rh	1	6	1648 - 1873	±5	6
	Sipp ²⁵⁾ - glass	UAC; t/c				1	32	960 - 1057	±7	0
	Sykes ²⁶⁾	RB; t/c	+	Pu/20Rh	Pu/20Rh	1	5	1673 - 1773	±5	5
	Urbain ⁷⁾	RC; Ar; p/m	+	Mo	Mo	1	7	1675 - 2312	±2	7
	Yasukouchi ²⁷⁾	RB; Ar; t/c	-	Pu/20Rh	Pu/20Rh	3	11	1773 - 1858		11
6. Al ₂ O ₃ - CaO- MgO- SiO ₂										
	Forsbacka ²⁸⁾	RB; Ar+5%CO; t/c	+	Mo	Mo	8	79	1853 - 2023		79
	Gul'tyai ²⁰⁾	Rotational; N ₂ ; t/c	-	C		63	315	1523 - 1823		292
	Hofmann ²⁹⁾	RB; t/c	-			22	69	1723 - 1873		47
	Johannsen ⁹⁾	RB; t/c	+	Pu/20Rh	Pu/20Rh	3	13	1523 - 1723	±2.3	13
	Kato ³⁰⁾	CBS; Air; t/c	-	Pt	Pt	3	15	1620 - 1749	±15	0

Kawai ²¹⁾	RB; t/c	-	C	C	22	42	1773 - 1873		0
Kim ³¹⁾	RB; Ar	-	Pu/10Rh	Pu/10Rh	4	8	1723 - 1773		8
Kita ³²⁾	OB; t/c	-	Pt	Pt	4	19	1523 - 1775		0
Lee ³³⁾	RB; Ar	-	Pu/10Rh	Fe	7	15	1673 - 1723		0
Machin ³⁴⁾	OB; Air; t/c	-	Pt	Pt	22	85	1523 - 1773		85
Machin ¹¹⁾	OB; Air; t/c	-	Pt	Pt	33	152	1523 - 1773		152
Machin ²³⁾	OB; Air; t/c	-	Pt	Pt	63	258	1523 - 1773		258
Mishra ³⁵⁾	RB; N ₂ ; t/c	-	C		18	179	1623 - 1848		179
Muratov ³⁶⁾	RB; t/c	-	Mo		9	57	1573 - 1923	±10	57
Prihod'ko ³⁷⁾		-			1	3	1573 - 1773		0
Scarfe ³⁸⁾	RB; Air	+	Pt	Pu/10Rh	7	58	1448 - 1873	±5	58
Sheludiyakov ³⁹⁾	Vibrational; t/c	-	Pt	Pt	1	18	1513 - 1683		18
Taniguchi ⁴⁰⁾ - melt	CBS	-	Pt	Pt	4	27	1373 - 1823	±1.1	27
- glass	FE; t/c				4	19	1003 - 1173		0
Tsybulnikov ⁴¹⁾	Vibrational; t/c	-	Mo	Mo	3	15	1773 - 1973		0
Vyatkin ⁴²⁾	Rotational; t/c	-	C		18	80	1573 - 1773		80
Yakushev ⁴³⁾	Vibrational; t/c	-	Mo	Mo	13	106	1734 - 1998		106

PEA – post-experimental analysis (analysis of slag composition after viscosity experiments); OB – oscillating bob, CBS – counterbalanced sphere, RC or RB – rotational crucible or bob, FE – fiber elongation, UAC – uniaxial compression, MP – micropenetration methods; t/c – thermocouple, p/m – pyrometer.

The rotational cylinder method appears to be the technique most commonly used to measure the slag viscosities in the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ system and its sub-systems. There are two modifications of this method: rotation of the inner cylinder (or bob) and rotation of the outer cylinder (or crucible). The rotational cylinder method is suitable for use over a wide range of slag viscosities. Other viscometry techniques commonly used to measure the viscosity of slags are the oscillating cylinder (normally bob) and falling (or counter-balanced) sphere methods. “Vibrational” or “Torsional” techniques indicate some modification of the oscillating cylinder method, while “Rotational” means the rotational cylinder method; details of the experimental setups and descriptions used in these cases were not published.

Most of the researchers used either Mo^{29,37,42,44)} or Pt (or Pt–Rh alloys)^{10,12,24,31–35,39,41)} for containers and sensors. These materials are more suitable for high temperature viscosity measurements in the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ system and its sub-systems compared to graphite used by Gul'tyai²¹⁾ and Kawai.²²⁾ Not all the investigators reported the atmosphere in which viscosity experiments were carried out. Nonetheless, at higher temperatures in the case of using molybdenum it is important to carry out experiments in neutral atmosphere (Ar, N₂) instead of air, which can oxidise molybdenum. There is also some evidence of solubility of gases such as argon or nitrogen in the molten silicate slags.⁴⁵⁾

One of the major sources of experimental errors in slag viscosity measurements is due to the contamination of the slag sample by container or/and sensor materials. The dissolution of the sensor and container can lead to changes not only in slag composition but also in container/sensor geometry. Measurements of the slag compositions after experiments reduce these potential errors. Temperature control using a thermocouple adjacent to the sample has better precision compared to an optical pyrometer. These and other considerations were used in the critical review of the data.

