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## ANALYSIS OF THE RHEOLOGICAL BEHAVIOUR OF SELECTED SEMI-SOLID SLAG SYSTEMS IN BLAST FURNACE FLOW CONDITIONS

## ANALIZA CHARAKTERU REOLOGICZNEGO WYBRANYCH STAŁO-CIEKŁYCH UKŁADÓW ŻUŻLOWYCH W WARUNKACH PRZEPŁYWU W WIELKIM PIECU

The rheological properties of liquid and semi-solid systems of slag and hot metal in a blast furnace are extremely important from the perspective of their dripping in the unit. The rheological nature and the values of the dynamic viscosity coefficient of liquid and semi-solid phases – slag and hot metal – determine the permeability of the zones in which those systems exist. The modelling of dripping processes and e.g. static and dynamic holding/retention of liquid in the bed, requires an accurate description of the rheological behaviour of slag and iron systems. Determining the liquid flow through the lump bed of the blast furnace is based on the assumption that liquids in the unit in the whole range of their occurrence are similar to a Newtonian ideal liquid. This study presents an analysis of the findings of high-temperature rheometric measurements of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO systems, liquid, semi-solid slags of the blast furnace type doped with TiO<sub>2</sub> and solids in the form of TiN. The tests were performed within a temperature range of 1310-1490°C. Also measurement results for glycerol solutions with concentrations of 86% and 100% at the ambient temperature, simulating blast furnace slags with various contents of solids – PC, anthracite – are presented.

*Keywords:* liquid slag viscosity, rheology, dripping zone, non-Newtonian flow

Właściwości reologiczne ciekłych i stałych-ciekłych systemów żużla i surówki w wielkim piecu mają diametralne znaczenie z punktu widzenia ich ściekania w agregacie. Charakter reologiczny, oraz wartości współczynnika lepkości dynamicznej ciekłych i stało-ciekłych faz: żużla i surówki determinują przewodność stref, w których systemy te występują. Modelowanie procesów ściekania oraz np. zatrzymanie/retencji cieczy w złożu, statyczne i dynamiczne, wymaga dokładnego opisanie zachowań reologicznych systemów żużla i surówki. Określenie przepływu cieczy przez złożo kawałkowe wielkiego pieca oparte jest na założeniu, że ciecze w agregacie w całym zakresie występowania, wykazują podobieństwo do cieczy doskonałej Newtona. W pracy zaprezentowano analizę wyników wysokotemperaturowych pomiarów reometrycznych układów CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO, ciekłych, stało-ciekłych żużli typu wielkopieczowego domieszkowanych TiO<sub>2</sub> oraz stałymi elementami w postaci TiN. Badania były wykonywane w zakresie temp. 1310-1490°C. Zaprezentowano także wyniki pomiarów dla roztworów gliceryny o stężeniu 86% i 100%, w temperaturze otoczenia, symulującej żużle wielkopieczowe z udziałem różnych zawartości stałych elementów: PCI, antracytu.

### 1. Introduction

Despite considerable research on slag system viscosity, the data available in the literature [1-23] is still too fragmentary and incomplete for us to be able to understand the structure and to anticipate the behaviour of the liquid and semi-solid silicate systems of the slags occurring in the metallurgical processes. For complex slag systems often experimental data is only available at selected temperatures and for a narrow range of concentrations. The authors [1] measured the viscosity coefficient of blast furnace slags doped with solids – spinel (MgAl<sub>2</sub>O<sub>4</sub>). The slag system analysed was in the form of 28CaO-10MgO-20Al<sub>2</sub>O<sub>3</sub>-42SiO<sub>2</sub> at a temperature of 1646K. The solid particle sizes were in three ranges: 0.10-0.21 mm, 0.21-0.44 mm, 0.44-0.99 mm. The slag com-

position was so selected that the slag was saturated with spinel at the measurement temperature, i.e. 1646K. In general, the shear rates analysed for low levels of solids (under 10%) were between 0.5 and 3s<sup>-1</sup>, whereas for high contents of solids they were from 0.3 to 1s<sup>-1</sup>. It was found that for a concentration of solids exceeding 8%, the slag-solid system analysed showed Bingham type behaviour. The shear stresses increased linearly as the shear rate increased; but at the zero shear rate the residual shear stress remained, which characterised the occurrence of the flow limit (up to 3Pa depending on the quantity and size of solid phase). The shear rate ranges applied in the study [1] correspond to the values of shear rate for a liquid-slag freely dripping in the coke bed.

The authors [1] made rheometric measurements for the case of very low shear rate values. However, the issue of the

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high values of shear rates still remains open – the effect of the mechanical impact of the reducing gas on liquids in the counterflow dripping in the lump bed. Additionally the possibilities for a change of their flow nature as a result of the impact of gas shear forces on liquids remain open.

The literature contains many published measurement results of the dynamic viscosity of metallurgical slags concerning fully liquid systems [3-8]. Scientists analyse the effect of the chemical composition, basicity and temperature on viscosity. Few research centres [1,10,11] have tackled such a complex subject of analysis, i.e. changes in the dynamic viscosity coefficient as a rheological characteristic of multicomponent liquid or semi-solid slag systems.

The rheological identification of a liquid is based on the general classification of liquids into Newtonian (ideally viscous) liquids – showing a linear dependence of the shear stress on the shear rate, and non-Newtonian liquids – showing non-linearity of the shear stress during changes in the shear rate. Newtonian liquids are characterised by a constant viscosity during a flow, independence of the shear rate and repeatability of the viscosity value during subsequent identical flows.

