

P. MIGAS*, M. KOROLCZUK-HEJNAK*

SEMI-SOLID STATE OF BLAST FURNACE SLAG ADMIXTURES OF Al_2O_3

ŻUŻLE WIELKOPIECOWE DOMIESZKOWANE Al_2O_3 W STANIE STAŁO-CIEKŁYM

The nature and properties of liquid solutions - metallurgical slags (used in the pig iron and steel production) affect the quality of the final product and processing time. The main object of the study was slag system: $CaO-SiO_2-MgO-Al_2O_3$, when the content of Al_2O_3 was raised to ca. 25% in liquid and semi-liquid state.

Measurements were performed using Searle's method of concentric cylinder systems. Graphite measuring systems were used for testing with two types of bobs: smooth and perforated. Rheological measurements were carried out for five slag systems in the temperature range between 1310-1500°C, shear rate values were changed in the wide range between $1s^{-1}$ to $150/180s^{-1}$. FactSage application was used to calculate the mass of solid phases precipitating from the slag volume for different chemical compositions at various temperatures. In the temperature range in which the solid phases occurred in the slag the analysed systems show non-Newtonian behaviour.

Keywords: liquid slags, rheology, non-Newtonian flow

Charakter oraz właściwości ciekłych żużli metalurgicznych (wykorzystywanych w procesach wielkopiecowym oraz stalowniczym) wpływa na jakość produktu oraz na czas prowadzonego procesu. W niniejszej pracy analizowano żużle typu $CaO-SiO_2-MgO-Al_2O_3$, domieszkowane do ok. 25% Al_2O_3 , w stanie ciekłym oraz stało-ciekłym.

Badania zostały wykonane przy użyciu rotacyjnej metody z koncentrycznymi cylindrami typu Searle'a. Narzędzia pomiarowe wykonano z grafitu, charakteryzowały się one gładkimi oraz perforowanymi powierzchniami. Badania reologiczne wykonano dla pięciu systemów żuźlowych w temperaturach 1310-1500°C. Prędkość ścinania w trakcie pomiarów zmieniana była od $1s^{-1}$ do $150/180s^{-1}$. Pakiet FactSage został wykorzystany do obliczenia masy fazy stałej, wytrącającej się z objętości żużla, dla różnych składów chemicznych, w różnych temperaturach. W temperaturach, w których zaobserwowano występowanie fazy stałej charakter reologiczny badanych układów żuźlowych odbiegał od zachowania ciała idealnego Newtona.

1. Introduction

When it comes to metallurgical processes involving slag and metal liquid phases, viscosity is one of the basic physical properties. It has direct influence on the kinetics of reactions taking place between the liquid metal and slag as well as on the flow of these phases in the metallurgical aggregates. That is why this property is a key parameter taken into account in the existing mathematical models as well as those that are currently being developed. The rheological character of liquid slag should be defined not only on the basis of chemical composition and temperature but also by means of rheological parameters such as t – a period of time during which the force is applied to the system, τ – shear stress, $\dot{\gamma}$ – shear rate [1].

The rheological parameters present in the actual metallurgical processes are very difficult to measure. These parameters include: the dynamics of the influence of the electric arc on the properties of liquid steel and slag in EAF, the dynamics of the influence of the gas reducer on the liquid slag and pig iron in the blast furnace, the phenomena connected to semi-liquid and liquid products moving down the blast furnace in counter-flow

with gas and then filling in the voids between the pieces of coke.

In all of above systems these factors influence the liquid slag and pig iron with a certain dynamic force and result in the occurrence of the shear stress in the layers of moving slag – thus changing the dynamic viscosity coefficient of the slag and in certain cases its rheological character. It is commonly assumed that fully liquid slag, which is a Newtonian fluid, does not change its viscosity under the influence of an applied force. In many cases liquid slag constitutes a heterogeneous system and its viscosity is affected by the contents of solid elements in the fluid. The solid elements precipitated while the temperature was being decreased (in the course of chemical reactions) due to changes in the chemical composition and as a result of elements entering slag from the outside (e.g. coal dust, carbides, nitrides insoluble in slag).

Solid-liquid slag systems are present in many metallurgical processes such as: the blast furnace process – powder coal injection (PCI), the cohesion zone and slag dripping; the arc furnace process – slag foaming, slag in the production of

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, AL. A. MICKIEWICZA 30, 30-059 KRAKOW, POLAND

chrome steel; COS – steel casting, casting powder, pig iron and steel refining – 3D technology, desulphurization, dephosphorization, desilicization.

The flow of non-Newtonian fluids in packed beds is important in many practical applications, and equations and theory for yield-stress fluids is unique, because a threshold pressure gradient is required to initiate flow. A number of macroscopic relationships, which are used for continuum-scale modelling have been proposed for non-Newtonian fluids and a few are applicable for yield-stress fluids. While these simple, closed form expressions are convenient when applicable, they are also quite restrictive in how they are applied [2, 20].

All these processes involve solid elements which precipitated from the solution or which were introduced to the slag system.

The high concentration of Al_2O_3 in slag in the blast furnace process is one of the factors determining the decrease in the liquidity of the slag. In order to limit the problems with the permeability in the lower parts of the blast furnace and the optimization of slag dripping, the pig iron production technology is characterized by a predefined level of Al_2O_3 ranging from 10 to 15% depending on the charging conditions of a particular steelworks. The applied technological conditions in modern blast furnaces are aimed at reducing the amount of slag in the process. They result from decreasing the amount of SiO_2 in the ore sinters, environmental conditions, improving the permeability and dripping of the process products. In such a situation decreasing the amount of slag triggers a significantly increase in Al_2O_3 concentration – even when the Al_2O_3 content in the used ore is at a constant level. Due to this fact it becomes vital to set clear guidelines concerning the upper limit of Al_2O_3 concentration in slag and its influence on the rheological parameters of the liquid and semi-liquid system [3].

Literature contains many published research results concerning the measurements of dynamic viscosity of metallurgical slag in fully liquid slag systems [4-7]. The authors did research into the influence of chemical composition, basicity and temperature on the viscosity. Few research centres [8,9] undertook a complicated subject and analysed the changes in the dynamic viscosity coefficient to provide a rheological description of liquid and solid-liquid multicomponent slag systems.

Rheology is a study of two different types of fluids [10, 11]:

- Newtonian fluids– (ideal viscosity) which show a linear relationship between the shear stress and the shear rate,
- Non-Newtonian fluids – which show non-linear relationship between the shear stress and changes in the shear rate.