The viscosity and temperature ranges investigated for different slags in the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ system and its MgO-containing sub-systems are summarised in **Table**

2. Measurements of the glass viscosity (higher than $10^8 \text{ Pa} \cdot \text{s}$)^{15,26,41)} are not included in this table. It can be seen from this table that the synthetic $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ slags examined by various researchers have a wide range of viscosities (from 10^{-1} to $10^3 \text{ Pa} \cdot \text{s}$) over a wide range of temperatures and compositions. Such great variation of slag viscosity values clearly indicates the need for a comprehensive modelling approach.

3. Optimisation Procedure

The optimisation procedure has been described in details in earlier publications.^{1,2)} Briefly, the methodology used in developing the QCV model in the present study involves

Table 2. Temperature and viscosity ranges reported for molten slags in the MgO-containing systems.

System	Range of temperatures, K	Range of viscosities, Pa·s
MgO-SiO ₂	1673–2461	0.02–2
Al ₂ O ₃ -CaO-MgO	1554–1964	0.1–6
Al ₂ O ₃ -MgO-SiO ₂	1523–2400	0.04–2·10 ³
CaO-MgO-SiO ₂	1573–2312	0.05–80
Al ₂ O ₃ -CaO-MgO-SiO ₂	1373–2023	0.08–3·10 ³

the following stages: 1) collect and carefully analyse all the experimental data available for the slag systems under investigation; 2) exclude unreliable experimental datasets from the model optimisation (using analysis of phase equilibria and trends in the activation and vaporisation energies obtained from experimental viscosity data); 3) evaluate the variability (internal scatter) of experimental data; 4) analyse the trends in the concentrations of structural units (SU) obtained from the quasi-chemical thermodynamic model; 5) calculate the masses and volumes of the structural units using mass balance and available ionic radii data; 6) optimise the model coefficients for the whole compositional range of the slag systems including all unary, binary, ternary etc sub-systems by repeating optimisation cycles from low- to high-order systems; 7) analyse the model parameters obtained during optimisation to understand general trends and dependencies; 8) repeat steps 6 and 7 until the

Table 3. Average weight and volume of structural units.

Average weight of structural unit ($\cdot 10^{-26} \text{ kg}$):
$m_{\text{SU}} = 4.99X_{\text{Si-Si}} + 5.64X_{\text{Al-Al}} + 9.31X_{\text{Ca-Ca}} + 11.93X_{\text{Fe-Fe}} + 6.69X_{\text{Mg-Mg}}$ $+ 5.32X_{\text{Al-Si}} + 7.15X_{\text{Ca-Si}} + 8.46X_{\text{Fe-Si}} + 5.84X_{\text{Mg-Si}} + 7.48X_{\text{Al-Ca}} + 8.79X_{\text{Al-Fe}}$ $+ 6.17X_{\text{Al-Mg}} + 10.62X_{\text{Ca-Fe}} + 8.00X_{\text{Ca-Mg}} + 9.13X_{\text{Fe-Mg}}$
Average volume of structural unit ($\cdot 10^{-29} \text{ m}^3$):
$v_{\text{SU}} = 1.92X_{\text{Si-Si}} + 3.04X_{\text{Al-Al}} + 5.79X_{\text{Ca-Ca}} + 4.34X_{\text{Fe-Fe}} + 3.99X_{\text{Mg-Mg}}$ $+ 2.43X_{\text{Al-Si}} + 3.50X_{\text{Ca-Si}} + 2.96X_{\text{Fe-Si}} + 2.83X_{\text{Mg-Si}} + 4.27X_{\text{Al-Ca}} + 3.65X_{\text{Al-Fe}}$ $+ 3.49X_{\text{Al-Mg}} + 5.03X_{\text{Ca-Fe}} + 4.84X_{\text{Ca-Mg}} + 4.16X_{\text{Fe-Mg}}$

Table 4. Parameters of the quasi-chemical viscosity model for fully liquid slags in the system $\text{Al}_2\text{O}_3\text{--CaO--FeO--MgO--SiO}_2$.

Activation energy ($\cdot 10^2 \text{ kJ/mol}$):

$$E_a = E_{a,\text{Si-Si}}X_{\text{Si-Si}} + E_{a,\text{Al-Al}}X_{\text{Al-Al}} + E_{a,\text{Ca-Ca}}X_{\text{Ca-Ca}} + E_{a,\text{Fe-Fe}}X_{\text{Fe-Fe}} + E_{a,\text{Mg-Mg}}X_{\text{Mg-Mg}} + E_{a,\text{Al-Si}}X_{\text{Al-Si}} + E_{a,\text{Ca-Si}}X_{\text{Ca-Si}} + E_{a,\text{Fe-Si}}X_{\text{Fe-Si}} + E_{a,\text{Mg-Si}}X_{\text{Mg-Si}} + E_{a,\text{Al-Ca}}X_{\text{Al-Ca}} + E_{a,\text{Al-Fe}}X_{\text{Al-Fe}} + E_{a,\text{Al-Mg}}X_{\text{Al-Mg}} + E_{a,\text{Ca-Fe}}X_{\text{Ca-Fe}} + E_{a,\text{Ca-Mg}}X_{\text{Ca-Mg}} + E_{a,\text{Fe-Mg}}X_{\text{Fe-Mg}}$$