In recent years many models for determining the aluminosilicate slag viscosity have been formulated and developed, including Urbain, KTH, Iida, QCV [2,4-7].

The slag viscosity ( $\eta$ ) depends considerably on the temperature and structure of the liquid [3,8]. It is a measure of the flowability of slags when a shear stress is applied. It is assumed that most slags and metallic liquids show Newtonian type liquid properties, where the viscosity is independent of the shear rate [9].

Liquid slags are built of, among others, discontinuous ionic structures; their activation energy is related to the type of ions and ionic complexes present in the system – as well as the interionic forces. As the type and size of ions change with the temperature, so does the activation energy.

To describe viscosity of slags containing a dispersed solid phase, the Einstein-Roscoe equation 1 is most often used. The following equation may be used to estimate viscosity of partially crystallised slags, containing up to 30% of the solid fraction within the system volume [12-13]:

$$\eta_S = \eta_L(1 - R\Phi_S)^{-n} \quad (1)$$

where:  $\eta_S$  and  $\eta_L$  are the apparent viscosity of the suspension and the viscosity of the fully liquid phase respectively,  $\Phi_S$  is the volumetric fraction of the solid phase. For equal size spherical particles, the constants  $R$  and  $n$  in the equation are 1.35 and 2.5 respectively. The inverse of the "R" value has a physical meaning of the maximum amount of the solid phase that can be accommodated by the liquid before the viscosity has reached an infinitely large value. The equation was derived assuming a uniform distribution of dispersed particles in the liquid.

In order to verify Einstein-Roscoe equation 1, A. Kondratiev et al. [12] tested four various, partially crystallised, tri-component slag systems of  $\text{Al}_2\text{O}_3$ -FeO-SiO<sub>2</sub>, also during cooling from 1773 to 1633K and heating from 1633 to 1723K. During a continuous measurement of the torque value changing with the temperature, a rapid increase in viscosity was

observed at a temperature of 1668K. Then the process of solid phase precipitation from the slag begins. The parameters adjusted to the model are  $R=1.29$  and  $n=2.04$ , and are comparable with the Roscoe model values. Slag systems with small contents of solids retain their Newtonian nature. For some cases – over 30% vol., others find that only 10% volumetric share of solids is sufficient to change the flow nature, and in some cases as much as 40% vol. is needed. Not only the quantity, but also the size and shape of the solid particles in the slag system will influence the change in its rheological nature [12].

Viscosity as a measure of viscous flow resistance depends largely on the mobility of the "components" contained in the liquid, such as atoms, molecules, ions or solid particles, which reflect respectively: bond, size and configuration of the liquid "components". In such a system a strong relationship between the measured viscosity and the structure occurs. Slags are partially polymeric substances and some of their properties (e.g. viscosity, density, electric and thermal conductivity) considerably depend on their internal structure.

The rheological parameters occurring in actual metallurgical processes are very difficult to measure, such as the dynamics of reducing gas impact on the liquid slag and the hot metal in the coke bed within the blast furnace, during their flow down counterflow with the gas.

It is universally assumed that the wholly liquid slag, freely dripping under the influence of the gravity force, will not change its viscosity under the influence of the force applied as it is a Newtonian liquid. The following will influence the slag viscosity – temperature, pressure and chemistry, but also the content of solids in the system [13]. They can originate from precipitation when the temperature decreases, or result from chemical reactions (carbides, nitrides insoluble in slag), or from penetrating into the slag from the outside e.g. unburned pulverised coal.

A. Shankar et al. [11] conducted tests of the dynamic viscosity coefficient, taking into account changes in the spindle rotational speed (five speeds 4 to 80 rpm) for the following slag systems: CaO-SiO<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub> and CaO-SiO<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> within a basicity range of 0.72-1.23 and within a temperature range from 1650 to 1873K. Due to an increase in the viscosity, it was concluded that solid particles were present in the system (at a temperature over 1673K), however their quantity was not determined. The authors [12] advanced a thesis that the viscosity depended largely on the quantity and size of the solid particles and complex ions present in the system. Also the degree of slag polymerisation, which depends on the silica activity, or possible Si-O-Si bonds and free O<sup>2-</sup> ions, also influences the viscosity. According to the authors [11], the coefficient of dynamic viscosity of slag is not affected by changes in the rotational speed of the rotary member [12].

Seok S., Jung S., Lee Y., Min D. [10] tested the viscosity of CaO-8%MgO-FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> in a dispersed semi-solid system saturated with 2CaO-SiO<sub>2</sub> – dicalcium silicate – within a temperature range of 1673-1873K. They measured viscosity at a temperature of 1873K for three various rotational speeds of the spindle (30, 60 and 100 rpm) and found that the viscosity results did not depend on the rotational speed.

In metallurgical processes, where also liquid phases – slag and metal – occur, viscosity is amongst the basic physi-

cal properties identifying liquids during their motion under the influence of forces. Therefore this property is a key parameter in existing and currently formulated mathematical models. It directly influences the kinetics of reactions occurring between the liquid metal and the slag, as well as the effect of the flow of these phases in metallurgical units. The dynamic viscosity of the liquid slag and iron is amongst the basic indicators participating in the analysis of permeability of the coke bed in the blast furnace and its static and dynamic holdup [14-16].

