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Viscosity calculations of mold slag in continuous casting

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ABSTRACT

Purpose: This paper deals with the mold slag viscosity calculations.

Design/methodology/approach: The study involved the analysis of the impact of the chemical composition and temperature on the viscosity. Calculations were performed using models Riboud - Zhao, Urbain, Kondratiev and the computer program FactSage using module viscosity. The results of this works charakterize the effect of temperature, addition of CaF_2 and Na_2O on the viscosity for two types of slag.

Findings: Slag 1 contained CaO/SiO_2 = 0.78 and the addition of Na_2O, slag 2 contained CaO/SiO_2 = 1.32 wihout Na_2O addition. Computer simulations revealed differences in the obtained values of viscosity. The use of the classical models: Riboud - Zhao and Urbain showed that at temperature 1200°C slag 2 contains larger content of CaO has the lowest viscosity at temperature 1500°C. The addition CaF_2 causes a similar effect on viscosity of both slags. The use of the Fact Sage software showed that the addition of Na_2O has a large influence on the viscosity. Slag 2 CaO/SiO_2 = 1.32 although more than slag 1 is obtained at temperature 1500°C higher viscosity values.

Research limitations/implications: Mathematical modeling of liquid mold slag viscosity based on classical and structural models and with the use of commercial software requires verification methods using scanning microscopy and nuclear magnetic resonance.

Practical implications: The computer calculations of the mold slag viscosity shown that the selection of the chemical composition of the slag is important for the species of the cast steel and the speed of casting. Results of calculations show that the change in viscosity of the slag in the process result from the content composition: CaO/SiO_2, CaF_2 and Na_2O content.

Originality/value: The results of the calculations indicate the reaction of CaF_2 with Na_2O, probably results of this reaction is NaF, which prevents the formation of cuspidine which has a high melting point, its presence increases the melting point of the slag.

Keywords: Mold slag; Slag viscosity; Viscosity models; $CaO-SiO_2-CaF_2$ system

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METHODOLOGY OF RESEARCH, ANALYSIS AND MODELLING

1. Introduction

Growing requirements regarding the surface quality of steel ingots obtained at high casting speed required deeper insight into the process mechanism, in which function of mold slag is of primary importance. The proper choice of slag allows to control the physico-chemical effects occurring in the slit between ingot and mould. Two main functions of the mould slag are the lubrication ant the control of heat flux.

The liquid layer of the mold slag is the result of powder melting. The grains of oxides in commercial powders are separated with carbon grains, which gradually oxidize in the mould. Carbon grains retard slag melting, what results in better thermal isolation of solid slag layer. The liquid slag flows into the space between the ingot and the mould walls, where it gradually solidifies at the mould side. In the upper region of the mould the slag is fully liquid. In the middle section of the mould the ca 0.1 mm thin layer of liquid slag preserves at the ingot side, which acts as a lubricating agent in vertical oscillating movement between mould and ingot. At the lower region of the mould the mould slag is fully solidified, what causes the occurrence of the gas (air) slit between the mould wall and solid slag layer adhered to the ingot. Figure 1 shows a typical schematic of interfacial gap phenomena in continuous casting mold.

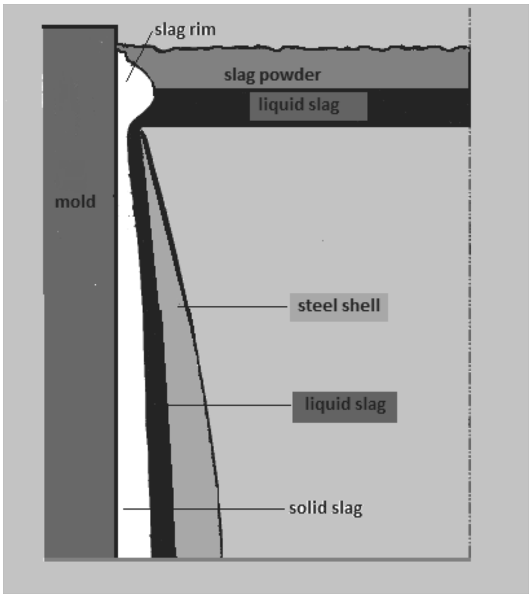

Fig. 1. Schematic of interfacial gap phenomena in continuous casting mold [1]

The studies of Yamauchi et al. [2,3] determined the total thickness of slag layer in the space between mould and ingot as well as the thickness of liquid slag layer, in dependence on slag viscosity, temperature, casting speed and position in the mold.