$$\left(2X_{\text{Al-Al}} + \sum_i X_{\text{Al-i}} \right)^\alpha \left(E_{a,\text{AlCa}}^{\text{ch/c}} \left(2X_{\text{Ca-Ca}} + \sum_i X_{\text{Ca-i}} \right)^\beta + E_{a,\text{AlFe}}^{\text{ch/c}} \left(2X_{\text{Fe-Fe}} + \sum_i X_{\text{Fe-i}} \right)^\beta + E_{a,\text{AlMg}}^{\text{ch/c}} \left(2X_{\text{Mg-Mg}} + \sum_i X_{\text{Mg-i}} \right)^\beta \right) + \frac{\left(2X_{\text{Al-Al}} + \sum_i X_{\text{Al-i}} + 2X_{\text{Ca-Ca}} + \sum_i X_{\text{Ca-i}} + 2X_{\text{Fe-Fe}} + \sum_i X_{\text{Fe-i}} + 2X_{\text{Mg-Mg}} + \sum_i X_{\text{Mg-i}} \right)^{\alpha+\beta}}{X_{\text{Si-Si}}}$$

where

$$\sum_i X_{\text{Al-i}} = X_{\text{Al-Si}} + X_{\text{Al-Ca}} + X_{\text{Al-Fe}} + X_{\text{Al-Mg}}, \quad \sum_i X_{\text{Ca-i}} = X_{\text{Ca-Si}} + X_{\text{Al-Ca}} + X_{\text{Ca-Fe}} + X_{\text{Ca-Mg}},$$

$$\sum_i X_{\text{Fe-i}} = X_{\text{Fe-Si}} + X_{\text{Ca-Fe}} + X_{\text{Al-Fe}} + X_{\text{Fe-Mg}}, \quad \sum_i X_{\text{Mg-i}} = X_{\text{Mg-Si}} + X_{\text{Al-Mg}} + X_{\text{Ca-Mg}} + X_{\text{Fe-Mg}}; \quad \alpha=3, \beta=1$$

and

$$E_{a,\text{Si-Si}} = 0.79 + 4.65X_{\text{Si-Si}}^2 + 4.98X_{\text{Al-Si}} + 2.34X_{\text{Ca-Si}} + 2.17X_{\text{Fe-Si}} + 2.77X_{\text{Mg-Si}}, \quad E_{a,\text{Al-Al}} = 1.30, \quad E_{a,\text{Ca-Ca}} = 0.82, \quad E_{a,\text{Fe-Fe}} = 0.50, \quad E_{a,\text{Mg-Mg}} = 1.16,$$

$$E_{a,\text{Al-Si}} = 2.78 - 0.96X_{\text{Ca-Si}} - 3.11X_{\text{Fe-Si}} - 0.38X_{\text{Mg-Si}} + 5.63X_{\text{Al-Ca}} + 7.48X_{\text{Al-Fe}}, \quad E_{a,\text{Ca-Si}} = 1.20 - 0.07X_{\text{Fe-Si}} + 0.22X_{\text{Mg-Si}} + 0.29X_{\text{Al-Ca}} + 0.37X_{\text{Ca-Fe}} + 2.00X_{\text{Ca-Mg}},$$

$$E_{a,\text{Fe-Si}} = 0.28 + 0.95X_{\text{Mg-Si}} + 1.20X_{\text{Al-Fe}} - 7.53X_{\text{Ca-Fe}} - 1.80X_{\text{Fe-Mg}}, \quad E_{a,\text{Mg-Si}} = 1.00 + 1.50X_{\text{Al-Mg}} + 1.00X_{\text{Ca-Mg}} + 2.70X_{\text{Fe-Mg}},$$

$$E_{a,\text{Al-Ca}} = 1.83 - 0.02X_{\text{Al-Fe}} + 0.56X_{\text{Al-Mg}}, \quad E_{a,\text{Al-Fe}} = (1/2)(E_{a,\text{Al-Al}} + E_{a,\text{Fe-Fe}}), \quad E_{a,\text{Al-Mg}} = 1.33, \quad E_{a,\text{Ca-Fe}} = (1/2)(E_{a,\text{Ca-Ca}} + E_{a,\text{Fe-Fe}}),$$

$$E_{a,\text{Ca-Mg}} = (1/2)(E_{a,\text{Ca-Ca}} + E_{a,\text{Mg-Mg}}), \quad E_{a,\text{Fe-Mg}} = (1/2)(E_{a,\text{Fe-Fe}} + E_{a,\text{Mg-Mg}}), \quad E_{a,\text{AlCa}}^{\text{ch/c}} = 1.90, \quad E_{a,\text{AlFe}}^{\text{ch/c}} = 1.20, \quad E_{a,\text{AlMg}}^{\text{ch/c}} = 1.29.$$