Many authors dealing with the modelling of effects in the dripping zone identify [14-15] the area of liquid products and their dripping as shown in Figure 1a and 1b.

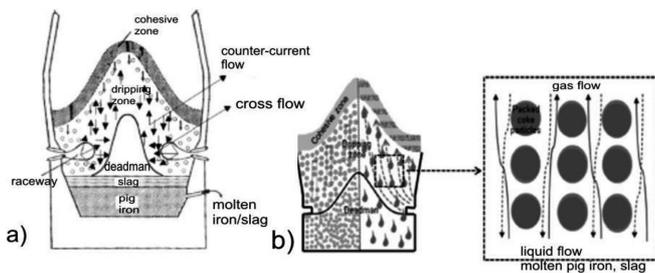


Fig. 1. Blast furnace dripping and cohesive zones [14,15]

Liquid slag systems in some areas of the blast furnace are not fully homogeneous. This results, among others, from their thermodynamic conditions, e.g. a change in the chemical composition, temperature decrease (e.g. dead-man, furnace walls zones), and also from reduction reactions occurring in specific conditions, in the case of various processes applied in this unit, e.g. reduction of ilmenite ores containing  $TiO_2$  [21]. When pulverised coal is injected, it often burns incompletely in the furnace, and escapes counterflow to the liquid in the coke bed. Examples of simulations of the effect of accumulation of the escaping unburned pulverised coal – PC on the change in the coke bed porosity are also presented in studies [17,18].

From the perspective of accumulation of unburned coal particles, based on the literature data [18], the static layer in the coke bed is the simulation area that has been divided into four zones (Figure 2a) depending on local porosities: the combustion zone (porosity –  $\epsilon_0 - 1.0$ ), the dead-man zone ( $\epsilon_1 - 0.25$ ), the dripping zone ( $\epsilon_2 - 0.5$ ) and the cohesion zone ( $\epsilon_3 - 0.4$ ). The porosity of the modelled areas varies from 0.25 to 1.0. The change in porosity in the aforesaid zones may be treated as a change in the shearing gap in rheometric measurements.

Figure 2b presents trajectories/paths of pulverised coal solid particle flow in the combustion chamber and in the coke bed. The results of the simulation of powder coal movement show that unburned powder movement coincides with the gas flow, these movements have different flow "trajectories" as shown in Figure 2b [18]. The unburned coal powder, accumulating in the bed, changes the bed properties by settling on coke lumps, and also by getting into the liquid slag and metallic phase and co-reacting with them.

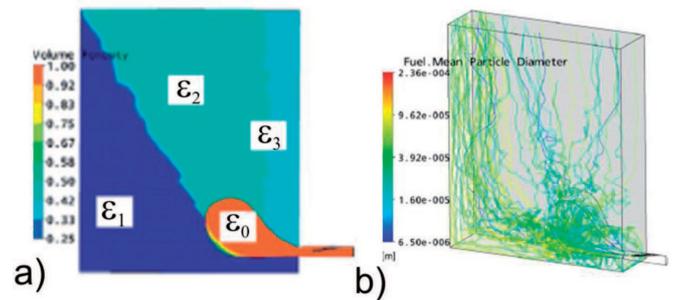


Fig. 2. Solid particles PC trajectories and porosity of the coke bed [18]

## 2. Experimental approaches

This study makes an attempt at rheological identification of the slag systems analysed and liquids simulating liquid slag in cold models, from the perspective of their behaviour in conditions of theoretical flows similar to shearing in the blast furnace lump bed. The rheological nature of liquid slag should be defined not only on the basis of changes in the chemical composition and temperature, but also by rheological parameters such as:  $t$  – time of force impact on the system,  $\tau$  – shear stress,  $\gamma$  – shear rate.

For various rheological gaps (cup/bob), depending on the critical value of the shear rate, the flow changes its nature from the laminar flow to the turbulent flow. These changes result from the limitation of measuring/testing capabilities of the dynamic viscosity coefficient for the system tested and the physical properties of the liquid tested (density, dynamic viscosity), as well as its structure and behaviour under the influence of shear stress.

Table 1 compares the rotational speeds of the spindle and the corresponding linear velocities of the gas flowing through the coke bed (for the 0,4 and 25m/s – appropriately column

TABLE 1

Calculated values for different measuring systems for linear velocities, shear rate and rotational speed of the spindle

Bobs diameter [mm]	Shearing gap bob/crucible [mm]	N° 1) Speed N [rpm]	Shear rate - $\gamma^*$ [s <sup>-1</sup> ]	N° 2) Speed N [rpm]	Shear rate - $\gamma^*$ [s <sup>-1</sup> ]	N° 3) Speed N [rpm]	Shear rate - $\gamma^*$ [s <sup>-1</sup> ]	Equipment max possible linear velocity of liquid system at the max. rotation speed for 3000 rpm [m/s]
11	9.5	70	9.8	44000	6164	690	96.7	1.73
15	7.5	55	9.6	33000	5758	510	88.9	2.36
16	7.0	50	8.72	30000	5235	480	83.8	2.51
27	1.5	25	22.3	18000	16043	300	267.4	4.24

with N<sup>o</sup> 1) and 3) in Table 1) and the assumed values of the linear velocity of dripping products (at the range 0,04m/s – column with N<sup>o</sup> 2) in Table 1) of processes in the dripping zone [14-16].