Newtonian fluids are characterized by a stable viscosity in the course of the flow, which is independent of the deformation rate and the repeatability of viscosity value in the course of subsequent identical deformations/flows. The viscosity of non-Newtonian fluids is referred to as apparent viscosity. It is dependent on the deformation rate, duration and pressure. In reality most fluids are non-Newtonian ones.

The rheological description of fluids includes viscous and elastic features. The viscous features can be determined by defining the flow curve, i.e. the relation between the shear

stress (triggered by shearing fluid) and the shear rate (velocity gradient existing in the flowing liquid). In order to determine the elastic features it is necessary to measure the normal stress in the course of a given viscous flow. Such analysis allows to determine the relationship between the deformation, the shear rate and the shear stress.

2. Selected rheological models for viscosity value calculation

Recently researchers have been developing and describing many models used to determine the viscosity of aluminosilicate slag: Urbain, KTH, Iida, QCV [12-16].

The viscosity (η) of slag is distinctly dependent on the temperature and structure of the fluid [10]. It is a measure of the ability of slag to flow when the shear stress is applied. Most slag and metallic fluids show the characteristics of Newtonian fluids, in case of which viscosity is independent of the shear rate [10]. As a result viscosity is defined by the Newton's equation (1):

$$\tau_{xy} = \eta \frac{dv_x}{dy} \quad (1)$$

where:

η – constant of proportionality, aka dynamic viscosity coefficient, Pas,

τ_{xy} – shear stress, Pa,

$\frac{dv_x}{dy}$ – the gradient of normal velocity to the shear stress, so called shear rate.

In some cases liquid aluminosilicates represent deviation from perfect Newtonian liquid body. Molten slags in ferrous metallurgy are liquid highly polymerized (additives Al_2O_3 , SiO_2) forming aluminosilicate network chains, by changing the chemical composition and the effect of free cations of some metals undergo intensive depolymerization. In a blast furnace during the dripping of the slag in particular conditions temperature, pressure and chemical composition may precipitate the solid elements forming the suspension of system, the nature of which will depend on the rheological character from the amount, the shape and size of the solid components in such system. The mean relative gap δ , the ratio of the mean gap between neighboring particles to particle diameter, is another important geometric parameter in predicting the rheological properties of concentrated suspensions. If the particle packing density Φ_m is known and it is assumed that, by adding a liquid medium, the particles are equally separated to a solid volume fraction of Φ , then by theoretical analysis δ is given by:

$$\delta = \left(\frac{\Phi_m}{\Phi} \right)^{\frac{1}{3}} - 1 \quad (2)$$

This parameter has been employed in many viscosity models. These models are based on the idea that, at high concentration, the flow of suspensions is dominated by the interaction between neighboring particles. The interaction force, and hence the viscosity, is proportional to δ^{-1} . At high solid-volume fraction the viscosity significantly increases as δ decreases, and as δ approaches zero the suspension becomes immobile. In case of slags, a liquid - between solid system elements - could create alumina-silicate chains, which providing changes of the rheological properties of suspension [17].

The literature referring to the topic contains numerous rheological models which make it possible to calculate the viscosity values for non-Newtonian fluids. The simplest models include [10]:

- Ostwald de Waele's a power law model

$$\tau = \eta \cdot \dot{\gamma}^n \quad (3)$$

where:

- τ – shear stress, Pa,
- η – viscosity of the fluid, Pas,
- $\dot{\gamma}$ – shear rate, s^{-1}
- n – flow coefficient.

- Herschel-Bulkley model

$$\tau = \tau_y + K \cdot \dot{\gamma}^m \quad (4)$$

where:

- τ – shear stress, Pa,
- τ_y – yield stress, Pa,
- $\dot{\gamma}$ – shear rate, s^{-1}
- K, m – constants.

- Bingham model

$$\tau = \tau_y + \eta_p \cdot \dot{\gamma} \quad (5)$$

where:

- τ – shear stress, Pa,
- τ_y – yield stress, Pa,
- η_p – plastic viscosity, Pas,
- $\dot{\gamma}$ – shear rate, s^{-1} .

The above mentioned models allow to calculate viscosity values of the plastic material which shows the characteristics of a solid body and sometime: slurry, suspensions or semi-solid liquids. It is elastic till the moment it exceeds the critical stress (known as yield point or yield stress) and then it deforms plastically (Bingham model). Herschel-Bulkley model, on the other hand, is a non-linear version of Bingham model. It illustrates the behaviour of plastic material which is characterized by shear thinning the moment the critical stress is exceeded.

There have been many mathematical models developed in order to describe the behaviour of real bodies. These models also include ones that allow to estimate the viscosity values of suspensions while taking into consideration the amount and shape of particles (and not only the shear rate and shear stress values which were taken into consideration by other rheological models). The above mentioned models include, among others, the Krieger-Dougherty equation [10].

$$\eta_{rel} = \left(1 - \frac{\Theta_{eff}}{\Theta_{max}}\right)^{-k\Theta_{max}} \quad (6)$$

where:

- η_{rel} – relative viscosity value, Pas,
- Θ_{eff} – solid phase volume fraction,
- Θ_{max} – maximum solid phase volume, equal to 0.68,
- k – constant equal to -2.5 (in relations to Einstein equation), in case of non-ideal suspensions k reaches values above 2.5.

Einstein equation was modified by Roscoe and that is how Einstein-Roscoe equation came into being:

$$\eta = \eta_0(1 - k\Theta_{eff})^m \quad (7)$$

where:

- η – viscosity of the suspension, Pas,
- η_0 – the viscosity of the liquid phase remaining in the system, Pas,
- Θ_{eff} – solid phase volume fraction,
- k – constant, for spherical molecules equal to 2.5,
- m – exponent, experimentally found to be equal to 1.35.

Carreau-Yasuda model is an equation used to model iron solutions in solid-liquid state. It is one of few models that contains a rheological parameter – shear rate. As a result, it takes into consideration changes in the viscosity coefficient under the influence of changing forces affecting the liquid metal.

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = [1 + (\lambda\dot{\gamma})^a]^{\frac{(n-1)}{a}} \quad (8)$$

where:

- η – viscosity of the suspension, Pas,
- η_0 – viscosity with the shear rate approaching 0, Pas,
- η_{∞} – viscosity with an infinitely high shear rate, Pas,
- λ – constant,
- $\dot{\gamma}$ – shear rate, s^{-1}
- a, n – constants, most commonly adopting the value equal to 2.