Mold slag is a multi-component oxide system. Liquidus and solidus temperatures can be determined only approximately. In the literature reliable data on liquidus and solidus temperature regard mainly the basic system CaO - SiO_2 - Al_2O_3 - Na_2O - CaF_2. Figures 2 and 3 shows the liquidus surface of the CaO - Al_2O_3 - SiO_2 system. Liquidus surface temperature exceeds 1673K with the exception of the occurrence region of phase pseudowollastonite phase [4].

Maximum liquidus temperature for CaO - SiO_2 - CaF_2 system occurs in the area of a cuspidine compound. Addition of CaF_2 to this compound lowers the liquidus temperature only if the CaO/SiO_2 (in wt pct) is 1/1.5. Excessive addition of CaF_2 increases liquidus temperature. Figure 4 shows the region of the liquid phase at the temperature 1573 K. Marked area corresponds to the chemical composition of slags, which are completely liquid below 1673 K.

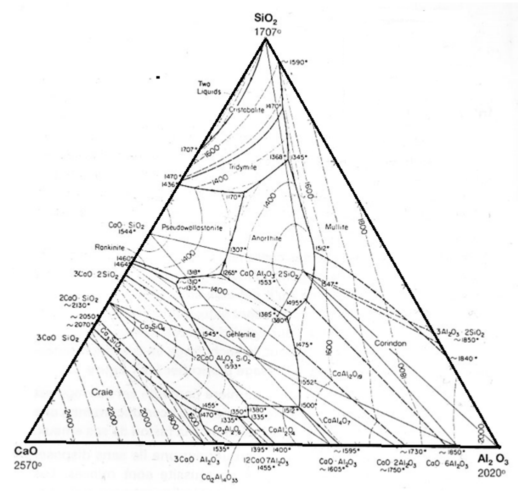

Fig. 2. CaO - SiO_2 - Al_2O_3 phase diagram [4]

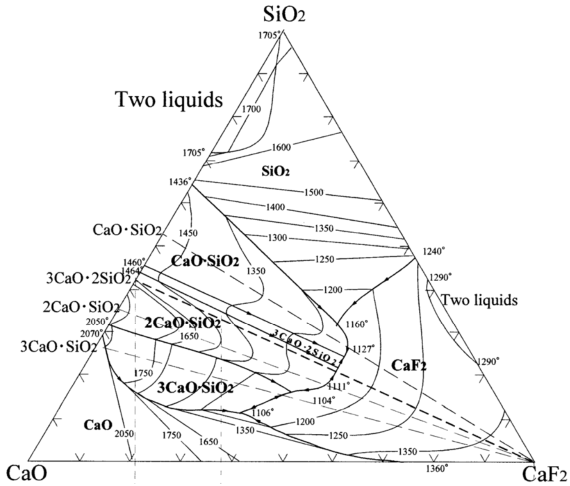

Fig. 3. CaO - SiO_2 - CaF_2 phase diagram [4]