Vaporisation energy (J/mol):

$$\Delta E_v = \exp(\epsilon_{v,\text{Si-Si}}X_{\text{Si-Si}} + \epsilon_{v,\text{Al-Al}}X_{\text{Al-Al}} + \epsilon_{v,\text{Ca-Ca}}X_{\text{Ca-Ca}} + \epsilon_{v,\text{Fe-Fe}}X_{\text{Fe-Fe}} + \epsilon_{v,\text{Mg-Mg}}X_{\text{Mg-Mg}} + \epsilon_{v,\text{Al-Si}}X_{\text{Al-Si}} + \epsilon_{v,\text{Ca-Si}}X_{\text{Ca-Si}} + \epsilon_{v,\text{Fe-Si}}X_{\text{Fe-Si}} + \epsilon_{v,\text{Mg-Si}}X_{\text{Mg-Si}} + \epsilon_{v,\text{Al-Ca}}X_{\text{Al-Ca}} + \epsilon_{v,\text{Al-Fe}}X_{\text{Al-Fe}} + \epsilon_{v,\text{Al-Mg}}X_{\text{Al-Mg}} + \epsilon_{v,\text{Ca-Fe}}X_{\text{Ca-Fe}} + \epsilon_{v,\text{Ca-Mg}}X_{\text{Ca-Mg}} + \epsilon_{v,\text{Fe-Mg}}X_{\text{Fe-Mg}})$$

where

$$\epsilon_{v,\text{Si-Si}} = 17.37 + 11.12X_{\text{Si-Si}} - 6.22X_{\text{Si-Si}}^2 + 1.06X_{\text{Al-Si}} + 0.04X_{\text{Ca-Si}} + 0.06X_{\text{Fe-Si}} + 0.05X_{\text{Mg-Si}}, \quad \epsilon_{v,\text{Al-Al}} = 13.59, \quad \epsilon_{v,\text{Ca-Ca}} = 13.02, \quad \epsilon_{v,\text{Fe-Fe}} = 11.25,$$

$$\epsilon_{v,\text{Mg-Mg}} = 14.25, \quad \epsilon_{v,\text{Al-Si}} = 20.08 + 9.00X_{\text{Ca-Si}}, \quad \epsilon_{v,\text{Ca-Si}} = 14.46, \quad \epsilon_{v,\text{Fe-Si}} = 9.60, \quad \epsilon_{v,\text{Mg-Si}} = 13.33, \quad \epsilon_{v,\text{Al-Ca}} = 16.88, \quad \epsilon_{v,\text{Al-Fe}} = (1/2)(\epsilon_{v,\text{Al-Al}} + \epsilon_{v,\text{Fe-Fe}}),$$

$$\epsilon_{v,\text{Al-Mg}} = (1/2)(\epsilon_{v,\text{Al-Al}} + \epsilon_{v,\text{Mg-Mg}}), \quad \epsilon_{v,\text{Ca-Fe}} = (1/2)(\epsilon_{v,\text{Ca-Ca}} + \epsilon_{v,\text{Fe-Fe}}), \quad \epsilon_{v,\text{Ca-Mg}} = (1/2)(\epsilon_{v,\text{Ca-Ca}} + \epsilon_{v,\text{Mg-Mg}}), \quad \epsilon_{v,\text{Fe-Mg}} = (1/2)(\epsilon_{v,\text{Fe-Fe}} + \epsilon_{v,\text{Mg-Mg}}).$$

agreement between model predictions and experimental data is comparable to the data variability over the whole range of conditions.

The final set of model parameters describing the experimental viscosities as well as the experimental activation and vaporisation energies in the $\text{Al}_2\text{O}_3\text{--CaO--FeO--MgO--SiO}_2$ system is given in **Tables 3 and 4**. It should be noted that in the quaternary system $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ there are ten types of structural units. The whole dataset is described with only 36 model parameters, that is effectively less than the number of the parameters in the previous modified Urbain model⁴⁷⁾ developed by the authors.

4. Comparison between Model Predictions and Experimental Data

Comparison of the predicted and experimental viscosities for the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ system is presented in a number of ways.

Figures 1(a)–1(e) show the predicted (QCV model) liquid viscosities [$\text{Pa}\cdot\text{s}$] as a function of wt $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{MgO})$ for $\text{MgO} = 5, 10, 15, 20, 25 \text{ wt}\%$ at $\text{SiO}_2 = 50 \text{ wt}\%$ and a range of temperatures (1 250–1 500°C). The liquidus compositions at each temperature predicted by FactSage^{48,49)} is also indicated in Fig. 1. It can be seen that the predicted QCV viscosities are non-linear with increasing alumina concentration due to the charge compensation effect, which is experimentally found⁵⁰⁾ to be present in some $\text{Al}_2\text{O}_3\text{--(MeO, Me}_2\text{O)--SiO}_2$ systems. However, the experimental data by Machin³⁵⁾ for the quaternary $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ do not appear to exhibit this behaviour, increasing linearly with an increase of Al_2O_3 . Some of the data reported by Machin³⁵⁾ appears to have been obtained at conditions below the liquidus, particularly some of the low temperature and high MgO data.