The equations responsible for calculations of changes in the shear rate critical value for a change in the flow nature for a specific density and rheological gap are presented in paper [20]. Results of shear rate critical for specific values of examples of countercurrent linear velocity of gas flow through the coke bed are presented in Table 1.

Based on the values obtained in Table 1, it seems impossible to obtain shear rates using the present equipment (with its design limitations) equivalent to those of gas impacting the liquid slags and hot metal in the dripping zone of the blast furnace. At present, the FRS1600 rheometer allows us to test the broadest range of changes in the measuring parameters of the group of equipment of this type. Additionally, changes in the physical properties (density, viscosity) of the tested liquid and semi-solid systems occurring in the process also influence the determination of the critical value of the shear rate for the specific case.

The capabilities of the FRS1600 device provide us with the opportunity to examine changes in the dynamic viscosity coefficient of liquids (hot metal, slag) during free dripping in the coke bed, corresponding to a laminar flow. However, the issue of the shearing impact of the gas on liquids moving in the opposite direction with exactly the same speed as in the actual process is still open to question.

Blast furnace slags also change their density when dripping between coke lumps; from very high for primary slags (FeO approx. 30%) – just under the cohesion zone, to lower values for final slags (Fe<1%) – in the hearth. Therefore, the change in chemical composition alters the dynamic viscosity coefficient, whilst the nature of the flow also changes within the same gas flow parameters, e.g. velocity, pressure in the coke bed.

When coke bed moves down the furnace, the coke particle sizes decrease as a result of the conditions prevailing over its entire path. An alteration in the free spaces between coke particles may be interpreted as a change of the shearing gap in rheometric measurements. This change affects the shear rate critical value for both specific experiment conditions and the measurement system. The shear rate critical value is responsible for the transition of the sheared system from a laminar flow into a different kind of flow.

An analysis of flows in the coke bed for blast furnace conditions is difficult from the perspective of numerical modelling and experimental research. At the moment, no high temperature models for examination of such effects exist. However, cold models are often created. These aim to describe the flow of pig iron and slag in the coke bed counterflow to the reducing gas [14-16].

Glycerol solutions are often used by researchers [14-16] in cold modelling. They model slag flowing through a packed coke bed and are applied alongside water solutions to model behaviour in the slag and pig iron dripping zone. Glycerol solutions were also chosen for rheometric tests. The crosslinking of the glycerol's internal structure may be compared with polymerised silicate liquids, such as silicate blast furnace slags.

Table 2 presents the chemical properties of liquids and solutions used in the cold modelling of flows in the coke bed. As can be seen, 80% glycerol solution (with a slightly lower dynamic viscosity coefficient [16]) is used in tests of liquid retention in the lump bed.

TABLE 2  
Liquids applied for physical modelling of flows in the coke bed [16]

Liquid	Concentration (wt%)	Density (kg/m <sup>3</sup> )	Viscosity* (Ns/m <sup>2</sup> )	Surface tension (N/m)
Water	–	1000	0.0010	0.0732
Aqueous solution of ethanol	96**	807	0.0016	0.0240
Aqueous solution of glycerol	80	1210	0.064	0.0652
Aqueous solution of CaCl <sub>2</sub>	35	1350	0.0059	0.0888
Aqueous solution of ZnCl <sub>2</sub>	75	1920	0.034	0.0809

\* Nominal value, \*\* Azeotrope

In this study, 86% and 100% glycerol solutions were used in order to obtain a broad range of changes in dynamic viscosity coefficient [22].

Table 3 presents a description of the content of solids for the systems in liquid glycerol solutions that were subjected to rheometric tests.

TABLE 3  
Liquid solutions and systems – concentration of fine particles

No sample	Type and $\varphi$ of fines	vol. fraction $\Phi$	No sample	Type and $\varphi$ of fines	vol. fraction $\Phi$
1	-	86%	15	-	100%
2	anthracite <90 $\mu$ m	0.05	16	anthracite <90 $\mu$ m	0.05
3		0.1	17		0.1
4		0.15	18		0.15
5		0.2	19		0.3
6		0.3			
7		0.5			
8	PC <100 $\mu$ m	0.05	20	PC<100 $\mu$ m	0.05
9		0.1	21		0.1
10		0.15	22		0.15
11		0.2	23		0.25
12		0.25	24		0.3
13		0.3			
14		0.5			

In low-temperature tests, two types of solids were used and their content in the system varied from 0.05 to 0.5 volumetric fraction.

Table 4 presents measurement diagrams used in high-temperature rheological measurements and at the ambient temperature. The tests were performed on a system with a perforated cylinder with a diameter of 16 mm.

TABLE 4  
Schema of measurements, particularly steps for “cold” experiments

Step	Shear rate - $\gamma \cdot [s^{-1}]$
1	20
2	30
3	log 20-50
4	log 50-20
5	5
6	150
7	5
8	150
9	0 - stop
10	2
11	8,725
12	200 or 150

Table 5 shows a comparison of the calculated values of the rotational speed and the shear rate of a specific spindle diameter – 16 mm, for a shear gap at a level of 7 mm. All experiments were conducted using this measuring system. Linear velocity ranges for freely dripping process products (slag, hot metal) are also presented at a level of 0.04 m/s or above. Values at this level are assumed for cold modelling of the liquid flow in the furnace dripping zone. The high values of the shear rates considerably exceed those that correspond to free dripping. Although they are not limit values for the velocity of gas flowing through the lump coke bed in the actual process, they do significantly expand the scope of rheometric examinations for blast furnace slags described above. The applied shear rates define the ranges of linear velocities of gas applied in cold modelling, e.g. 0.4 m/s [15]; in this case, it varied between 0.023 and 0.963 m/s.