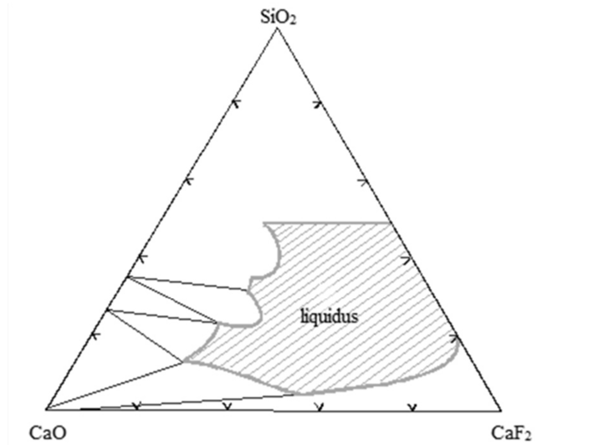

Fig. 4. Liquid phase range for the system: CaO - SiO_2 - CaF_2 at 1673 K [5]

The present work is focused on the factors, which determine the mold slag viscosity. The analysis employs the viscosity calculations with the use of the models of Kondratev, Riboud [6,7] and the quasi-chemical model operating within the FactSage program. The model calculations regarded two types of slag of considerably different chemical composition, which are frequently used in continuous casting of steel. The influence of concentration of CaO, SiO_2 and CaF_2 on slag viscosity at various process temperature was studied. The results of calculations were verified in comparison with the authors' experimental results. The results of calculations were verified in comparision with the authors experimental results.

2. The subject of study

The calculations and experimental investigations were carried out for two kinds of slags. Their chemical composition is given in Table 1.

Table 1.
The chemical composition of mold slags studied in the present work

Slag composition [mass %]	SiO_2	CaO	MgO	Al_2O_3	Na_2O
Slag 1	34.4	27.0	3.9	4.7	11.8
Slag 2	27.5	36.5	2.75	4.5	-

3. Models of mold slags viscosity

The following models have been employed in the present work [6-14]:

a. Riboud model [6,7]

This model is applicable for the slags of following chemical compositions (in mole %):
SiO_2 (28-48%), CaO (13-52%), Al_2O_3 (0-17%), CaF_2 (0-21%), Na_2O (0-27%).

The mold slag is the liquid mixture of chemical compounds, predominantly oxides. These oxides are of four categories, depending on their chemical character:

- SiO_2 "acidic oxides" category contains: SiO_2, P_2O_5, TiO_2, ZrO_2,
- Al_2O_3 "amphoteric oxides" category contains Al_2O_3 and B_2O_3,
- CaO "alkaline oxides" category contains: CaO, MgO, FeO, Fe_2O_3, MnO, NiO, CoO, ZnO and Cr_2O_3,
- Na_2O "alkaline oxides" category contains Na_2O, K_2O, LiO_2.

Accordingly, the following cumulative molar fractions are defined:

$$X'SiO_2 = X_{SiO2} + X_{P2O5} + X_{TiO2} + X_{ZrO2} \quad (1)$$

$$X'Al_2O_3 = X'_{Al2O3'} + \{X'_{B2O3'}\} \quad (2)$$

$$X'CaO = X_{CaO} + X_{MgO} + X_{FeO} + X_{Fe2O2} + \{X_{MnO} + X_{NiO} + X_{CrO} + X_{ZnO} + X_{Cr2O3}\} \quad (3)$$

$$X'Na_2O = X_{Na2O} + X_{K2O} + \{X_{Li2O}\} \quad (4)$$

Additionally, the molar fraction of CaF_2 - X_{CaF2} must be taken into account. Thus, the following condition is fulfilled:

$$X'_{SiO2} + X'_{Al2O3} + X'_{CaO} + X'_{Na2O} + X_{CaF2} = 1 \quad (5)$$

Viscosity is expressed as the function of temperature:

$$\eta = A \cdot T \cdot e^{B/T} \quad (6)$$

where A and B parameters are the functions of liquid slag composition expressed in cumulative molar fractions:

$$A = exp\,(-19.81 + 1.73X'_{CaO'} + 5.82X_{CaF2} + 7.02\,X'_{Na2O'} - 35.76X_{Al2O3} \quad (7)$$

$$B = 31140 - 23896\,X'_{CaO'} - 46356X_{CaF2} - 39159X'_{Na2O'} + 68833X'_{Al2O3'} \quad (8)$$

b. Riboud model adopted by Zhao et al.