Iso-viscosity curves for $\text{MgO} = 5, 10, 15$ and $20 \text{ wt}\%$ and $T = 1\,500^\circ\text{C}$ are shown in **Figs. 2(a)–2(d)**; the liquidus is calculated by FactSage^{48,49)}. It can be seen that viscosities decrease with increasing MgO for the same $\text{Al}_2\text{O}_3/\text{CaO}/\text{SiO}_2$ ratio in the melt. An area of fully liquid slag gradually decreases in extent with increasing MgO concentration and moves towards higher concentrations of SiO_2 (**Figs. 2(a)–2(d)**). The trends in the slag viscosities in this MgO-containing system are similar to those in the $\text{Al}_2\text{O}_3\text{--CaO--SiO}_2$ system.

It is very important to compare the experimental results from different studies. Variability of the experimental data has been calculated for each slag system using the method recently suggested.¹⁾ All experimental data for each sub-system have been sub-divided into small compositional areas (within 5 mol%) and the best fit of the Eyring viscosity equation for each small compositional area was found by adjusting appropriate parameters. Since the compositional areas were so small, the true viscosity values could have been fitted within them with very high precision. Further details of calculation of the variability were published elsewhere.¹⁾ The overall deviations from these fits can then be taken as an indicator of the variability of experimental data for each sub-system.

The model evaluation parameter by Mills *et al.*⁵¹⁾ was used to compare the experimental data and predicted viscosities:

$$\Delta = \frac{1}{N} \sum \left| \frac{(\eta_n)_{\text{calc}} - (\eta_n)_{\text{ex}}}{(\eta_n)_{\text{ex}}} \right|$$

where N is a number of points and n is a particular slag system, the subscripts “calc” and “ex” refer to the calculated and experimental viscosities at a given composition and process conditions. **Table 5** presents the number of accepted points for the model optimisation, the variability of the experimental data, and model evaluation parameters comparing the QCV model predictions and the experimental measurements for each sub-system in the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ system.

Comparison between calculated and experimental viscosities [$\text{Pa}\cdot\text{s}$] for the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ system and all its sub-systems is given in **Fig. 3**. It can be shown that majority of the points are within $\pm 20\%$ interval, showing good agreement with the experimental data over a wide range (8 orders of magnitude) of viscosity values.

Variability of the experimental data and the model evaluation parameters for the QCV model developed for the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ and its various sub-systems are shown in **Fig. 4**. It should be pointed out that the variability provides an estimation of the best achievable agreement in a given slag system. Thus, the relative measure of agreement between model predictions and experimental data can be taken as the difference between the model evaluation parameter and variability.

5. Analysis of QCV Model Parameters

The activation and vaporisation energies are complex, structurally-related parameters and even in the simplest monatomic fluids (*e.g.* liquid H_2) cannot be calculated from first principles. The activation energy E_a is proportional to the height of the potential barrier that has to be overcome by a structural unit to move to the available hole. The activation energy in liquid oxides depends on the character and quantitative effect of interactions between different ions composing the liquid slag.⁵²⁾ The energy of vaporisation ΔE_v is related to the concentration of the holes in the liquid or free volume of the liquid.⁵²⁾ The activation and vaporisation energies can be approximately evaluated by methods of statistical and quantum mechanics or using combined semi-empirical methods.⁵³⁾

The analysis of the activation and vaporisation energies is important for understanding the mutual interactions between different structural units in the slag, for evaluating the relationship between the slag viscosity and internal structure and, finally, for reliable prediction of the viscosity. Improvements to the predictive power of the viscosity model should necessarily be based on this knowledge. The analysis of the “experimental” activation and vaporisation energies was used in the optimisation of the quasi-chemical viscosity model parameters.

The procedure for calculating the experimental activation and vaporisation energies as previously been outlined^{1,2)} is as follows. Since the weight and volume of the structural units were calculated from mass balance and ionic radii data, respectively, the slag viscosity is determined by the values of the activation and vaporisation energies. The “experimental” activation and vaporisation energies can then be found using the Eyring equation $\eta = AT^{1.5} \exp(B/T)$ by adjusting constants A and B to fit the experimental viscosities at each particular composition. These “experimental” values of A and B are proportional to the activation E_a and vaporisation ΔE_v energies that can be used for further analysis and model development.

Figures 5(a)–5(b) show the activation and vaporisation energies in the binary ($\text{AlO}_{1.5}$, * CaO , ‘ FeO ’, MgO)– SiO_2 systems as a function of the SiO_2 content. The experimental

* The $\text{Al}_2\text{O}_3\text{--SiO}_2$ model parameters were recalculated per one Al cation for comparison with other binary data.

Fig. 3. Agreement between the predicted (QCV model) and experimental liquid viscosities in the Al_2O_3 -CaO-MgO-SiO₂ system.