TABLE 5  
Share rate and velocity levels for experiments performed

Bob diameter [mm]	Speed – N [rpm]	Shear rate – $\gamma [s^{-1}]$	Linear velocity – V [m/s]
16	27	5	0,023
	50	8,72	0,042
	287	50	0,24
	860	150	0,72
	1146	200	0,963

Figure 3 presents a comparison of the values of the dynamic viscosity coefficient of a blast furnace slag substitute with 86% and 100% glycerol solutions.

Figure 3 presents changes in the dynamic viscosity coefficient as a function of shear rate for the basic blast furnace slag within a temperature range of 1340-1500°C with 86% and 100% glycerol solutions in an ambient temperature range of 25-30°C. All the obtained values of the slag dynamic viscosity coefficient are within the range of values represented by the

glycerol solutions. The variability of the parameter values remained consistent across the entire range until the slag began intensively transforming into its solid state – increasing the dynamic viscosity coefficient values within the temperature range of 1370-1340°C. This effect is shown in Figure 4 as an increase in the value of the viscosity coefficient. This may indicate the precipitation of solid crystals in the system, but it could also mark an intensive change in the network/ structure of the liquid residual in the system. Changes in the value of the slag viscosity coefficient of a standard CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO system are at Figure 5 and its chemical composition are presented in Table 6 (for basic slag).

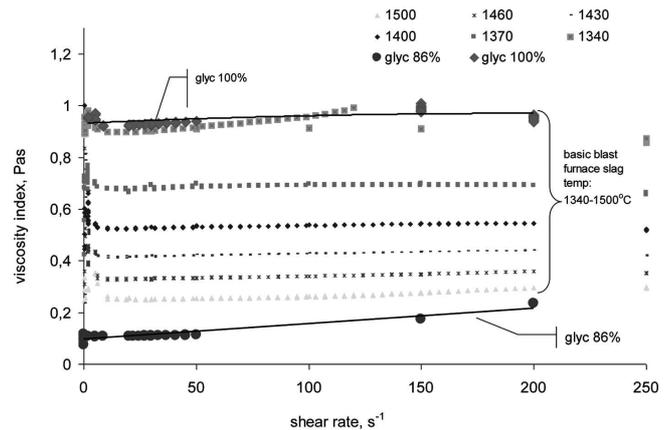


Fig. 3. Viscosity curves for basic blast furnace slag and glycerol solutions

Figure 4 presents the flow curves for various tested and analysed liquid systems of slags and glycerols.

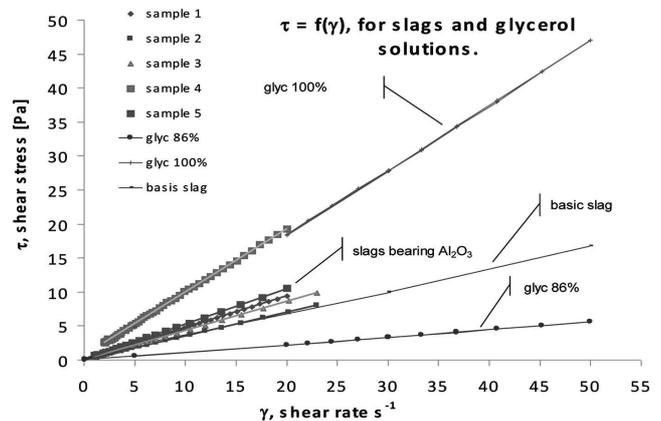


Fig. 4. Flow curves for various rheological liquids

Flow curves for samples of blast furnace slag substitutes doped with Al<sub>2</sub>O<sub>3</sub> described in the paper [13] and “standard” hearth slag used in the blast furnace, as well as flow curves for pure 86% and 100% glycerol solutions can be observed here. The results relate to rheometric tests for slags with Al<sub>2</sub>O<sub>3</sub> (samples 1-5) at a temperature of 1450°C and at a temperature of 1460°C for the basic slag. The glycerol solutions were examined at an ambient temperature of 25-30°C. All results were obtained within a shear rate range of up to 50s<sup>-1</sup>. The shear rates correspond to the free dripping of slag in the coke bed for the so-called static suspension of the burden without gas flowing through the bed. It can be seen that in these shear

rate ranges, all the systems behave like liquids similar to Newtonian ideal bodies; meaning their viscosities do not depend on shear rates and that for the specific minimum values  $\gamma$ , they do not show a flow limit. The possibility of them being Bingham bodies can be ruled out within these ranges of  $\gamma$ . Apart from the blast furnace process itself, other metallurgical processes, such as sintering, foaming slag in EAF [23,24], hot metal or steel refining and desulphurisation processes, are also important in the rheology of liquid and semi-liquid systems.

In low temperature tests, an anthracite fraction of up to  $90\mu\text{m}$  and pulverised coal – PC – which is applied in industrial conditions in the blast furnace, were used. Figure 5 presents pictures from a scanning microscope (SEM) of solid particles added to the glycerol liquid system.