The models which allow to calculate the viscosity of suspensions in metallurgy can be used to estimate the viscosity values of solid-liquid slag systems, fluxes and salt in semi-solid state.

3. Experimental method

In order to measure the dynamic viscosity coefficient a force needs to be applied to the liquid system, and as a result the system is set into motion. The application of the force causes one layer of fluid to be transported towards another. Internal structures in the fluid, their polymerisation or depolymerisation cause the measurements to be more complicated. The dynamic viscosity is the best property of liquid glass and slag [17] when it comes to analysing the internal structure of these fluids.

As far as the measurement methods are concerned, the method of concentric cylinders in two systems (Coute's and Searl's [10]) is the most popular way to measure the dynamic viscosity coefficient. In case of Coute's system there is a moving external cylinder, and a motionless internal one. In the second system, Searl's one, there is a moving internal cylinder and a motionless external one.

Figure 1 presents graphite measurement tools used by authors to conduct rheological research into liquid and solid-liquid slag systems. The researchers used one type of cup (inner diameter – 30 mm) and three different types of bob geometry: a smooth bob (diameter 15 mm) with a flat basis, a perforated bob (diameter 16 mm) with a conical basis and a smooth bob (diameter 27 mm) with a conical basis. The 15 mm and 16 mm bobs are used to conduct research in the

conditions of wide rheological fissure (7.5 mm and 7.0 mm respectively) used to study high viscosity systems – hundreds and thousands of Pas. In case of slag we are dealing with decimal parts of Pas. As far as slag is concerned, research in the conditions of wide rheological fissure is conducted mainly for solid-liquid states.

The 27 mm bob makes it possible to measure substances with very low viscosity values amounting to hundredths and thousandth parts of Pas.

The bob which was used to study liquid and solid liquid systems had the diameter of 16 mm and a perforated side surface in order to ensure the simple shear of the fluid and the most linear distribution of velocity in the fissure possible. From the point of view of this rheological research into fluids such a size of fissure is better. In case of this research the fissure measured 7 mm.



Fig. 1. Measurement systems used [19,21,22]

The bob with the biggest diameter (27 mm, presented in Fig. 1) together with the cup can be treated as a standard measurement system (according to ISO 3219). The other two bobs are nonstandard measurement systems and were selected due to the character of the analysed fluid. Nonstandard measurement systems are calibrated by using model fluids that have a defined value of the viscosity coefficient in given temperature. In case of the described research the system was calibrated on model oils in room temperature by selecting appropriate values of conversion coefficients (C_{SR} and C_{SS}). They can be described as follows:

$$\tau = C_{SS} \cdot M \tag{9}$$

$$\dot{\gamma} = C_{SR} \cdot n \tag{10}$$

where: τ – shear stress, Pa; $\dot{\gamma}$ – shear rate, s^{-1} ; M – torque, Nm; n – rotational speed, rpm.

Figure 2 shows a high temperature rheometer scheme. It is equipped with a pipe furnace which makes it possible to obtain temperatures up to 1530°C. The measuring head and the cooling system are the main parts of the rheometer. The

rheometer is also equipped with an air bearing which enables precise measurements for low viscosity values amounting to several mPas. Both the head and the furnace are operated remotely using a computer. There is a thermocouple in the furnace, which allows to measure the temperature. The resistance pipe furnace with a mullite pipe is controlled by means of Eurotherm. Inert gas (argon, its purity – 5.0) is introduced into the furnace. It allows to maintain a protective atmosphere in the course of long rheological measurements.

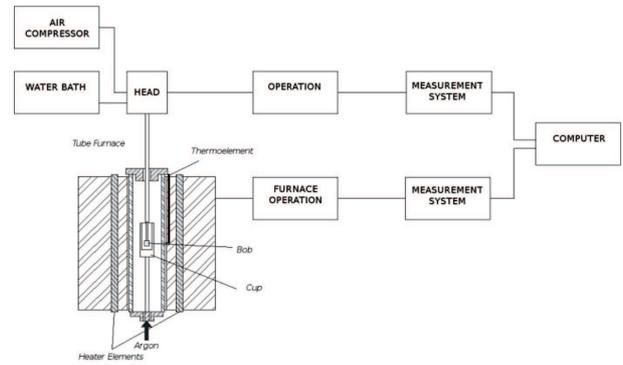


Fig. 2. Scheme of a high temperature rheometer FRS1600 [19-22]

The rheological research focused on multi-component slag of the blast furnace type in the system $CaO-SiO_2-Al_2O_3-MgO$. This slag was obtained by means of a synthesis of pure components in liquid form: CaO – calcined powder, SiO_2 – analytically pure quartz, Al_2O_3 – analytically pure, MgO – analytically pure calcined powder (E. Merck company). Before the components were weighed, they had been dried in the temperature of 120°C for 5 hours. Then they were carefully mixed. Slag was melted in an induction furnace (in a graphite cup). The chemical composition of slag was analysed using an XFR spectrometer TWIN-X. The results of this analysis can be found in Table 1.

TABLE 1

Percentage and mass chemical composition of slag used for this research

Components	1		2		3		4		5	
	%	g	%	g	%	g	%	g	%	g
CaO	44.23	22.11	41.61	20.81	40.34	20.17	37.66	18.83	35.56	17.78
MgO	6.46	3.23	6.07	3.04	5.88	2.94	5.49	2.74	5.18	2.59
Al_2O_3	7.07	3.54	12.76	6.38	15.60	7.80	21.29	10.65	25.65	12.83
SiO_2	42.24	21.12	39.55	19.78	38.18	19.09	35.56	17.78	33.61	16.80

4. Results analysis

In order to determine the content of solid phases in the slag system the researchers carried out equilibrium calculations (using FactSage software) of solid phase precipitation. The chemical composition and temperature of the analyzed slag constituted boundary conditions for which researchers calculated the type and amount of solid particles precipitating from the system. The mass of the sample used for this rheological experiment was 50g – this mass was used to calculate the mass content of particular oxides in the system. The obtained results are shown in Table 2.

The types of possible solid precipitations in the analyzed slag systems were also studied: sample 1 – $\text{MgOCa}_3\text{O}_3\text{Si}_2\text{O}_4$ – merwinite, CaSiO_3 – pseudowollastonite; sample 4 – $\text{Ca}_2\text{Al}_2\text{SiO}_7$ – gehlenite; sample 5 – $\text{Ca}_2\text{Al}_2\text{SiO}_7$ – gehlenite. In case of sample 2 and 3 solid particles appear only when the temperature rises over 1270°C or 1250°C respectively. These temperatures are theoretical ones and were not applied in the course of rheological experiments. Table 2 shows results for selected samples – sample 1, 4 and 5.