Fig. 4. Variability of experimental data and model evaluation parameter in the Al_2O_3 -CaO-FeO-MgO-SiO₂ system.

Fig. 5. Predicted and experimental (a) activation and (b) vaporisation energies in the binary $\text{AlO}_{1.5}$ -CaO, 'FeO', MgO-SiO₂ systems.

Fig. 6. Predicted and experimental (a) activation and (b) vaporisation energies in the binary Al_2O_3 -(CaO, 'FeO', MgO) systems.

values of the activation and vaporisation energies (open squares) have been calculated from the accepted experimental data (see Table 1) as described above. Clearly, the activation and vaporisation energies in all cases increase systematically with increasing silica concentration; the values for $\text{AlO}_{1.5}$ -SiO₂ system are greater than those for both CaO-SiO₂ and MgO-SiO₂ systems, which are in turn greater than those for the 'FeO'-SiO₂. This might be taken as evidence of that Al^{3+} cation is a weaker modifier (or "network-breaker") than others; Ca^{2+} and Mg^{2+} cations are also weaker modifiers than Fe^{2+} . The activation and vaporisation energies achieve their maximum values at $X_{\text{SiO}_2}=1$, which can obviously be related to high "network-forming" ability of the silicon dioxide resulted in high viscosities.

Figures 6(a)-6(b) represent the activation and vaporisation energies in the binary Al_2O_3 -(Ca, Fe, Mg)O systems. Activation and vaporisation energies in the Al_2O_3 -CaO

have a maximum at 40–50 mol% of Al_2O_3 . The experimental data available only for the Al_2O_3 -CaO system corresponds to those in Table 1. Al^{3+} cation is well-known^{50,54)} to have so-called amphoteric behaviour in the melt, i.e. Al can act both as a modifier and as a network-former. The experimental data in the Al_2O_3 -CaO system indicate that the activation and vaporisation energies have a maximum at a certain slag composition; this non-linear behaviour can be taken as some evidence of network-forming ability of Al^{3+} cation in the slag. Values of the maximal activation and vaporisation energies are less than those in the pure SiO₂.

A comparison between the experimental and calculated activation and vaporisation energies in the CaO-MgO-SiO₂ and CaO-'FeO'-SiO₂ systems at ~40 mol% SiO₂ as a function of molar CaO/(CaO+MeO), Me=Mg, Fe is shown in Figs. 7(a)-7(b). It can be seen that the activation energy in the MgO-SiO₂ system at SiO₂=40 mol% is greater than

Fig. 7. Predicted and experimental (a) activation and (b) vaporisation energies in the ternary CaO-(FeO, MgO)-SiO₂ systems.

that in the FeO-SiO₂. This might indicate that again Fe²⁺ cation is a stronger modifier than Mg²⁺. It can also be seen from Fig. 7 that the scatter of the activation energy values obtained from the experimental data in ternary systems is greater than that in binary systems.

Figures 8(a)–8(b) show the experimental (see Table 1) and calculated (QCV model) activation and vaporisation energies for the ternary Al₂O₃-(Ca, Fe, Mg)O-SiO₂ systems at SiO₂=50 mol% as a function of molar ratio Al₂O₃/(Al₂O₃+CaO+MgO). The activation energy in the Al₂O₃-CaO-SiO₂ has a maximum at molar Al₂O₃/(Al₂O₃+CaO) ≈ 0.5, which is a result of the charge compensation effect. This effect was experimentally found^{8,50} to take place in the systems Al₂O₃-(Me₂O, MeO)-SiO₂ and was also referred to as “amphoteric behaviour” of Al₂O₃.^{50,54} The charge compensation effect occurs if Al³⁺ occupies tetrahedral coordination positions provided the excess negative charge for Al³⁺ is compensated by the presence of alkali (K⁺, Na⁺ etc.) or alkaline earth (Ca²⁺, Mg²⁺ etc.) cations, thus keeping or forming the network structure instead of breaking it. As a result the slag viscosity has a maximum at molar Al₂O₃/(Al₂O₃+MeO) close to 0.5. In the Al₂O₃-MgO-SiO₂ this effect is present but less pronounced, the deviation from linear behaviour being approximately half that in the Al₂O₃-CaO-SiO₂ case (see Fig. 8). There is no reliable experimental data in the Al₂O₃-FeO-SiO₂ system⁴⁷; the activation and vaporisation energies therefore were predicted to be almost linear with alumina concentration.

Figure 9 provides a comparison between the activation energies of viscous flow of pure oxides and the parameter z/r , where z and r are the formal charge and ionic radius of a cation, respectively. This parameter z/r was found^{54,55} to be a reasonable estimation of the relative bond strength of different cations. It is possible to calculate parameter z/r using ionic radii from the work by Shannon⁴⁶ for a cation with the known coordination number. The network-forming oxides (GeO₂ and SiO₂) were known^{54,55} to be mostly four-coordinated in silicate melts; for all the other oxides (modifiers and amphoteric) a range of possible coordination numbers (IV, VI, and VIII) was used.⁴⁶ Iron cations Fe²⁺

Fig. 8. Predicted and experimental (a) activation and (b) vaporisation energies in the ternary Al₂O₃-(CaO, FeO, MgO)-SiO₂ systems.