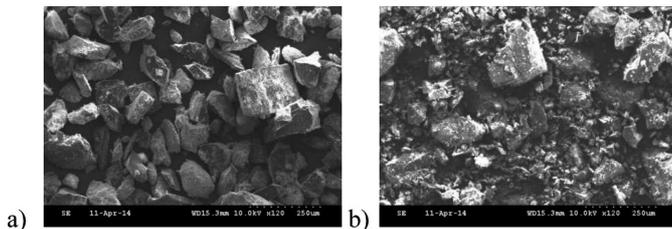


Fig. 5. Solid fine particles for “cold” experiments a) anthracite  $<90\mu\text{m}$ , magnification x120, b) pulverised coal – PC, magnification x120

The applied measurement programmes presented in Table 6 were the same as for tests of semi-solid systems with glycerol solutions. The shear rate values varied within broad limits corresponding to possible shear rates occurring in the blast furnace for liquids and gas.

Picture/photo 6a and 6b present images of the size and shape of solid, synthetic TiN particles used in the tests with slags of the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO system. The chemical composition of the examined slags is presented in Table 7.

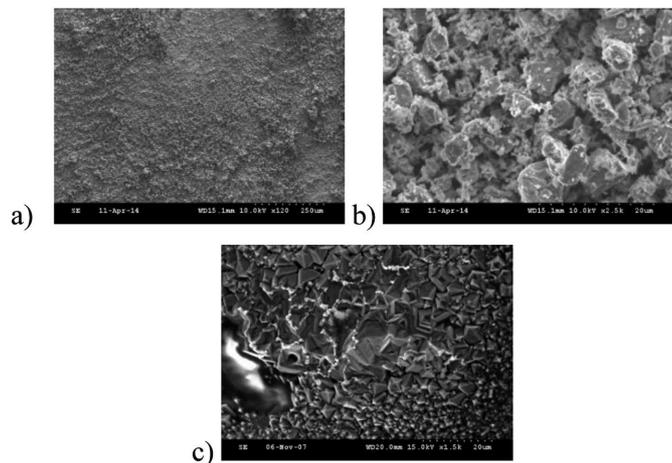


Fig. 6. Solid fine particles for high temp experiments: slags-TiN; a) TiN, magnification x120, b) TiN, magnification x2,5k c) Ti(C,N) in slag, magnification x1,2k

Slag systems doped with solids in the form of titanium compounds were also examined – Fig. 6a and 6b. These compounds may occur under particular process conditions – when adding rutile to the process. Due to the similarity of the shape of the solids used, the effect on the rheological behaviour of

the systems was not examined. Figure 6c presents precipitated inclusions resulting from the reduction of TiO<sub>2</sub> with carbon in the slag system. Table 6 presents the chemical composition of slags doped with TiN.

TABLE 6  
Chemical compositions of blast furnace slags doped with TiN

	Sample description	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiN
		%				
1	Basic slag	43.71	7.97	8.50	39.10	0.00
5	TiN ( <i>min</i> 5,81%TiO <sub>2</sub> )	41.28	6.89	7.52	36.99	3.44
6	TiN ( <i>max</i> 5,81%TiO <sub>2</sub> )	40.99	6.85	7.46	36.70	4.14
7	TiN ( <i>min</i> 29,73%TiO <sub>2</sub> )	34.65	6.53	7.55	30.45	17.67
8	TiN ( <i>max</i> 29,73%TiO <sub>2</sub> )	32.64	6.49	7.47	28.87	21.58
10	TiN ( <i>max</i> 1,45%TiO <sub>2</sub> )	42.96	6.83	7.89	38.25	0.78
11	TiN ( <i>max</i> 2,81%TiO <sub>2</sub> )	42.65	6.96	7.80	38.24	1.67

Figure 6c presents a (SEM) picture of the solid components of titanium compounds precipitated from the liquid system, formed as a result of TiO<sub>2</sub> reduction with the carbon contained in the crucible walls. These solid precipitations were identified in the slag matrix. The comparable size of solid particles can also be observed. Their shapes are irregular and they slightly differ from each other.

Figure 7 presents flow curves for the blast furnace slag doped with solid particles of synthetic TiN. The tests were performed within a temperature range of 1340-1500°C with a TiN content of 1.67%. This value was calculated using the FactSage thermodynamic database for reduction to the equilibrium state for the corresponding TiO<sub>2</sub> content of 2.81%.

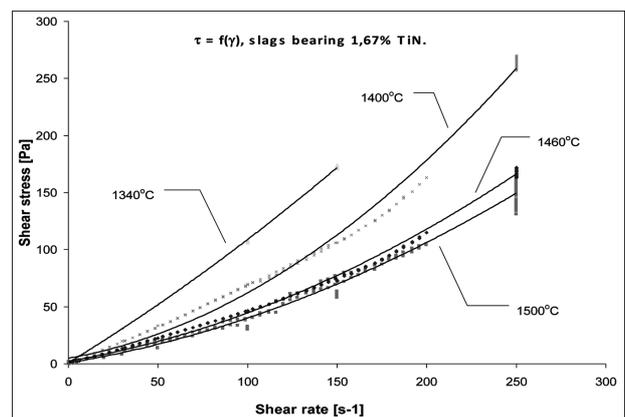


Fig. 7. Flow curves for slags bearing solid particles – TiN

The test results for samples of slags doped with TiN were presented in paper [13]. A slight deviation from rectilinearity can be observed with an increase in the shear rate. These deviations become more significant when the temperature decreases. Figure 9 presents flow curves for slags doped with TiO<sub>2</sub> at a level of 2.81% at temperatures of 1340-1500°C.