Viscosity is expressed as the function of temperature:

$$\eta = A \cdot T \cdot e^{B/T} \quad (6)$$

where A and B parameters are the functions of liquid slag composition expressed in cumulative molar fractions:

$$A = exp\,(-20.81 + 1.73X'_{CaO'} + 5.82X_{CaF2} + 7.02\,X'_{Na2O'} - 35.75X_{Al2O3} \quad (9)$$

$$B = 31140 - 23896\,X'_{CaO'} - 46351X_{CaF2} - 39519X'_{Na2O'} + 68833X'_{Al2O3'} \quad (10)$$

c. Urbain model [6-8]:

This model classified the various slag into the three categories:

- glass formers:

$$X_G = X_{SiO2} \quad (11)$$

- network modifires:

$$X_M = X_{CaO} + X_{MgO} + X_{CaF2} + X_{FeO} + X_{MnO} + X_{CrO} + X_{NiO} + X_{K2O} + 2X_{TiO2} + X_{ZrO2} \quad (12)$$

- amphoterics compounds:

$$X_A = X_{Al2O3} + X_{B2O3} + X_{Fe2O3} + X_{Cr2O3} \quad (13)$$

Urbain model makes use of the Weymann equation:

$$\eta = A \cdot T \cdot e^{1000B/T} \quad (14)$$

where:

$$\ln A = -(0{,}29B + 11{,}57) \tag{15}$$

The B is calculated by equations:

$$a = \frac{x_M}{x_M + x_A} \tag{16}$$

$$B_i = a_i + b_i a + c_i a^2 \tag{17}$$

where a, b, c are the constans

$$B = B_0 + B_1 X_{SiO_2} + B_2 X^2{}_{SiO_2} + B_3 X^3{}_{SiO_2} \tag{18}$$

B_0, B_1, B_2, B_3 can be calculated from equation 19-21. These parameters are introducted into Equation 18.

$$B_0 = 13.8 + 39.9355\,\alpha - 44.049\,\alpha^2 \tag{19}$$

$$B_1 = 30.481 - 117.1505\,\alpha + 139.9978\,\alpha^2 \tag{20}$$

$$B_2 = -40.9429 + 234.0486\,\alpha - 300.04\,\alpha^2 \tag{21}$$

$$B_3 = 60.7619 - 153.9276\,\alpha + 211.1616\,\alpha^2 \tag{22}$$

d. Kondratiev model [7,9]

Kondratiev and Jak modified the Urbain viscosity model for calculate viscosities multi - component slags. Equation for the viscosity of the solution oxide (Pa·s) according to this model is the following:

$$\eta = A \cdot T \cdot \exp\left(\frac{B \cdot 10^3}{T}\right)\eta \tag{14}$$

where A and B are related to the relationship:

$$-\ln A = m \cdot B + n \tag{23}$$

B is a function of the composition of the slag, expressed in mole fraction, m and n are empirical parameters.

$$B = \sum_{i=0}^{3} b_i^0 \cdot \left(X_{SiO_2}\right)^i + \sum_{i=0}^{3}\sum_{j=1}^{2}\left(b_i^{'j} \cdot \frac{x_{CaO}}{x_{CaO}+x_{FeO}} + b_i^{''j} \cdot \frac{x_{CaO}}{x_{CaO}+x_{FeO}}\right) \cdot a^j \cdot \left(X_{SiO_2}\right)^j \tag{24}$$

A is a function of the chemical composition of the slag

$$a = \frac{x_{CaO} + x_{FeO}}{x_{CaO} + x_{FeO} + x_{Al_2O_3}} \tag{25}$$

parameter m is expressed as:

$$m = m_{SiO_2} \cdot X_{SiO_2} + m_{CaO} \cdot X_{CaO} + m_{Al_2O_3} \cdot X_{Al_2O_3} + m_{Feo} \cdot X_{Feo} \tag{26}$$