Fig. 9. The activation energies of viscous flow as a function of z/r parameters for pure oxides.

and Fe³⁺ were assumed to be in a high-spin (HS) state, which is likely to be the case in silicate melts.⁵⁶ The activation energies of Al₂O₃, CaO, FeO, MgO, SiO₂ were calculated by the present viscosity model; values of the activation energy for pure GeO₂ and PbO were estimated from the experimental data^{57,58} using the Eyring equation; and the activation energies of K₂O, Na₂O and Fe₂O₃ were taken from the preliminary optimisation of the present model.

It can be seen from this figure that there is a correlation between the activation energy of viscous flow E_a and the relative bond strength z/r . Network-formers (such as GeO₂ and SiO₂) have higher z/r and E_a values, while modifiers (such as CaO, K₂O, Na₂O) have lower z/r and E_a values. Aluminium oxide has greater values of z/r and E_a parameters than all other modifiers, which may point to its amphoteric behaviour. From this point of view the ferric oxide is closer to CaO, FeO and others than Al₂O₃, so it might be expected that Fe₂O₃ may act in the melt mostly as a modifier. It can also be seen from Fig. 9 that the model values of the activation energy are generally in a good accordance with the overall trend.

6. Comparison of Viscosity Models

A number of reviews on the slag viscosity models have recently been published in the literature.^{51,59–61)} In some cases^{51,61)} comparisons of a number of viscosity models with the viscosities of some selected slag compositions were reported, but in general there is still a need for a systematic and accurate analysis of viscosity models' performance over a wide range of slag compositions and temperatures. In the present paper those viscosity models that have all the parameters available and are applicable to the Al_2O_3 – CaO – MgO – SiO_2 systems and its sub-systems are analysed and compared with the experimental data that have been collected, analysed and used for the development of the QCV viscosity model.

Urbain^{50,62)} published a method of estimating viscosity of multi-component slags using the Urbain model for the ternary Al_2O_3 – CaO – SiO_2 and Al_2O_3 – MgO – SiO_2 systems. The general formalism developed by Urbain describes slag viscosities in terms of the Weymann–Frenkel equation $\eta = AT \exp(10^3 B/T)$, where T is the absolute temperature, the pre-exponential parameter A was shown^{50,62)} to be linked to the parameter B with the so called “compensation law”, and the parameter B is proportional to the activation energy and expressed through the polynomial functions of compositions.^{50,62)}

Several viscosity models have been developed on the basis of the Urbain formalism. Riboud *et al.*,⁶³⁾ using the Urbain model with corrected compositions dependences of A and B , successfully applied it to describe the viscosities of some industrial mould fluxes (in the Al_2O_3 – CaO – Na_2O – SiO_2 – CaF_2 system). In the Kalmanovich–Frank (KF) model⁶⁴⁾ the parameters A and B of the Urbain model have

been modified to describe viscosities of the particular coal ash slags.

Browning *et al.*⁶⁵⁾ developed the “T-shift” model for describing the viscosity of particular coal ash slags. The model showed satisfactory agreement for some synthetic slags, but cannot be recommended for using in the whole compositional range reported. Using a regression analysis Utigard and Warczok⁶⁶⁾ developed the viscosity model (UW) for the copper/nickel fayalite-type smelting slags.

The comparison of the models cited above for the Al_2O_3 – CaO – MgO – SiO_2 system and its sub-systems is given in Figs. 10(a)–10(b). Apart from the QCV model each of these models^{62–66)} was developed to describe experimental data over a limited range of compositions, and Figs. 10(a)–10(b) clearly demonstrate that they do not provide accurate predictions of viscosities over the whole range of slag compositions in the quaternary system.

A number of fundamental slag viscosity models (Iida,⁶⁷⁾ NPL,⁶⁸⁾ Zhang,^{69,70)} KTH⁷¹⁾ and Tanaka⁷²⁾) based on the structural considerations have been developed for different slag systems, including the Al_2O_3 – CaO – MgO – SiO_2 system. Independent comparison of these models with the experimental data is not possible, because the additional information on the structural (thermodynamic) models, their coefficients, and calculation procedures used is not available in the literature. The reader is therefore referred to these individual publications.

7. Industrial Application of the Al_2O_3 – CaO – MgO – SiO_2 QCV Viscosity Model

The development of the QCV model for the Al_2O_3 – CaO – MgO – SiO_2 system makes it possible to predict slag viscosi-

Fig. 10. Comparison between predictions of different models and experimental data in the Al_2O_3 – CaO – FeO – MgO – SiO_2 : (a) unary and binary systems; (b) ternary and higher-order systems.

ties in composition ranges where little or no experimental viscosity data are available, particularly in complex industrially important slag systems. In the present paper this point is illustrated with reference to the reduction smelting of chromite ore fines with coal—in spite of the fact that slag viscosity plays an essential role in the process, no experimental data have been found for this composition range. Chromite ore consists of complex spinel $(\text{Fe}, \text{Mg})\text{O} \cdot (\text{Al}, \text{Cr}, \text{Fe})_2\text{O}_3$. As the ore is dissolved in CaO-SiO_2 slag (formed from gangue and fluxes), the $(\text{Al}_2\text{O}_3 + \text{MgO})$ concentration in the liquid slag phase progressively increases. The iron and chromium oxides are reduced to the Fe–Cr alloy.