Very slight deviations in the rheological nature of the system tested from the similarity to the Newtonian ideally viscous liquid can be observed in Figure 8. These deviations are much smaller than those presented in Figure 7. This may indicate that the titanium oxide dissolving in the ionic silicate

solution does not influence the rheological nature of the system to a great extent. The addition of components comprising the anion framing (network structure) influences the value of the dynamic viscosity coefficient without changing the rheological nature of the liquid at the examined temperatures and shear rates. By comparing both Figures 7 and 8, one may observe the significant effect of the addition of solids to the system on the increase of the shear stress/dynamic viscosity of the system. For titanium oxide addition, these values are significantly lower at each of the temperatures. A change in the rheological nature of the slag systems tested can also be observed.

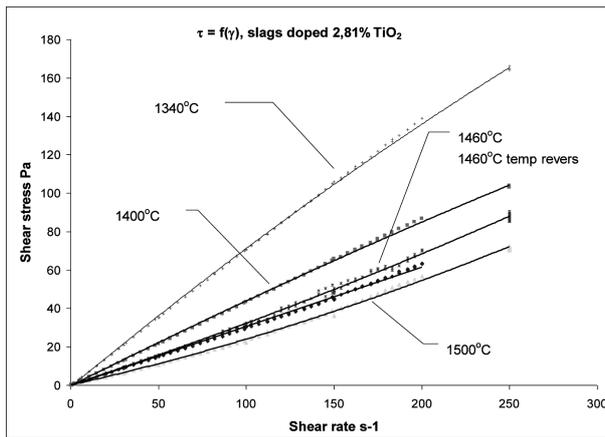


Fig. 8. Flow curves for slags doped with  $\text{TiO}_2$

The analysed glycerol solutions cover the whole range of shear stresses occurring in slags in the specific experiment conditions. It may be observed that 100% and 86% glycerol solutions within the range of values of shear stress and dynamic viscosity (Figures 5 and 6) cover the range of values obtained for the blast furnace slags applied. Nevertheless, it seems necessary to use at least these two solutions for the cold modelling of dripping effects within the blast furnace.

Figure 9 presents a change in the dynamic viscosity coefficient of glycerol solutions for various intervals of shear rate changes.

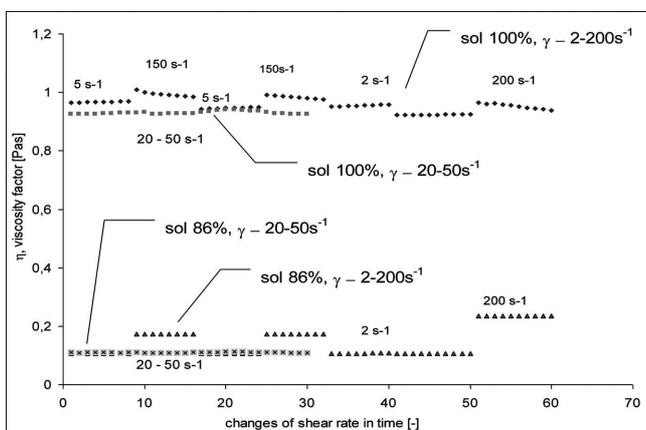


Fig. 9. Viscosity changes in steps (a and b etaps)

Figure 9 shows that "smooth" shear rate changes between 20 and  $50\text{s}^{-1}$  do not change the viscosity coefficient – thus indicating the Newtonian nature of the system within this time interval. However, step changes of shear rate from low to high values cause changes in the viscosity coefficient. This may

indicate deviations from the previous nature of the system or a change in the type of liquid flow from laminar to another (transient, turbulent). Unfortunately, there is no method for measuring the dynamic viscosity coefficient for these types of flows.

Figures 10a and 10b present flow curves of semi-solid systems of 100% glycerol with the addition of anthracite within various ranges of the volumetric fraction. The addition of solids to a liquid causes an increase in the shear stress/dynamic viscosity at the same values of shear rate. It can be observed that systems within the shear rate ranges up to  $50\text{s}^{-1}$  possess the rheological nature of an ideally viscous liquid – Figure 10a. When the shear rate increases to within a range of  $50\text{--}200\text{s}^{-1}$ , however, slight deviations towards a shear-thinning liquid are observed – Figure 10b. This may be caused by various factors, including a change in the behaviour of solids in the liquid (e.g. sedimentation, coagulation or others) or a potential change in the flow nature of a given system.