FactSage application enables to make thermodynamic calculations for selected systems in the equilibrium states. Researchers calculated the quantitative and qualitative chemical composition of slag systems for selected samples in given process conditions. The application does not, however, provide a possibility to calculate the rate of solid elements precipitation from the system. In order to be absolutely sure whether the solid precipitations actually exist during the measurement and in order to obtain homogenous temperature in the entire sample before the measurement, it was necessary to stabilise the system by mixing the sample in given temperature with the aim of obtaining constant viscosity values.

The viscosity of suspensions (especially in high temperatures) is the subject of many research projects and theoretical modelling. Researchers most commonly use Einstein's equation [8, 21] or its possible modifications to calculate the dynamic viscosity values of solid-liquid slag systems. The theoretical equations do not, however, account for the influence of the shape of solid particles suspended in the fluid on the viscosity measurements of the suspension. That is why, in such equations it is assumed that there are constant coefficients determining a factor of nodularity shape of particles. Equation (11), which is a modification of equation (7), was used for calculations during which a possible shape of solid particles was taken into account [21].

$$\eta = \eta_L(1 - f)^m \quad (11)$$

where:

η – coefficient of the dynamic viscosity of the suspension, Pas,

η_L – coefficient of dynamic viscosity of the fully liquid part of the fluid that remained in the system (without solid particles), Pas,

f – volume fraction of the solid phase,

m – a constant in the equation,

F – factor of nodularity shape of particles.

Using Urbain's model it was possible to calculate the dynamic viscosity of fully liquid slag remaining in the system

for a given chemical composition. The following value of η_L was obtained:

$$m = \frac{\ln \frac{\eta}{\eta_L}}{\ln(1 - f)} \quad (12)$$

$$m = \frac{3F - 2}{3F(1 - 2F)} \quad (13)$$

Equations (11), (12) and (13) were used to calculate the value of dynamic viscosity coefficient of the solid-liquid system and coefficient m . In the first case the value of coefficient m and of viscosity were calculated for an assumed possible shape of the solid element (characterized by coefficient $F=0.33333$). Table 2 (for selected samples 1, 4, 5) presents a comparison of dynamic viscosity coefficient values obtained in the course of measurements (with a constant shear rate value and temperature) and values calculated using Einstein-Roscoe model.

TABLE 2
A comparison of experimental results and calculations made using Einstein-Roscoe model

N ^o	n [rpm]	T [°C]	η_{measur} [Pa s]	η_{cal} [Pa s]
1	15	1310	53.08	18,90
	150		15.86	18,90
	15	1320	25.72	13,73
	150		10.78	13,73
	15	1330	0.796	11,23
	150		0.768	11,23
	15	1340	0.727	9,18
	150		0.695	9,18
4	15	1310	91.92	31,78
	150		31.90	31,78
	15	1320	40.71	27,80
	150		-	27,80
	15	1330	36.46	24,38
	150		23.35	24,38
	15	1340	27.42	21,26
	150		18.15	21,26
5	15	1310	45.72	55,24
	150		15.91	55,24
	15	1320	32.44	47,72
	150		16.28	47,72
	15	1330	20.66	41,11
	150		13.81	41,11
	15	1340	19.89	35,91
	150		12.98	35,91

Then calculations were made using the same set of equations but the values of coefficient m_{calcul} and F_1, F_2 were estimated for a measured value of dynamic viscosity coefficient η_{measur} . It was done in order to compare the results with possible table indicators (Table 3) characterizing the shape of solid particles in the system. The values of dynamic viscosity

calculated using the model – η_{cal} and the measured – $\eta_{measure}$. were shown in Table 2. After comparing the calculated values of coefficients F to those from the table (see Table 3) it became clear that the values are closest to each other in case of sample 1, the level is comparable to the one characterized by spherical shape of the solid element. The values obtained for sample 5, however, are higher than those calculated, which suggests a significant influence of solid inclusions or a total change in the shape of the solid element in the direction of an prolate spheroid. It may mean that the Al_2O_3 concentration in slag influences not only the amount of solid elements in the system, which is obvious, but also their size and shape.

TABLE 3
Shape factor F as a function of the relation between the axes of the nodular particles [23]

Axial ratio (z/x)	Shape factor (F)	Description
$\rightarrow 0$	0	oblate spheroid
0.002	0.00157	
0.02	0.01532	
0.1	0.06959	
0.2	0.12476	
1	0.33333	sphere
2	0.41322	
10	0.48986	
20	0.49663	prolate spheroid
200	0.49994	
2000	0.49999	
$\rightarrow \infty$	0.5	

The behaviour and influence of Al_2O_3 on the dynamic viscosity coefficient value in liquid siliceous systems shows similarity to SiO_2 . The oxide can also behave as an element cross-linking the fluid structure in the case of systems with higher basicity. Tetrahedral ion AlO_4^{4-} can be produced in such systems. It is characterized by high durability due to a big charge capacity – which compensates for the cation (Ca^{2+}). The production of AlO_4^{4-} ion can cause an increase in the resistance of flow. That is why, the viscosity models used to estimate the dynamic viscosity coefficient show lower viscosity by approx. 40% than the one obtained in the course of measurements. It is true, however, that there are few experimental data available in literature that could explain this discrepancy [21].

Figure 3 presents a comparison between the dynamic viscosity coefficient values calculated using Einstein-Roscoe model and the values measures using the FRS1600 rheometer.

Figure 3 shows clearly that the values of the variable $\eta_{calculate}$ reach on average higher values than in the case of the variable $\eta_{measure}$. Furthermore, one can notice the influence of the shear rate variable, which is not taken into account in the case of E-R equation. The viscosity values for the rate $\dot{\gamma}-150s^{-1}$ are lower for each of the presented samples than in the case of $\dot{\gamma}-15s^{-1}$. The calculated values of the coefficient F and the calculated values of the dynamic viscosity coefficient

as well as their comparison to the rheological character of the solid-liquid slag system suggest that it is necessary to consider the influence of the shear rate on the obtained dynamic viscosity coefficient value. E-R model is based on an assumption that the solid elements are spherical in shape when it comes to the rheological description of the solid-liquid system. In the case of the analysed slag solid elements have a totally different shape and size. These observations are in line with those presented by the authors [9], who drew conclusions concerning the application of Einstein-Roscoe model in determining the dynamic viscosity coefficient of liquid slag systems.

