Prediction and measurement of the coal slag viscosity including the influence of solid particle fractions

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Abstract: The flow behavior of slag in entrained flow gasification reactors is influenced by the local environment (temperature, oxygen partial pressure, etc.) and essentially depends on the knowledge of the slag viscosity. This is in turn influenced by the possible presence of solid phases. This work therefore forms the beginning of a systematic investigation of the influence of individual solid phases occurring in the slag on the slag viscosity. Among the most often occurring solids in slag is tridymite (SiO_2). The influence of tridymite and also of cristobalite on the viscosity of slags was analyzed as function of the solid volume fraction by applying the Einstein-Roscoe model. The parameters used in this model were obtained from a comparison of experimental and predicted viscosity values for various slag systems. Reintroduction of the determined parameters to the modeling of the viscosity resulted in a good agreement with the experimental data.

Keywords: viscosity, molten oxide, modeling, slag, thermodynamics.

1. Introduction

In the ongoing discussions about energy supply, several gasification techniques of bituminous and lignite coals [1] are currently receiving more and more attention. Equally, there is concern about the emission of CO_2 from other high temperature processes like the blast furnace. The project Virtuhcon at TU Bergakademie Freiberg aims at providing a better understanding of such high temperature processes (gasifiers and blast furnace alike). In order to give insight in the details of these processes and to reduce the costs for complex experiments and prototype plants these processes are modeled requiring a multidisciplinary approach. Although some of the models are already quite advanced, model validation and the determination of necessary input parameters is still necessary.

As the formation of slag is common to high temperature processes and its properties significantly influence the process performance, knowledge of the thermophysical properties of slag is essential. For example, in an entrained flow gasifier the slag forms a solid protective layer on the water cooled inner walls while the liquid slag flows on top of it [1]. The flow behavior of the slag is determined by its viscosity which is therefore one of the most important input parameters for the modeling. Due to the extreme conditions (e.g. high temperatures) required for the experimental measurement of slag viscosity it is desirable to provide a method to make predictions. However, most of the empirical models available in the literature are only suited for fully liquid slags [2]. In high melting slags a fraction of solid particles is frequently formed that modifies the slag viscosity. In such cases the conventional models need to be combined with the Einstein-Roscoe model (ER-Model) that allows the inclusion of the solid particle fraction (equ. 1):

$$\eta = \eta_0 \cdot (1 - a \cdot f)^{-n} \qquad \text{(equ. 1)}$$

where a and n are parameters and f is the volume fraction of the solid phase. η_0 is the viscosity as obtained from the literature models (without solid particle contribution) and η is the final viscosity in Pa·s [3].

The present work is the beginning of a systematic study of the influence of solid phases on the viscosity of slags with the aim of defining a and n values in the ER-model for particular solid phases. In this work, the influence of tridymite particles on the viscosity of a Al_2O_3-CaO-SiO_2 slag (sample 1) [4] and a SiO_2-Fe_2O_3-FeO slag (sample 2) [5] was investigated, while the influence of cristobalite particles – another crystalline SiO_2 phase - was determined for a binary CaO-SiO_2 slag (sample 3).

2. Data selection and experimental section

Experimental viscosity data from various slag systems form the basis of the analysis of the solid particle influence and the determination of the ER-parameters. Therefore, a literature screening was carried out using a newly developed software tool [6]. This screening revealed that anorthite, hematite and tridymite are among the most often occurring solid phases in slag. Tridymite was finally chosen out of these, because for anorthite the slag composition is practically identical to the solid phase which indicates glassy behavior rather than the influence of particles in the viscosity data. For hematite, there is the problem of Fe^{2+}/Fe^{3+}. The actual experimental viscosity data for this study were then either taken from the entries in the database tool ([6]) or from our own measurements:

- From the database (literature data): sample 1 [4] and sample 2 [5] were selected from the database and were found to contain tridymite as the solid phase according to thermodynamic calculations.
- From own measurements: sample 3 is a 31.5CaO-68.5SiO_2 (mass%) mixture that was found to contain cristobalite as solid phase according to the stabilities of the SiO_2 modifications in the binary system. Though not containing tridymite, this sample was chosen because it contains another SiO_2 modification, i.e. cristobalite.