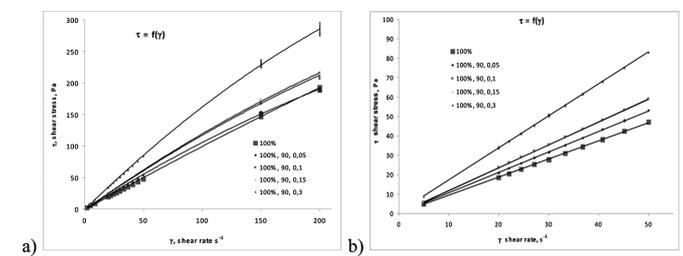


Fig. 10. Flow curves for different shear rate levels; a) up to  $200\text{s}^{-1}$ , b) up to  $50\text{s}^{-1}$

The flow nature of the 86% glycerol solution shows similarities to a Newtonian liquid within a shear rate range up to  $100\text{s}^{-1}$ . Between 100 and  $200\text{s}^{-1}$ , the glycerol shows an increase in the viscosity coefficient and, at the same time, demonstrates slight deviations from Newtonian behaviour. The addition of solid PC particles from 0.25 to 0.5 volumetric fraction to the glycerol solution causes deviations in the system analysed from the Newtonian nature towards a shear-thinning system. The addition of solid PC particles from 0.05 to 0.2 does not cause a change in the rheological nature of the liquid-solid system analysed.

The addition of solids between the limits of 0.05 and 0.5 volumetric fraction causes an increase in the dynamic viscosity coefficient over two times as large as that of pure glycerol solutions. For the 86% glycerol solution this increase in the viscosity coefficient is higher than for the 100% solution. The addition of the same amount of solids ( $90\mu\text{m}$ , PC) to a liquid that is "less" crosslinked in the same conditions causes a higher increase in the viscosity coefficient than for a liquid with a higher viscosity – "more" crosslinked. The increase of the viscosity coefficient in the same conditions is higher for PC particles than for  $90\mu\text{m}$  particles.

Figures 11a and 11b present viscosity changes in the 100% glycerol solution doped with solid particles corresponding with the changes in the shear rate. The graphs present findings from the programmed stages from Table 5 (first four stages, stage a and b, Table 5). It can be observed that for the applied changes in shear rate value, the systems behave as ideally viscous liquids regardless of the volumetric fraction of solid particles and their size. For a volumetric fraction of

0.1, the dynamic viscosity coefficient is higher for PC solid particles than for  $90\mu\text{m}$  particles, but it is similar for a fraction at a level of 0.3. The addition of PC solids of 0.3 volumetric fraction causes the system to start showing deviations towards a liquid whose viscosity depends on the nature of shear rate changes. However, such behaviour cannot be observed for  $90\mu\text{m}$  particles.

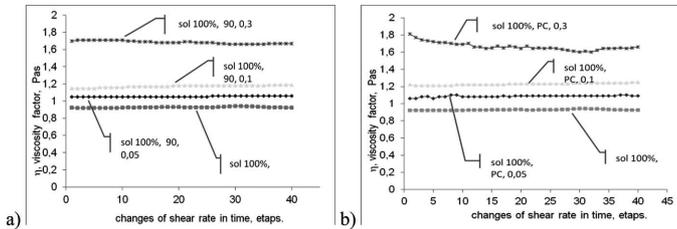


Fig. 11. Relationships between viscosity factors and changes of shear rate in steps

Apart from changes in shear rate for glycerol and slags, changes of  $\tau$  in various time intervals of shear rate changes are also worth considering.

### 3. Conclusions

Based on the conducted tests and analyses, one can conclude that:

- within the shear rate range of  $2\text{-}50\text{s}^{-1}$  the systems analysed – glycerol solutions, semi-solid systems – are similar to a Newtonian ideal liquid. Under this value the systems tested started to demonstrate slight deviations from ideally viscous liquids

- for the slag systems analysed a similar tendency may be noticed, the limit value of the shear rate shifts upwards far above  $100\text{s}^{-1}$

- the effect of solid particle size can be observed in the content at a level of 0.3 volumetric fraction in the liquids tested

- solids introduced to the system in the form of anthracite and PC do not change the values of shear stresses for the same values of shear rates. It is most visible in volumetric fraction of solid particles over 0.3

- the effect of changes in the nature of the shear force applied (variable or step) may be observed. This may be seen as the effect of time on the value of viscosity for a specific constant value of shear rate. For smooth changes of its value in the range of  $20\text{-}50\text{s}^{-1}$ , the system remains Newtonian. However, for step changes between the low shear rate values of  $2\text{-}5\text{s}^{-1}$  and high values of  $150\text{-}200\text{s}^{-1}$ , a slight but step change in the viscosity value can be observed. This indicates deviations from an ideally viscous liquid

- a change in the value of shear stress/dynamic viscosity at the same shear rates (for 100% glycerol) occurs in the ranges of volumetric fraction of solid particles of 0-0.05; 0.1-0.15; 0.3; the higher the content of solids in the system the higher the deviation from linearity in the flow curves. This indicates changes in flow nature or in the internal structure of the system, which is confirmed by the findings presented [10-12].

At high temperatures within the range of free dripping through the bed, the rheological nature of fully liquid slags

shows similarities to a Newtonian ideally viscous body. However, when solids are present in the liquid, the system deviates from this nature, also when strong mechanical forces have an impact on the liquid.

In order to obtain a more extensive knowledge of the rheological nature of liquid and semi-solid slag systems, it is necessary to continue research for as high shear rates as possible. This seems appropriate from the point of view of the mechanical impact a gas has on a liquid. Such application of very high shear rates could arise from very high linear velocities of blast furnace gas flowing through the lump bed counterflow to the liquid.

It seems necessary to use at least these two glycerol solutions for cold modelling of dripping effects within the blast furnace. During numerical or physical modelling, it is also worth considering not only the conformity of the liquid dynamic viscosity coefficient values, (glycerol, slag), but also their rheological nature.

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