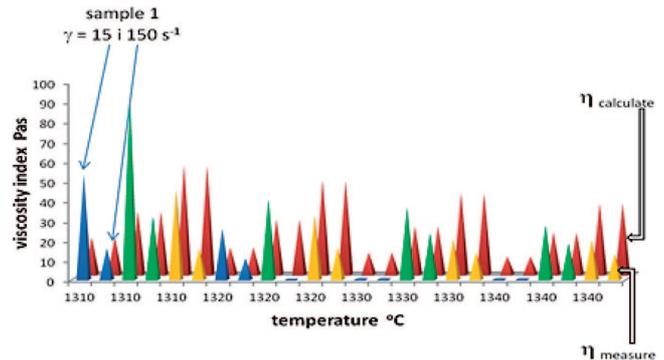


Fig. 3. Comparison of research results and calculations

Table 4 presents the measurement schemes which were conducted for all samples. The obtained changes of the programmed parameters (among others) were shown in Fig. 4.

TABLE 4
Protocol used for the measurement of rheological properties

Measurement stage	$\dot{\gamma}$ [s ⁻¹]	Process in temp.
Step I	15	cooling/homogenisation
Step II	A) 15-150(log) B) 150-15(log)	Const.
Step III	A) 15-180(log) B) 180-15(log)	Const.
Step IV	A) 30, 60, 80, 120, 80, 60, 30, B) 5, 200, 15, 200, 15, 150, 15, 150,	Const.

The charts presented in Figure 6 show the changes in dynamic viscosity coefficient for sample 5 in temperatures ranging from 1340 to 1320°C according to the scheme – step I, II, III, IV. During step I the system cooled down to the set temperature thanks to constant mixing at the shear rate of $15s^{-1}$. This was done in order to achieve its homogenization. When the sample obtained comparable/stable values of dynamic viscosity coefficient, the second measurement step began. Step III and IV are different configurations of the changes in the shear rate – they were presented in Table 4. Applying higher shear rates causes the dynamic viscosity coefficient values to decrease. Applying lower shear rates causes the dynamic viscosity coefficient values to increase. Similar behaviour was true for sample 1 and 4. Samples 2 and 3 do not show this kind of behaviour nor such significant changes in viscosity. This supports the calculations concerning solid particles in the

system – particles which should have appeared in temperatures which are lower than those for samples 1, 4 and 5.

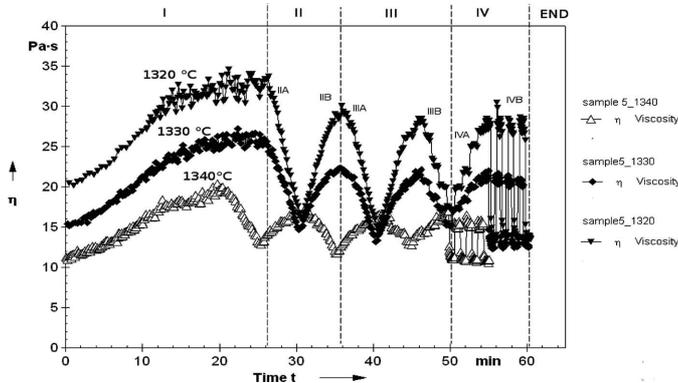
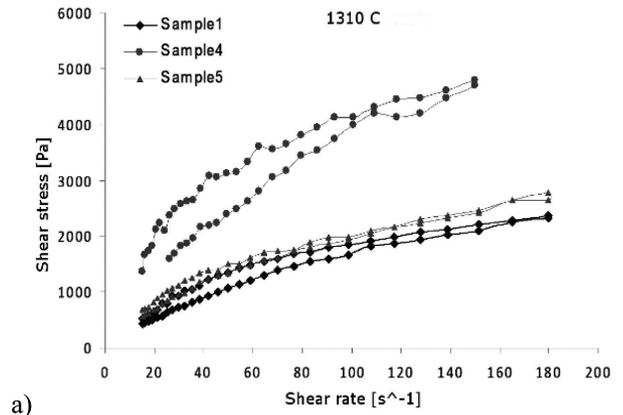


Fig. 4. Changes in the dynamic viscosity coefficient values with time for sample 5, for different $\dot{\gamma}$, for temperatures 1320-1340°C

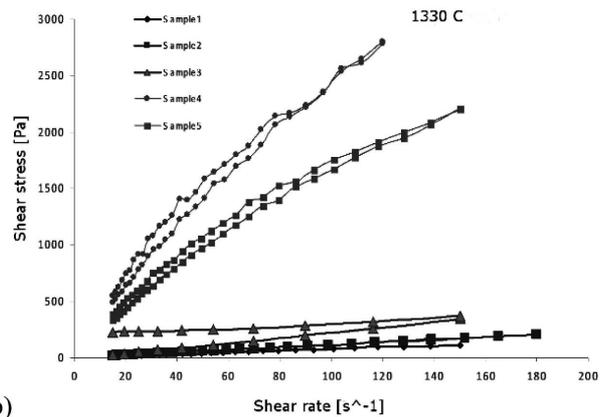
After removing the shear stress the value of the dynamic viscosity coefficient of the system increases. In case of decreasing the value of dynamic viscosity coefficient for high shear rates the system behaves as if its internal structure (aluminosilicates chains) of the liquid part is ordered to the shear direction. It is also possible that due to the centrifugal force of the rotating bob the solid particles present in the system are pushed away of bob surface and their order changes. This phenomenon can be verified by changing the value of the dynamic viscosity coefficient in step III and IV where a high shear rate was applied during a given time period and then the shear rate was dramatically decreased for the same time period. Consequently, it was possible to observe sudden changes in the viscosity values, which could explain the above mentioned behaviour of the internal structure of the system. Figure 5a and 5b present the flow curves for selected samples in the following temperatures: 1310, 1330, 1350, 1420°C.

One can notice considerable differences between the shape of curves in given measurement temperatures for particular contents of Al_2O_3 in the sample. The higher concentration of Al_2O_3 in given temperature, the higher dynamic viscosity coefficient value. The flow curves are also less linear. It can be concluded that the rheological character of the analysed system to a large extent depends on the temperature and the Al_2O_3 content. As a result, the rheological character depends on the amount (size and shape) of solid elements in the system and on the character of the residual fluid in the system.