Parameters used in the calculations presented in Table 2.
The parameters m and n are as follows:

$$m_{SiO_2} = 0.212 \; m_{CaO} = 0.587 \; m_{Al_2O_3} = 0.370 \; m_{FeO} = 0.665$$

Table 2.
The viscosity Kondratiev model parameters for the system CaO - SiO_2 - Al_2O_3 [5,8]

j/i		0	1	2	3
b_i^0	0	13.31	36.98	-177.70	190.03
$b_i^{'j}$	1	5.50	96.20	117.94	-219.56
	2	-4.68	-81.60	-109.80	196.00
$b_i^{''j}$	1	34.30	-143.64	368.94	-254.85
	2	-45.63	129.96	-210.28	121.20

Model calculations were carried out for slag in the system SiO_2 - Al_2O_3 - CaO of the composition given in Table 1. The content of components in percentage by mass converted into mole fractions.

e. Quasichemical Model - Fact Sage [10]

Model allows to determine the viscosity of the liquid phase: slag or glass. Model relates directly to the structure of the slag. The structure is calculated by using the thermodynamic description of the model. Module of the viscosity uses thermodynamic base Ftoxid for calculations by means of Fact Sage software.

4. The results of calculations

First viscosity calculations were made for the slag consisting of the oxides of the primary system: CaO - SiO_2 - Al_2O_3. Simulation were performed using the model of Kondratiev [7,9]. The calculation was carried out at a temperature of 1550°C for the slags composition shown in Table 1. The content of components in the slag were converted to mole fractions. Results of viscosity calculations are shown in the Fig. 5.

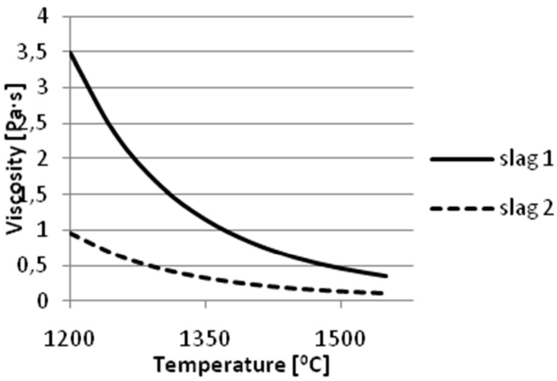

Fig. 5. Dependence of slags 1 and 2 viscosity on temperature calculated from the Kondratiev model [7,9]

In the next step, the calculation were performed for slag consisting of oxide system: CaO, SiO_2, Al_2O_3, Na_2O with variable CaF_2 content in the range from 1 to 14%. The results of the calculations by means of different models are shown in the Figs. 6-11. Figures 6-7 shows the results of calculations made by the Riboud - Zhao model [6,7].

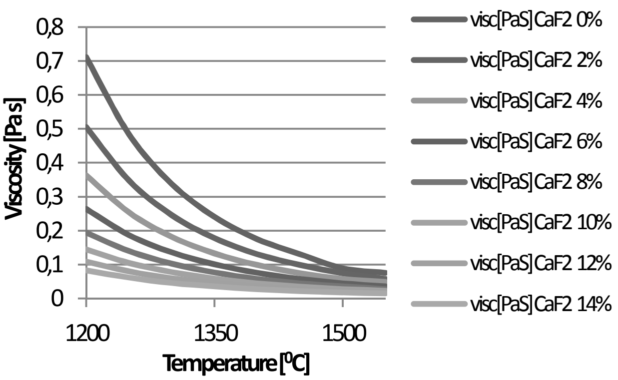

Fig. 6. Temperature dependence of viscosity of slag 1 containing CaF_2 calculated by the model Riboud - Zhao [6,7]