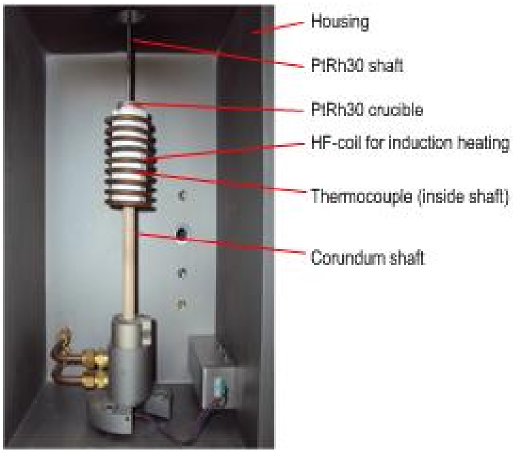

Fig. 1: Detail of measurement chamber of the viscometer (Bähr Thermoanalyse GmbH)

Fig. 2: Image of the viscometer during the measurement.

Viscosity (η) measurements for sample 3 were done on a rotational viscometer (Bähr Thermoanalyse GmbH, Germany) using a crucible/spindle system made of a 70Platinum-30Rhodium alloy (mass-%) – see Fig. 1 & 2. The binary slag was prepared from CaO (Sigma Aldrich, 99.9 % purity) and SiO_2 (Sigma Aldrich, 99.8 %) powders that were dried for 6 hours at 900 °C before mixing. The composition of 31.5CaO-68.5SiO_2 was chosen to yield a liquid/solid mixture according to the CaO-SiO_2 phase diagram with eutectic temperature close to 1437 °C. The sample composition was verified using X-ray fluorescence analysis.

3. Results and discussion

3.1 Modeling approach

As already mentioned the Einstein-Roscoe Model makes use of the factors *a* and *n* in addition to the solid volume fraction *f* and these two parameters were to be determined in this work as a measure for the influence of tridymite and cristobalite particles. The *a*-parameter is a measure of the achievable packing density. It is 1.35 for spherical particles without size distribution, which results in a maximum packing density of 74% (f=0.74). The lower limit is of course a=1 for other particle shapes and size distributions. The factor *n* is often set to 2.5 [3]. Wright et al. [7] proposed *a*-values of 4.24, 3,29 and 3.56 and *n*-values of 1.28, 2.36 and 2.24 for fine, medium and coarse spinel particles, respectively, based on their analysis of viscosity data. In the present work, the application of the ER-model was done according to the approach from Wright et al. [7], who analyzed the influence of the addition of $MgAl_2O_4$ spinel particles on the viscosity of a 28CaO-10MgO-20Al_2O_3-42SiO_2 slag.

Table 1: Viscosity models used in this work

Model	Reference	Abbreviations
ANNliq	[6]	-
BBHLW	[8]	-
Duchesne	[9]	-
Kalmanovitch-Frank	Secondary citation in [10]	Kalm.-F.
Lakatos		-
Riboud		-
Shaw		-
Streeter		-
Urbain		-
Watt-Fereday		Watt-F.

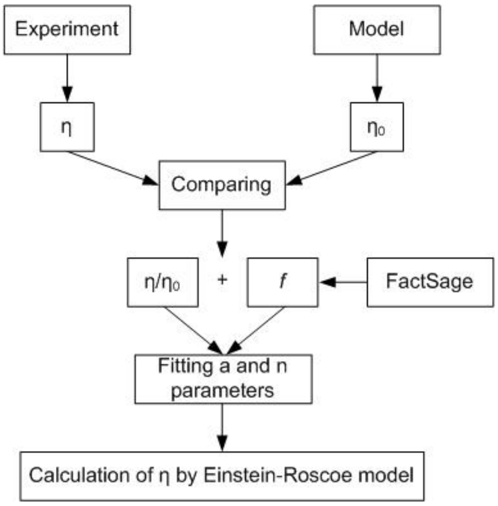

Fig. 3 Scheme showing the steps involved in the application of the ER-model

In the present work this approach was carried out in such a way (see also the scheme in Fig. 3) that the experimental data from either literature or own experiments were combined with model calculations that yield η_0 in order to obtain the relative viscosity η/η_0. Various models were used in the calculation that are accessible via the database tool [6]. As the Einstein-Roscoe (ER) model increases the predicted viscosity values as a function of the amount of solid phase, only models can be used that underestimate the viscosity as compared to the experimental values. In total, 10 models were employed in the present work. Except for the ANNliq model, which is based on an artificial neural network, all other models are empirical models developed from measurements of artificial, natural or industrial slags (see Table 1for a list of models).