Figure 6a and 6b show the flow curves for the systems which are theoretically fully liquid and do not contain solid elements. The lack of solid elements was proved on the basis of thermodynamic equilibrium calculations conducted using FactSage application. In case of the temperature of 1420°C presented in Fig. 6b and in the case of higher temperatures rectilinear relations of the flow curves were obtained. Such a character of the curves can point to a similarity between the analysed fluid and the ideally viscous body – the Newtonian body.

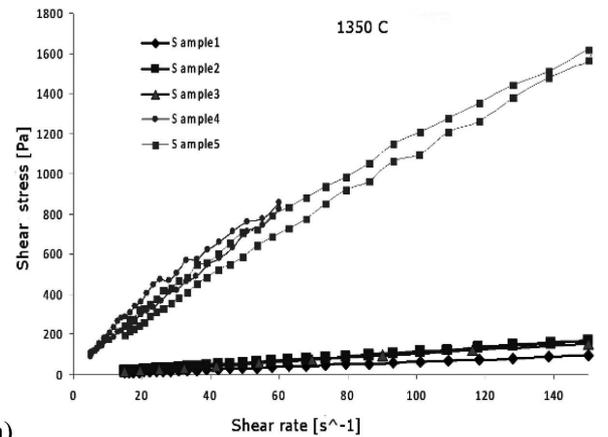


a)

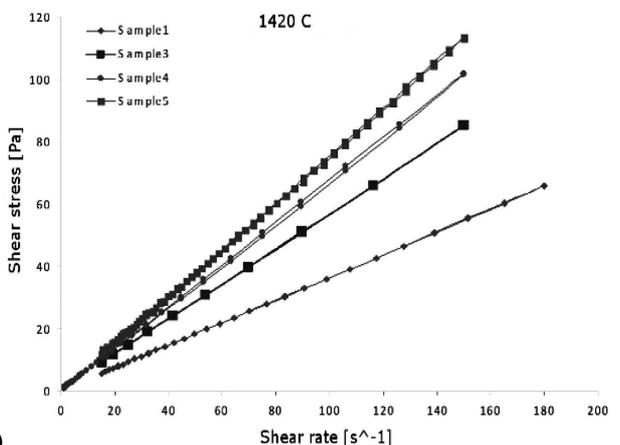


b)

Fig. 5. Flow curves in the temperature of 1310°C and 1330°C



a)



b)

Fig. 6. Flow curves in the temperature of 1350°C and 1420°C

By analysing the flow curves – their nonlinear character and the existence of a flow boundary - τ_o – one can conclude that the slag with solid elements does not show any similarity to the Newtonian fluids. One can suppose that it is a shear thinning fluid (with a viscous-elastic character). This phenomenon is typical of polymer solutions, suspensions of solid particles and others. Shear thinning can be treated as the result of the orientation of the dispersed polymer molecules or asymmetrical particles or as the result of immobilization of the part of liquid phase. For low shear rates the molecular attraction forces dominate over hydrodynamic ones and lead to the formation of structural aggregates. When the shear rate increases, however, the hydrodynamic forces (which are produced because of the flow area) become more significant. As a consequence, aggregates are gradually broken into smaller elements and the value of dynamic viscosity coefficient of the suspension falls.

The internal structure of the fluid determines the dynamic viscosity coefficient values and affects the rheological character of the analysed system. Applying the force results in transporting one of the layers of the fluid towards another. Longer chains or other structural units appear in the fluid. Their arrangement and depolymerisation make the measurement issues much more complicated.

Table 5 shows calculated theoretical values of the NBO/T and Q indices. It has been agreed that these variables characterise respectively the degree of polymerisation and depoly-

merisation of the liquid slag. Factor Q usually describes degree of polymerization of liquid slags and glasses. Author [23] presents the relation between factor Q and NBO. The paper presents the values for all slag samples in temperatures corresponding to solid-liquid and fully liquid systems. In the case of sample 1 in the temperature of 1350°C the system is fully liquid. For samples 2 and 3 the system becomes fully liquid in the temperature of 1310°C. Samples 4 and 5 reach that state in the temperature of 1350°C and 1390°C respectively. It can be assumed that the values of NBO/T and Q^n describe the structure of liquid slag systems, in this case the residual liquid phase in the system.

Frequently, the degree of polymerization is quantitatively characterized by structure-chemical parameter NBO/T (non-bridging oxygen per tetrahedral). This parameter is defined as the ratio of free oxygen ions to the total number of networking ions $NBO/T = (2O - 4T)/T$, where T is total number of networking ions and O is the number of oxygen ions in the system [24, 27].

$$\frac{NBO}{T} = \frac{\sum_{k=1} n_i X_i^{n+}}{X_T} \quad (14)$$

where:

M_i^{n+} – number of cations i modifying the network structure of the n^+ charge.

X_T – the number of ions in tetrahedral coordination.

TABLE 5

Analysis of the residual liquid phase in the system

N ^o sample	Temp	MgO	SiO ₂	CaO	Al ₂ O ₃	$Y_{NBO} = \sum_{k=1} n_i X_i^{n+}$	$X_T = T$	NBO/T	Q	
	[°C]	[%]								
1	1310	5.96	42.65	43.33	8.07	0.89194	0.50777	1.8	2.2	Q ²
	1320	6.05	42.64	43.74	7.57	0.91200	0.50068	1.8	2.2	Q ²
	1330	6.23	42.46	43.95	7.36	0.92483	0.49558	1.9	2.1	Q ²
	1340	6.23	42.29	44.17	7.13	0.93514	0.49167	1.9	2.1	Q ²
	1350	6.46	42.24	44.22	7.08	0.94111	0.48912	1.9	2.1	Q ²
2	1310	6.08	39.55	41.61	12.76	0.76681	0.54198	1.4	2.6	Q ³
3	1310	5.88	38.18	40.34	15.60	0.67645	0.56928	1.2	2.8	Q ³
4	1310	5.92	36.67	37.40	20.01	0.52018	0.61883	0.8	3.2	Q ³
	1320	5.81	36.37	37.47	20.35	0.51113	0.62106	0.8	3.2	Q ³
	1330	5.68	36.07	37.54	20.71	0.50100	0.62366	0.8	3.2	Q ³
	1340	5.56	35.75	37.62	21.07	0.49137	0.62604	0.8	3.2	Q ³
	1350	5.48	35.56	37.66	21.30	0.48479	0.62775	0.8	3.2	Q ³
5	1310	6.28	36.10	34.42	23.20	0.39391	0.66069	0.6	3.4	Q ³
	1320	6.14	35.78	34.57	23.52	0.38580	0.66253	0.6	3.4	Q ³
	1330	6.00	35.45	34.72	23.84	0.37751	0.66441	0.6	3.4	Q ³
	1340	5.85	35.12	34.87	24.16	0.36905	0.66633	0.6	3.4	Q ³
	1350	5.70	34.78	35.02	24.49	0.36040	0.66829	0.5	3.5	Q ³
	1360	5.55	34.44	35.18	24.83	0.35153	0.67030	0.5	3.5	Q ³
	1370	5.39	34.09	35.34	25.18	0.34247	0.67235	0.5	3.5	Q ³
	1380	5.24	33.73	35.50	25.53	0.33320	0.67445	0.5	3.5	Q ⁴
	1390	5.18	33.61	35.56	25.66	0.32986	0.67521	0.5	3.5	Q ⁴