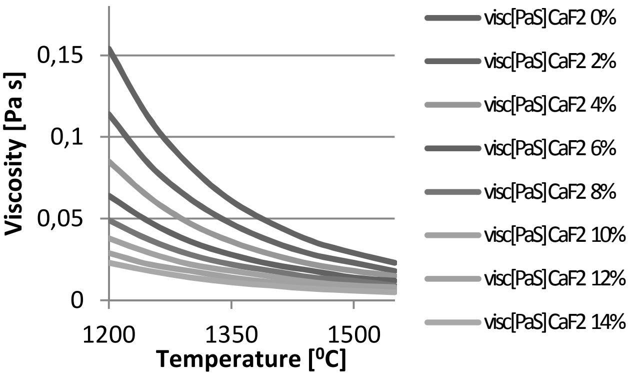

Fig. 7. Temperature dependence of viscosity of slag 2 containing CaF_2 calculated by the model Riboud - Zhao [6,7]

Figures 8-9 show the results of calculations made by the Urbain model [6,7,8].

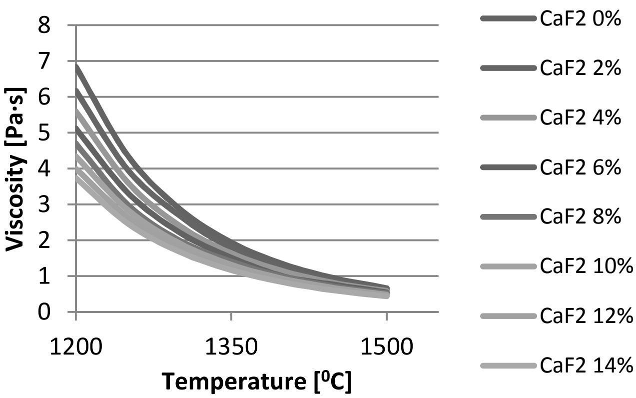

Fig. 8. Temperature dependence of viscosity of slag 1 containing CaF_2 calculated by the Urbain model [6-8]

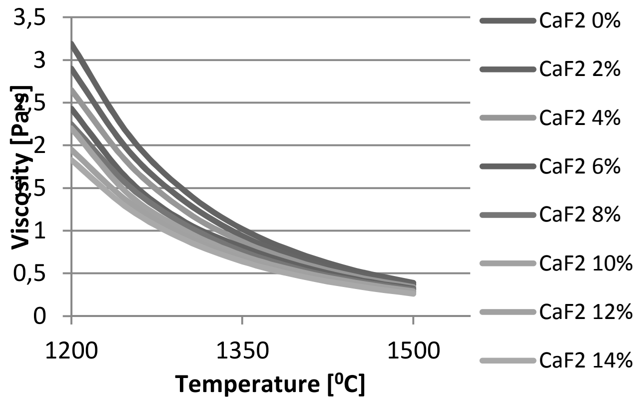

Fig. 9. Temperature dependence of viscosity of slag 2 containing CaF_2 calculated by the Urbain model [6-8]

Figures 10-11 show the results of calculations made FactSage program [10].

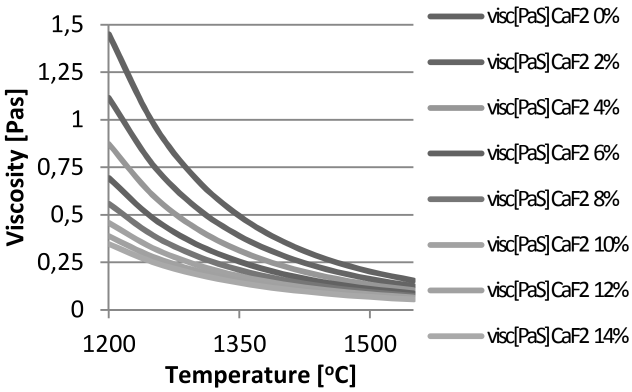

Fig. 10. Temperature dependence of viscosity of slag 1 containing CaF_2 calculated by means of Fact Sage program [10]