The solid particle volume fraction f was calculated using the software FactSage [11] from the thermodynamics of the respective systems. It has to be noted that η and f are of course functions of the composition and temperature of the system. The volume fractions were calculated to be between 0.03 to 0.18, which corresponds to validity range of the ER-model [7]. The relative viscosity data η/η_0 were then plotted as a function of the particle volume fraction f, from which a and n were determined by applying a non-linear least squares fit. Finally, the obtained parameters were reintroduced into the various viscosity models combined with the ER-model and the calculated viscosities were compared to the experimental ones.

3.2 Influence of the solid phases and the parameters a and n in the ER-model

Experimental viscosity data for samples 1-3 are shown in Fig. 4-6 and data summarized in Table 2. The data of sample 1 (6.1Al_2O_3-22.0CaO-71.9SiO_2, mole%) show the evolution of viscosity as a function of temperature, while sample 2 (SiO_2-Fe_2O_3-FeO, see Table 2 for details) is an example for the viscosity as a function of composition and solid particle volume fraction f, respectively. Sample 3 (31.5CaO-68.5SiO_2, mole%) shows the viscosity as a function of temperature. In case of samples 2 and 3 pronounced increase of the viscosity from f~0.024 and f~0.065 were noticed.

Table 2: Composition, temperature, measured viscosity and solid volume fraction f for samples 1-3 [4, 5].

	Composition			Temp.	η.	f.
	molar-%			K	Pa s	-
Sample 1	Al2O3	CaO	SiO2			
	6.1	22.0	71.9	1573	12794	0.177
				1623	4624	0.135
				1673	1820	0.087
				1723	828	0.028
Sample 2	FeO	Fe2O3	SiO2			
	49.46	11.25	39.29	1573	1.086	0.026
	50.17	9.98	39.85		0.904	0.025
	51.23	8.08	40.69		0.652	0.024
	54.26	2.63	43.1		0.269	0.016
Sample 3	CaO	SiO2				
	31.5	68.5		1811	249.5	0.073
				1813	159.1	0.070
				1814	78.9	0.069
				1815	139.4	0.068
				1816	70.7	0.067
				1817	12.6	0.066
				1818	30.8	0.065
				1819	11.2	0.064
				1820	7.8	0.063
				1830	5.8	0.051
				1840	4.7	0.039
				1850	5.9	0.027
				1860	5.1	0.013
				1870	4.8	0.000

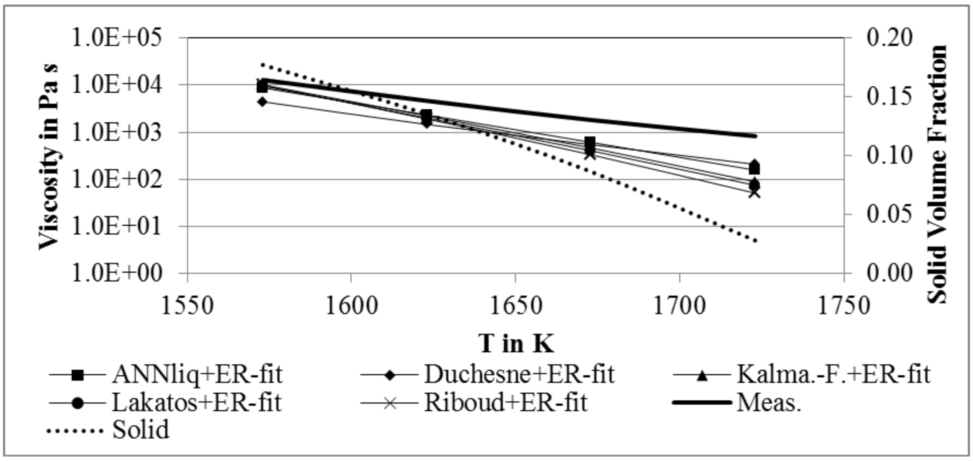

Fig. 4: Viscosity predictions of sample 1 with application of the ER model; see Table 4 for the values of *a* and *n*.