Table 6 presents data concerning NBO/T and Q indices for two-component systems CaO-SiO₂ [21]. By comparing the obtained values from Table 5 to the results obtained by the authors [23] one can conclude that the obtained depolymerisation numbers (Q², Q³, Q⁴) of the residual liquid part of the system have similar values. These values seem to prove for example: that there is a chain, 3-dimensional and sheet structure, that anion complexes are formed in solid-liquid and liquid solutions of the analysed slag.

TABLE 6
Structural indices NBO/T, Q for different two-component systems [19]

		NBO/T	Q	
SiO ₄ ⁴⁻ (monomer)	2CaO.SiO ₂	4	0	BOF slag
Si ₂ O ₇ ⁶⁻ (polyhedral)	2CaO.2SiO ₂	3	1	Mould flux; billets; Q=1
Si ₂ O ₆ ⁴⁻ (chain)	CaO.SiO ₂	2	2	BF slag Q>2 Mould flux; Q=2.5
Si ₂ O ₅ ²⁻ (sheet)	CaO.SiO ₂	1	3	Glasses, Coal slags
Si ₂ O ₅ ²⁻ (3-dim)	SiO ₂	0	4	Glasses

In paper [23] the author presented a structural analysis of liquid alumina-silicate systems corresponding to the blast furnace slag, among others to the CaO-SiO₂-Al₂O₃ system. The author concludes that for the systems with the chemical composition corresponding to the blast furnace slag and the Al₂O₃ content up to 25%, the depolymerisation numbers are – 2, 3, 4. The aluminium oxide has the following property – depending on the chemical composition of the ionic solution in which it is present, it can form complex anions by substituting the Si⁴⁺ ion with the aluminium ion in the form of in Al³⁺ in the tetrahedral system or by behaving like an amphoteric oxide. In case of high temperatures (1823K) the values of the NBO/T index for the CaO-SiO₂-Al₂O₃ system (with the basicity of B₁-1.3) are predominantly at the level of 1 and 2. It can mean that the cross-linked silicate structure has an inclination for polymerisation if the content of Al₂O₃ admixture increases. If the Al₂O₃ concentration goes up by over 10%, the values of NBO/T are at the level of 3 and 4 – which can mean that depolymerisation of the structure takes place and that the aluminium oxide is a factor contributing to the modification of the cross-linked structure of the system [24]. The above mentioned observations are comparable to the results obtained in this paper.

As far as slag samples 1, 4 and 5 are concerned, one can notice that in the presented conditions the amount of solid phase in case of sample 4 (with constant value of Q=3) allows to obtain the highest shear stress values (Fig. 5a, 5b, 6a). This can mean that the obtained amount of solid phase in the system and the cross-linking influence of the Al₂O₃ admixture in the fluid remaining in the state of equilibrium with the solid elements result in obtaining the highest viscosity values (with $\dot{\gamma}$ – const) as well as in changes in character. In case of sample 5 lower shear stress values were obtained in the same exper-

imental conditions. The viscosity values were lower, which suggests that the increase in the Al₂O₃ concentration in the system affects not only the amount of solid elements (which increases) but also the modification of the internal structure of the residual fluid in the system. If one compares sample 4 and 5, one will notice that the amount of solid elements in the system increases but the shear stress values decrease. In case of sample 1 the amount of solid elements precipitated in the system increases, but the Al₂O₃ concentration in slag makes Al³⁺ behave like a factor modifying the structure of the fluid by decreasing the shear stress values. Despite the precipitation of the solid particles the solid-liquid system for sample 1 shows similarity to an ideally viscous Newtonian body.

5. Conclusions and observations

On the basis of the conducted research and calculations the following conclusions can be made:

- In case of the slag system CaO-SiO₂-MgO-Al₂O₃ in a fully liquid state, in the temperature of 1400°C the analysed liquid ionic solutions resemble ideal Newtonian fluid [17, 23],
- In the analysed systems with solid particles the character of the fluid changes – it is no longer a Newtonian fluid but a shear thinning one (pseudoplastic) [19,20] and increase $\dot{\gamma}$ – shear rate influences the value of the dynamic viscosity coefficient. The calculations and measurements show that a particle content of approx. 11% changes the character of fluid from a Newtonian one to a shear thinning fluid [21].
- Calculating the value of factor *F* (which characterizes the shape of solid elements in the network of chain complex anions) showed how important this factor is from the point of view of not only the viscosity changes but also the rheological character of the fluid. The type and amount of solid elements in the system and the type of complex anion networks (in a fully liquid system as well as in the liquid residual part in the solid-liquid one) is an important subject from the point of view of the changes in viscosity and the rheological character of the fluid. In case of solid-liquid slag systems it seems that the verification of the Einstein-Roscoe model is necessary.
- Adding Al₂O₃ to the slag systems causes the amount of solid particles to increase in higher temperatures. It also leads to the polymerization of the viscous part of the residual liquid for the Al₂O₃ concentration at the level of 21,29% and then alternately depolymerisation for the Al₂O₃ concentration at the level of 25.65%. The slag system changes its character from Newtonian to pseudoplastic.

The issues concerning the internal structure of highly polymerised slag systems containing solid elements (as presented above) still remain to be studied. So does the influence of the applied shear stress on such a system as it leads to changes in the dynamic viscosity coefficient and possible changes in the rheological character of the fluid. The following stages of research will concentrate on verifying the influence of the shape of solid elements and other concentrations in the

system on the rheological character and the viscosity coefficient value of slag.