Using FactSage the liquidus and the concentrations of the various structural units can be calculated for any bulk composition and temperature. Using the new QCV model the viscosities of the fully liquid slags can be predicted. **Figure 11** shows lines of constant viscosity for the system $\text{SiO}_2\text{--CaO--}(\text{Al}_2\text{O}_3 + \text{MgO})$ at 1600°C . Conventional submerged arc furnace (SAF) ferrochromium smelting slags contain only 2–10 wt% CaO. The slags used in direct ferrochrome smelting however have high CaO concentrations. It can be seen that in fully liquid slags, increasing CaO/SiO₂ ratio results in significantly decreased viscosity for the same $\text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{MgO})$ ratio. The 1600°C liquidus isotherms for slags with $\text{MgO}/\text{Al}_2\text{O}_3$ ratios of 0.75, 1.00 and 1.25 are also shown in Fig. 11. The effect of increasing $(\text{Al}_2\text{O}_3 + \text{MgO})$ concentration for a given CaO/SiO₂ ratio on viscosities is complicated reflecting a number of complex processes, including the changing charge compensation effects, in the slag.

The predicted effects of increasing $(\text{Al}_2\text{O}_3 + \text{MgO})$ for $\text{MgO}/\text{Al}_2\text{O}_3 = 1$ at different CaO/SiO₂ weight ratios (0.8, 1.0 and 1.2) are illustrated in **Fig. 12** at 1600°C . It can be clearly seen that the viscosities of liquid slags are not monotonic functions of weight ratio $(\text{Al}_2\text{O}_3 + \text{MgO})/(\text{Al}_2\text{O}_3 + \text{MgO} + \text{CaO} + \text{SiO}_2)$; maxima in the viscosities correspond to 0.08–0.15 $(\text{A} + \text{M})/(\text{A} + \text{M} + \text{C} + \text{S})$. The volume fractions of solids change almost linearly with increasing $(\text{Al}_2\text{O}_3 + \text{MgO})$ and appear to be relatively insensitive to CaO/SiO₂ for values between 0.8–1.2. The liquid slag viscosities vary from 0.1 to 0.37. At $\sim 0.33 \text{ AM/AMCS}$ spinel starts to crystallise out of the liquid.

Figure 13 shows the effect of different $\text{MgO}/\text{Al}_2\text{O}_3$ wt ratios (0.75, 1.00 and 1.25) on the slag viscosities and proportions of solids at 1600°C . Again, the viscosities are predicted to initially increase with increasing $(\text{Al}_2\text{O}_3 + \text{MgO})$ and subsequently decrease. The behaviour of the system is not greatly affected by $\text{MgO}/\text{Al}_2\text{O}_3$ ratio.

The effect of temperature on the liquidus and liquid slag viscosities is given in **Fig. 14**. It can be seen that liquidus area increases and viscosities decrease with increasing temperature.

8. Conclusions

A quasi-chemical viscosity model has been developed for liquid slags in the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ system; this model is directly related to the internal slag structure. The structures of the slags have been determined from the second nearest neighbour bond concentrations extracted from the modified quasi-chemical thermodynamic model of the system available in the FactSage package. The viscosity model parameters are valid for the whole range of compositions in the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ system.

An experimental dataset of ~ 2200 points has been used to optimise the model parameters. The average agreement between the model predictions and experimental data over the whole composition range in the $\text{Al}_2\text{O}_3\text{--CaO--MgO--}$

Fig. 11. Liquidus and viscosities predicted for the system $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ at 1600°C .

Fig. 12. Effect of CaO/SiO₂ on slag viscosity and volume fraction of solids at 1600°C for $\text{MgO}/\text{Al}_2\text{O}_3 = 1.0$.

Fig. 13. Effect of $\text{MgO}/\text{Al}_2\text{O}_3$ on slag viscosity and volume fraction of solids at 1600°C for $\text{CaO}/\text{SiO}_2 = 1.0$.

SiO_2 system is within 20%. The analysis of the activation and vaporisation energies showed that the general trends of these parameters are consistent with current understanding of the internal structures of multi-component slags.

A comparison of different viscosity models and experimental data in the $\text{Al}_2\text{O}_3\text{--CaO--MgO--SiO}_2$ system and its sub-systems reveals that the quasi-chemical viscosity model performs reasonably well over the whole range of compositions and temperature within the slag system investigated.

Fig. 14. Effect of temperature on slag viscosities in the system $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$ for $\text{MgO}/\text{Al}_2\text{O}_3 = 1.0$.

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