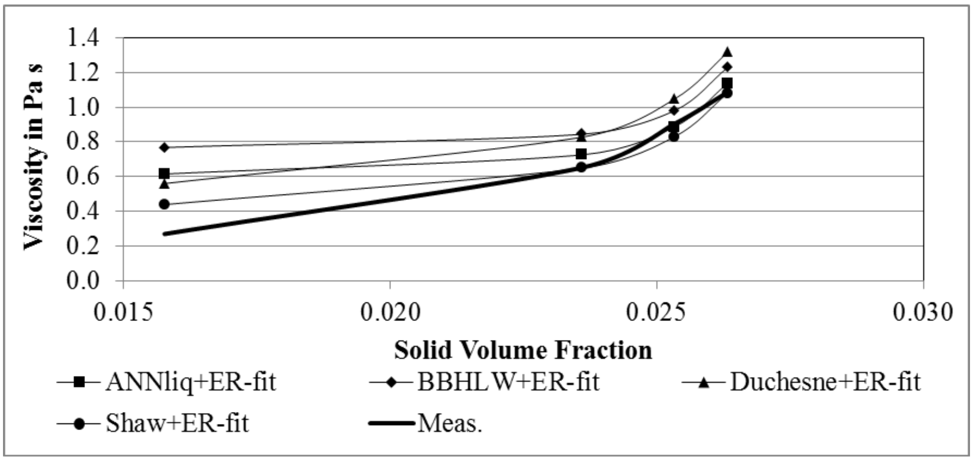

Fig. 5: Viscosity predictions of sample 2 with application of the ER model, see Table 4 for the values of *a* and *n*

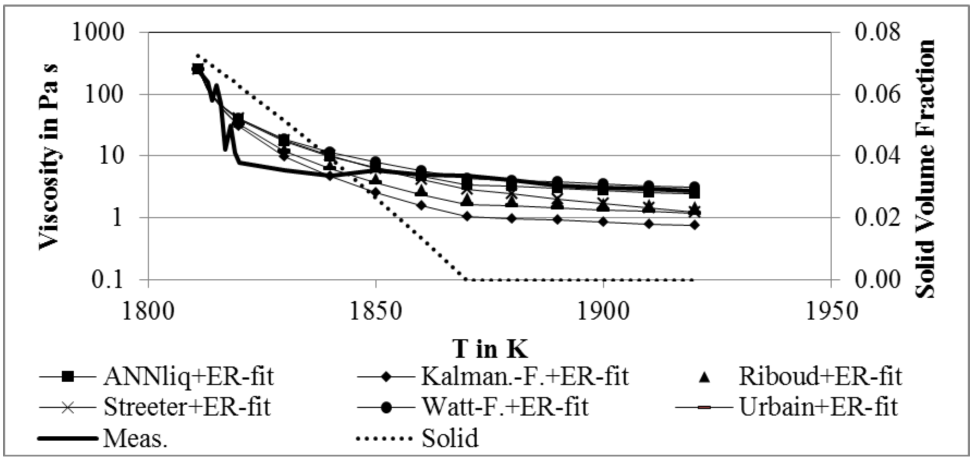

Fig. 6: Viscosity predictions of sample 3 with application of the ER model, see Table 4 for the values of a and n.

In Fig. 7 the experimental viscosity of sample 3 is compared to the modeled ones without inclusion of the ER-contribution. It can be seen that neither model is able to predict the strong increase in viscosity above *f*~0.065. A similar situation was also found for the other two samples. Of course, in none of the models the influence of the solid particle fraction is included.

Application of the Einstein-Roscoe (ER) model to the various viscosity predictions improves the predicted viscosities and can also describe the strong increase of the viscosity observed in samples 2 and 3, as can be seen from Fig. 4-6. These calculations were performed using the *a* and *n* parameters as determined by the fit of the relative viscosity as a function of the solid volume fraction. The relative viscosities used in the data fit, the obtained *a* and *n* parameters for the samples and the calculated viscosities are given in Table 3-5.