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REFERENCES

- [1] Y. Sasaki, H. Urata, M. Iguchi, M. Hino, Stress Relaxation Behavior with Molten CaO–SiO₂–Al₂O₃ Slag, *ISIJ International* **46**, 3, 385-387 (2006).
- [2] M.T. Balhoff, K.E. Thompson, Modeling the Steady Flow of Yield-Stress Fluids in Packed Beds **50**, 12 *AIChE Journal*, 3034-3048 December 2004.
- [3] K. Sunahara, K. Nakano, M. Hoshi, T. Inada, S. Komatsu, T. Yamamoto, Effect Of High Al₂O₃ Slag On The Blast Furnace Operations, *ISIJ International* **48**, 4, 420-429 (2008).
- [4] S. Seetharaman, K. Mukai, Du Sichen, Viscosity of slags – an overview, *Steel Research International* **76**, 4, 267-278 (2005).
- [5] S. Seok, S. Jung, Y. Lee, D. Min, Viscosity of highly basic slags, *ISIJ Int.* **47**, 8, 1090-1096 (2007).
- [6] N.N. Viswanathan, F-Z. Ji, Du Sichen, S. Seetharaman, Viscosity Measurements on Some Fayalite Slags, *ISIJ International* **41**, 7, 722-727 (2001).
- [7] A. Shankar, M. Görnerup, A.K. Lahiri, S. Seetharaman, Experimental Investigation of the Viscosities in CaO–SiO₂–MgO–Al₂O₃ and CaO–SiO₂–MgO–Al₂O₃–TiO₂ Slags, *Metallurgical And Materials Transactions B* **38B**, 12, 911 (2007).
- [8] A. Kondratiev, B. Zhao, S. Raghunath, P.C. Hayes, E. Jak, New tools for viscosity measurement and modeling of fully liquid and partly crystallised slags, *Proceedings of EMC 2007*.
- [9] S. Wright, L. Zhang, S. Sun, S. Jahanshahi, Viscosity of a CaO–MgO–Al₂O₃–SiO₂ Melt Containing Spinel Particles at 1646K, *Metallurgical And Materials Transactions B* **31B**, 2, 97-104 (2000).
- [10] J. Ferguson, Z. Kębłowski, *Reologia stosowana płynów*, Wydawnictwo MARCUS, Łódź 1995.
- [11] A. Kondratiev, P.C. Hayes, E. Jak, Development of a Quasi-chemical Viscosity Model for Fully Liquid Slags in the Al₂O₃–CaO–‘FeO’–MgO–SiO₂ System. Part 1. Description of the Model and Its Application to the MgO, MgO–SiO₂, Al₂O₃–MgO and CaO–MgO Sub-systems, *ISIJ International* **46**, 3, 359-367 (2006).
- [12] A. Kondratiev, P.C. Hayes, E. Jak, Development of a Quasi-chemical Viscosity Model for Fully Liquid Slags in the Al₂O₃–CaO–‘FeO’–MgO–SiO₂ System. Part 2. A Review of the Experimental Data and the Model Predictions for the Al₂O₃–CaO–MgO, CaO–MgO–SiO₂ and Al₂O₃–MgO–SiO₂ Systems, *ISIJ International* **46**, 3, 368-374 (2006).
- [13] A. Kondratiev, P.C. Hayes, E. Jak, Development of a Quasi-chemical Viscosity Model for Fully Liquid Slags in the Al₂O₃–CaO–‘FeO’–MgO–SiO₂ System. Part 3. Summary of the Model Predictions for the Al₂O₃–CaO–MgO–SiO₂ System and Its Sub-systems, *ISIJ International* **46**, 3, 375-384 (2006).
- [14] A. Kondratiev, P.C. Hayes, E. Jak, Development of a Quasi-chemical Viscosity Model for Fully Liquid Slags in the Al₂O₃–CaO–‘FeO’–MgO–SiO₂ System. The Experimental Data for the ‘FeO’–MgO–SiO₂, CaO–‘FeO’–MgO–SiO₂ and Al₂O₃–CaO–‘FeO’–MgO–SiO₂ Systems at Iron Saturation, *ISIJ International* **48**, 1, 7-16 (2008).
- [15] A. Kondratiev, E. Jak, Review of Experimental Data and Modeling of the Viscosities of Fully Liquid Slags in the Al₂O₃–CaO–‘FeO’–SiO₂ System, *Metallurgical And Materials Transactions B* **32b**, 1015, December 2001.
- [16] K.C. Mills, S. Sridhar, *Ironmaking & Steelmaking* **26**, 262-268 (1999).
- [17] D. He, N.N. Ekeré, Structure Simulation of Concentrated Suspensions of Hard Spherical Particles, *AIChE Journal* **47**, 1, 53-59, January 2001.
- [18] G. Handfield, G.G. Charette, Viscosity and structure of industrial high TiO₂ slags. *Canadian Metallurgical Quarterly* **10**, 3 (1971).
- [19] P. Migas, M. Korolczuk-Hejnak, M. Karbowniczek, Rheological characteristic of liquid iron solutions and co-occurring slags, *Hutnik. Wiadomości Hutnicze*, 4, 196-202, April 2012.
- [20] R. Przyłucki, S. Gólak, B. Oleksiak, L. Błacha, Influence of an induction furnace’s electric parameters on mass transfer velocity in the liquid phase, *Metalurgija* **52**, 1, 67-70 (2012).
- [21] M. Korolczuk-Hejnak, P. Migas, Analysis of selected liquid steel viscosity, *Archives of Metallurgy and Materials* **57**, 4, 963-969.
- [22] M. Korolczuk-Hejnak, P. Migas, Selected Grades Of Steel As Rheologically Defined Liquid Bodies, *Archives Of Metallurgy and Materials* **57**, 2, 583-591 (2012).
- [23] A.R. Boccaccini, S. Riaz, C. Moisescu, On the viscosity of glass-crystal systems. *Journal Of Materials Science LETTERS* **20**, 1803-1805 (2001).
- [24] K. Mills, The estimation of slag properties, Department of Materials, Imperial College, London, UK, Short course presented as part of Southern African Pyrometallurgy 2011.
- [25] I. Sohn, D.J. Min, A reviewer of the relationship between viscosity and the structure of calcium-silicate based slags in ironmaking, *Steel Research International* **83**, 7, 611-630.
- [26] M. Korolczuk-Hejnak, P. Migas, Selected Grades Of Steel As Rheologically Defined Liquid Bodies, *Archives of Metallurgy and Materials* **57**, 2, 583-591.
- [27] R.G. Kuryeva, Influence of Pressure on the Refractive Index and Relative Density of Glasses in the CaO–Al₂O₃–SiO₂ System, *Glass Physics and Chemistry* **34**, 1, 37-41 (2008).