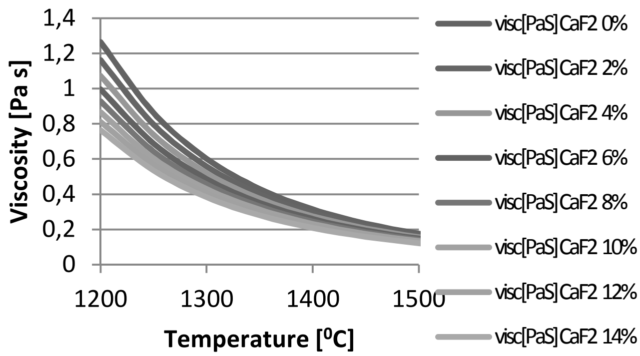

Fig. 11. Temperature dependence of viscosity of slag 2 containing CaF_2 calculated by means of Fact Sage program [10]

Figures 12-13 show the effect of temperature on the viscosity of the slag 1 and 2.

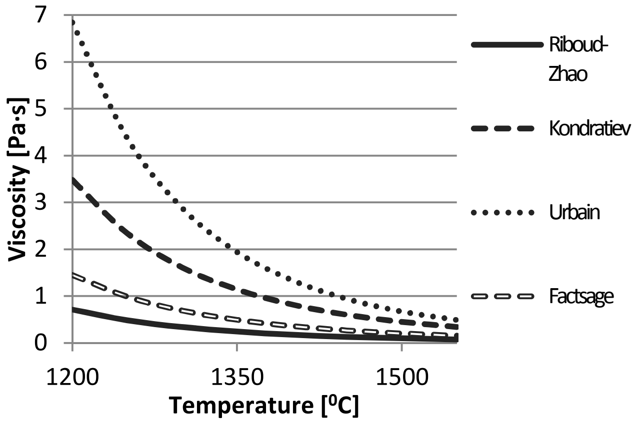

Fig. 12. Effect of temperature on the viscosity of the slag 1

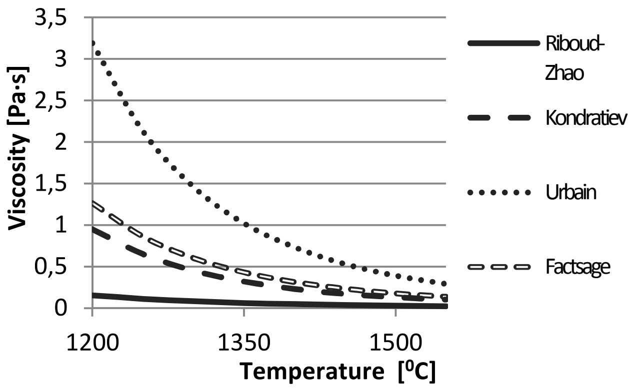

Fig. 13. Effect of temperature on the viscosity of the slag 2

Figures 14-15 show the effect of the addition CaF_2 on the viscosity of the slags 1 and 2.

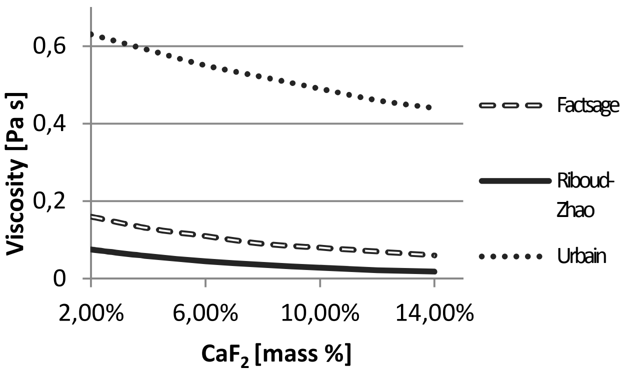

Fig. 14. Effect of the addition CaF_2 on the viscosity of the slag 1 at temperature 1500°C