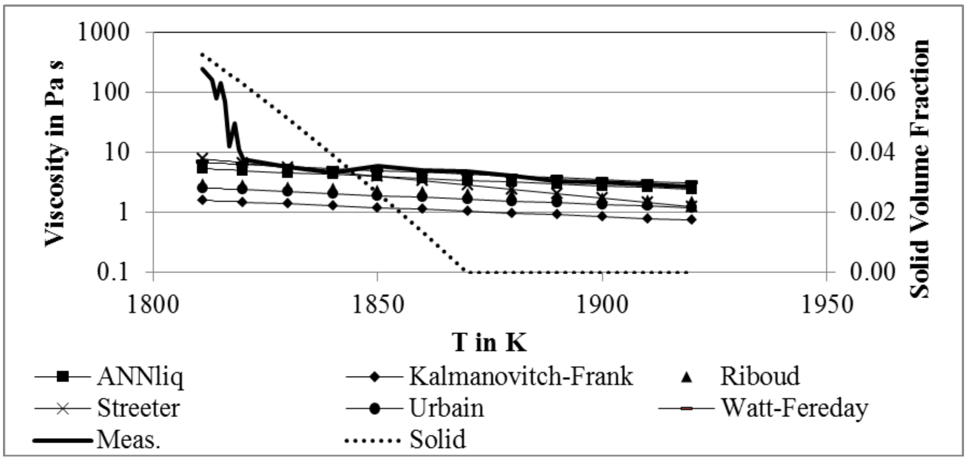

Fig. 7: Viscosity predictions of sample 3 without application of the ER model

Table 3: Calculated viscosity η_0 w/o influence of particles and η/η_0 fraction

	η_0						η/η_0					
Sample 1	ANNliq	Duchesne	Kalm.-F	Lakatos	Riboud		ANNliq	Duchesne	Kalm.-F	Lakatos	Riboud	
	Pa s	Pa s	Pa s	Pa s	Pa s		-	-	-	-	-	
	633.8	3905.5	360.5	236.9	130.1		13.64	0.31	21.37	36.04	68.70	
	342.8	1444.0	184.8	127.1	74.5		6.94	0.24	10.89	18.41	32.40	
	190.9	542.5	98.7	72.5	44.2		2.98	0.39	4.31	7.12	11.55	
	109.7	208.8	54.7	43.6	27.0		1.00	1.00	1.00	1.00	1.00	
Sample 2	ANNliq	BBHLW	Duchesne	Shaw			ANNliq	BBHLW	Duchesne	Shaw		
	Pa s	Pa s	Pa s	Pa s			-	-	-	-		
	0.157	0.268	0.537	0.121			7.15	4.53	2.41	8.81		
	0.173	0.293	0.508	0.133			5.46	3.56	2.17	6.63		
	0.202	0.336	0.474	0.153			3.45	2.42	1.76	4.09		
	0.349	0.516	0.439	0.229			1.00	1.00	1.00	1.00		
Sample 3	ANNliq	Kalm.-F	Riboud	Streeter	Urbain	Watt-F	ANNliq	Kalm.-F	Riboud	Streeter	Watt-F.	Urbain
	Pa s	Pa s	Pa s	Pa s	Pa s	Pa s	-	-	-	-	-	-
	5.4	1.6	3.0	7.8	2.6	6.77	46.09	152.10	81.47	31.14	36.76	95.70
	5.3	1.6	3.0	7.6	2.5	6.66	29.71	97.16	52.16	20.32	23.78	61.27
	5.2	1.6	3.0	7.4	2.5	6.61	14.64	46.72	25.36	9.91	11.83	29.66
	5.2	1.6	2.9	7.3	2.5	6.56	26.39	85.98	46.14	18.36	21.15	54.26
	5.2	1.5	2.9	7.2	2.5	6.50	13.30	42.21	22.92	9.15	10.77	26.83
	5.1	1.5	2.9	7.1	2.4	6.45	2.06	4.63	3.03	1.09	1.85	3.27
	5.1	1.5	2.9	6.9	2.4	6.40	5.65	16.61	9.35	3.74	4.69	10.78
	5.0	1.5	2.9	6.8	2.4	6.35	1.82	3.81	2.59	0.95	1.65	2.76
	5.0	1.5	2.8	6.7	2.4	6.30	1.15	1.58	1.41	0.47	1.12	1.36
	4.6	1.4	2.7	5.6	2.2	5.83	0.84	0.53	0.83	0.33	0.88	0.70
	4.3	1.3	2.5	4.8	2.1	5.41	0.69	0.02	0.55	0.30	0.76	0.39
	4.0	1.2	2.3	4.0	1.9	5.02	1.07	1.24	1.16	0.77	1.06	1.15
	3.7	1.1	2.2	3.4	1.8	4.67	0.97	0.92	0.98	0.81	0.98	0.95
	3.4	1.0	2.1	2.9	1.7	4.35	1.00	1.00	1.00	1.00	1.00	1.00

Table 4: Parameters a and n for fitted models of sample 1 to 3

Sample	Model						
Sample 1	Factor	ANNliq	Duchesne	Kalmanovitch-Frank	Lakatos	Riboud	
	a	1.683	5.648	1.000	1.000	1.000	
	n	7.391	0.009	17.080	18.947	22.284	
Sample 2	Factor	ANNliq	BBHLW	Duchesne	Shaw		
	a	35.941	36.564	36.320	35.642		
	n	0.678	0.463	0.286	0.786		
Sample 3	Factor	ANNliq	Kalmanovitch-Frank	Riboud	Streeter	Watt-Fereday	Urbain
	a	13.341	12.958	13.171	13.353	13.401	13.119
	n	1.128	1.802	1.429	1.000	1.019	1.520

Table 5: Viscosities of classical ER (a=1.35; n=2.5) and ER with fitted a, n for sample 1 to 3.