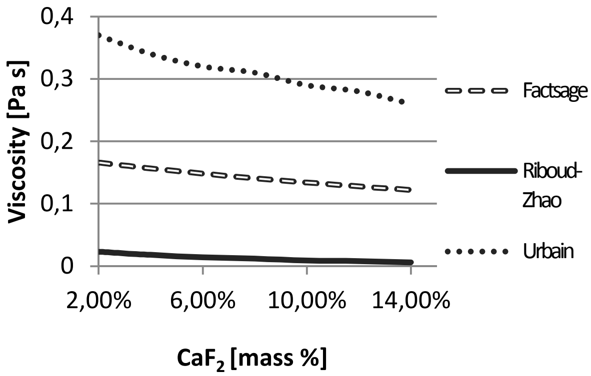

Fig. 15. Effect of the addition CaF_2 on the viscosity of the slag 2 at temperature 1500°C

For better comparison of the results obtained with the use of various methods, the viscosity values at 1500°C were collected in Table 3.

Table 3.
The values of viscosity [Pa·s] at 1500°C calculated with the use of various models

Viscosity Model	Slag 1			
	CaF_2 0%	CaF_2 4%	CaF_2 10%	CaF_2 14%
Riboud and Zhao	0.089	0.058	0.028	0.018
Urbain	0.67	0.59	0.49	0.44
Kondratiev	0.45	-	-	-
Fact Sage	0.20	0.13	0.08	0.06
Viscosity Model	**Slag 2**			
	CaF_2 0%	CaF_2 4%	CaF_2 10%	CaF_2 14%
Riboud and Zhao	0.029	0.018	0.09	0.006
Urbain	0.39	0.34	0.29	0.26
Kondratiev	0.13	-	-	-
Fact Sage	0.17	0.15	0.13	0.12

5. Conclusions

Empirical viscosity models allow to calculate viscosity ionic solutions containing fluorides. The present work discussed the impact of CaF_2 addition and temperature on the viscosity of the oxide system investigated. The results of calculations made with the use the models of viscosity and the Fact Sage program indicate discrepancies due to the calculation method used and the assumptions made in the models. The results of calculations in the form of viscosity dependence on temperature obtained from various models were illustrated in Figures 6-15. The behavior of slags 1 and 2 differs significantly. Slag 1 indicates considerably higher viscosity at all temperatures than slag 2. The same is valid for 4 - components slags on the basis of slags 1 and 2 with the same CaF_2 additions. This difference stems from the proportions between SiO_2 and CaO (CaO/SiO_2 = 0.78 for slag 1 and 1.32 for slag 2). It should be noted that considerable content of Na_2O in slag 1 does not strongly influence the viscosity.

The results obtained on the ground of various viscosity models show strong discrepancy. The viscosity values for fixed values of temperature and slag composition decrease from model to model in the following order:L Urbain - Kondratiev - Fact Sage - Riboud. In all cases the typical decrease of viscosity with growing temperature was revealed.

The addition of calcium fluoride affects the viscosity as well as the range of fully liquid slag. Calcium fluoride melting point is 1360°C. The influence of CaF_2 content on the viscosity decrease was observed for both slags1 and 2, at all considered versions of model calculations. However, the impact of CaF_2 addition is stronger in the case of slag 1.

This difference may be partly attributed to the presence of Na_2O in slag 1. The following reaction may take place: $CaF_2 + Na_2O = 2\ NaF$

In this case, the F^- fluoride ion is bound to the cation Na^+ and is not associated with cation Ca^{2+}, which prevents the release of the cuspidine compound that increases the liquidus temperature of slag. Calculations made with using models Urbain and Riboud - Zhao did not confirm this phenomenon results observed in the calculation variant with Fact Sage. However, they showed that the addition of CaF_2 to the slag with a higher content of CaO lowers the viscosity more than the slag with a higher content of SiO_2.

The obtained results suggest, that the most commonly used viscosity models yield very different results. To explain this discrepancy more experimental data are needed.

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