Sample 1	ANNliq	Duchesne	Kalm.-F	Lakatos	Riboud	
	Pa s	Pa s	Pa s	Pa s	Pa s	
	8664	4416	10053	9504	9999	
	2317	1462	2215	1998	1903	
	612	546	464	403	332	
	157	209	89	75	51	
Sample 2	ANNliq	BBHLW	Duchesne	Shaw		
	Pa s	Pa s	Pa s	Pa s		
	1.14	1.23	1.32	1.08		
	0.89	0.98	1.05	0.83		
	0.73	0.84	0.83	0.65		
	0.61	0.77	0.56	0.44		
Sample 3	ANNliq	Kalm.-F.	Riboud	Streeter	Urbain	Watt-F.
	Pa s	Pa s	Pa s	Pa s	Pa s	Pa s
	253.62	251.21	252.40	245.72	251.75	254.68
	122.43	124.62	123.70	124.53	123.60	122.46
	95.69	94.77	95.29	98.76	94.78	96.46
	77.91	74.52	76.22	81.31	75.40	79.24
	65.30	60.13	62.69	68.70	61.65	67.01
	55.91	49.53	52.68	59.19	51.49	57.87
	48.68	41.49	45.02	51.76	43.74	50.80
	42.94	35.24	39.02	45.80	37.67	45.16
	38.28	30.29	34.20	40.91	32.83	40.56
	16.91	9.89	13.21	17.81	12.06	18.97
	9.90	4.65	7.05	9.97	6.19	11.55
	6.54	2.58	4.35	6.22	3.70	7.87
	4.63	1.59	2.91	4.12	2.41	5.71
	3.45	1.05	2.08	2.85	1.67	4.35

The solid phase present in sample 1 is tridymite. The values for a and n vary between 1 and 5.648 and 0.009 and 22.284, respectively, for the various models. In sample 2 the solid phase is also tridymite, factors a and n vary between 35.642 and 36.564 and 0.286 and 0.786, respectively. The a and n values in sample 3 vary between 12.958 and 13.401 and 1 and 1.802. Note that in this sample the solid phase is cristobalite. These values clearly deviate from the usual values of a=1.35 and n=2.5, but the use of these original values did not result in a considerable improvement of the viscosity predictions. The high values for a are required to model the strong and abrupt increases in the observed viscosities already at low solid volume fractions. The a parameter is related to the shape and size distribution of the particles, but also to their achievable maximum volume fraction. Therefore, in case of strong viscosity increases at low solid volume fractions high a values are automatically obtained. Wright et al. [7] also investigated the particle influence on the viscosity of slag in a similar f range. Their maximum a value is 2.5 and the maximum n value is 3.4. However, the viscosity increase observed in the work of Wright et al. [7] was not as abrupt as in the present work.

4. Conclusion

The current data suggest that the presence of crystalline SiO_2 phases (tridymite and cristobalite) have a significant influence on the viscosity of silica rich slags. This was in particular observed for samples 2 and 3. In terms of the Einstein-Roscoe model such a strong influence is reflected by the high values of a and n as determined by fitting the relative viscosities as a function of the solid volume fraction.

However, the limits of the application of the ER model were also noticed in this work:

- Silica containing slags often have the tendency to solidify in a glassy state. Increase in the viscosity may therefore partially be due to this glassy behavior. A systematic study including a detailed analysis of the solidification behavior would be needed to clarify this situation.
- The present calculation of the solid volume fraction was done under the assumption of equilibrium. However, supercooling is usually observed in the formation of crystalline phases during cooling of the sample. The actual solid volume fraction may therefore be smaller than under true equilibrium conditions. Again a more detailed study is needed to elucidate this problem.

It can therefore be concluded that a start has been made in a systematic investigation of the influence of solid particles to the slag viscosities with respect to their nature and quantity. More information is required in terms of viscosity data and detailed studies of the solidification behavior of silicate slags.

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