VISCOSITY OF ALUMINO-OLIVINE SLAGS

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ABSTRACT

The development of continuous converting of copper matte points out an olivine type of converting slag as an optimal solution from the point of view of refractory corrosion and copper losses.

Modification of the olivine slag by addition of alumina should make another improvement of the slag properties, allowing for the use of quartz, lime and clay as three fluxes.

Measurements of the viscosity of the synthetic olivine slag with addition of alumina and cuprous oxide, in the wide range of temperatures, permitted to determine the optimal range of composition of alumino-olivine converting slag. The continuous measurement of the slag viscosity using roto-visco technique in linearly decreasing temperature allowed additionally for determination of slag liquidus temperature.

The utilization of three fluxes creates conditions for auto-melting, which is very attractive for currently developed new process of continuous converting in a packed ceramic bed.

INTRODUCTION

The new process of continuous copper mate converting in a ceramic packed bed [3, 4] requires new fluxes and type of slag.

The principle of continuous converting process is shown schematically in Figure 1. The vertical, cylindrical reactor is filled with ceramic grains, such as a scrap of chromo-magnesite bricks. The copper matte flows continuously into reactor and is dispersed in the surface of packed bed flowing downwards through a porosity of the packed bed. Tuyeres in side walls are injected air enriched in oxygen into the packed bed. At the surface of matte veins and drops the oxidation reactions take place with oxygen in counter current flowing gas. Produced iron oxides need to be slagged.

Various processes of continuous converting are using the olivine slag (FeO-CaO-SiO_2) as the most attractive solution. Some smelters were considering the application of the olivine slag. The application of olivine slag in the new process is limited because two fluxes quartz and lime do not melt at the range of converting temperatures 1250-1300°C.

The mix of three fluxes is fed onto the packed bed surface: quartz, clay, lime ore limestone. Three major components of the fluxes (FeO, CaO, SiO_2) form the initial slag, which melts and flows down through a porosity of packed bed. Iron oxides react with this slag forming converting slag of a system FeO - Fe_2O_3 - CaO - SiO_2 - Al_2O_3 - Cu_2O.

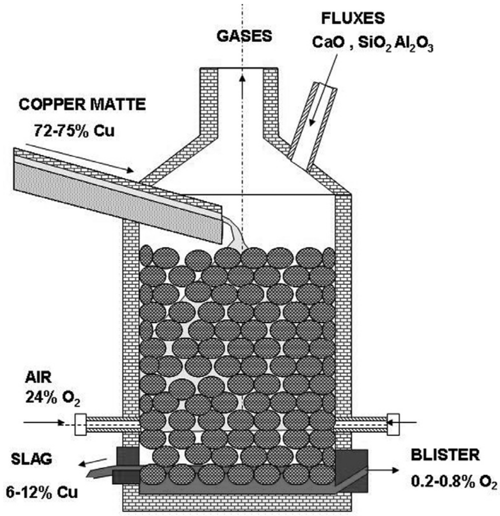

Figure 1: Principle of continuous matte converting in a packed bed

Next, the oxidation of a copper sulphide produces blister copper and partly cuprous oxide, which dissolves in the slag.

The blister copper separates from the slag on the furnace hearth and is continuously evacuated by siphon. The slag is tapped out through the tapping hole in the furnace side wall.

The alumino-olivine slag viscosity was measured by [1]. The slag viscosity is shown in Figure 2 for 5% and 15% of Al_2O_3 content for temperature 1300°C.

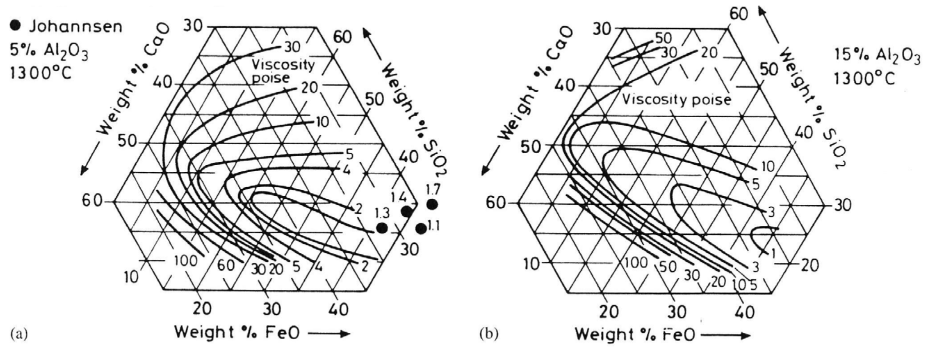

Figure 2: Viscosity of synthetic slag system FeO-CaO-SiO_2-Al_2O_3 at 1300°C

The aim of this work is to determine the viscosity of alumino-olivine (FeO-CaO-SiO_2-Al_2O_3) slag in a wide range of temperature and the effect of Cu_2O on the viscosity decrease.

METHODOLOGY

Preparation of Synthetic Slag

Two types of master olivine slag have been made, corresponding to chemical composition of slag A1 and B1 in Table 1.

Chemically pure SiO_2, Fe_2O_3, Fe (powder) and CaO were mixed in the proportion requires by defined slag composition and melted in MgO crucible at 1300°C in purified nitrogen atmosphere. The slag was stirred and the crucible quenched in water. Next, the master slags A1 and B1 were mixed with 5, 10, 15 or 18% of Al_2O_3, melted again in MgO crucible at 1300°C in purified nitrogen atmosphere and quenched in water.

Additionally, the slag B4 (Table 1) were used as master slag in which the addition of 5% and 10% Cu_2O was made.

The chemical assay of all used slags is presented in Table 1.

For illustration of chosen two types of olivine slag the composition are shown in the background of ternary diagram in Figure 3 as points A and B.

The slag preparation and measurements of viscosity were carried out in purified nitrogen, what does not define the oxygen potential, introducing error related to presence of magnetite. However, the x-ray diffraction did not find magnetite in the slags.

Table 1: Chemical composition of synthetic slags

No.	wt% content				
	FeO	CaO	SiO_2	Al_2O_3	Cu_2O
A1	36.0	30.0	34.0	0	0
A2	34.2	28.5	32.3	5.0	0
A3	32.4	27.0	30.6	10.0	0
A4	30.6	25.5	28.9	15.0	0
A5	29.5	24.6	27.9	18.0	0
B1	56.0	10.0	34.0	0	0

B2	53.2	9.5	32.3	5.0	0
B3	50.5	9.0	30.6	10.0	0
B4	47.6	8.5	28.9	15.0	0
C1	47.6	8.5	28.9	10.0	5.0
C2	44.8	8.0	27.2	10.0	10.0

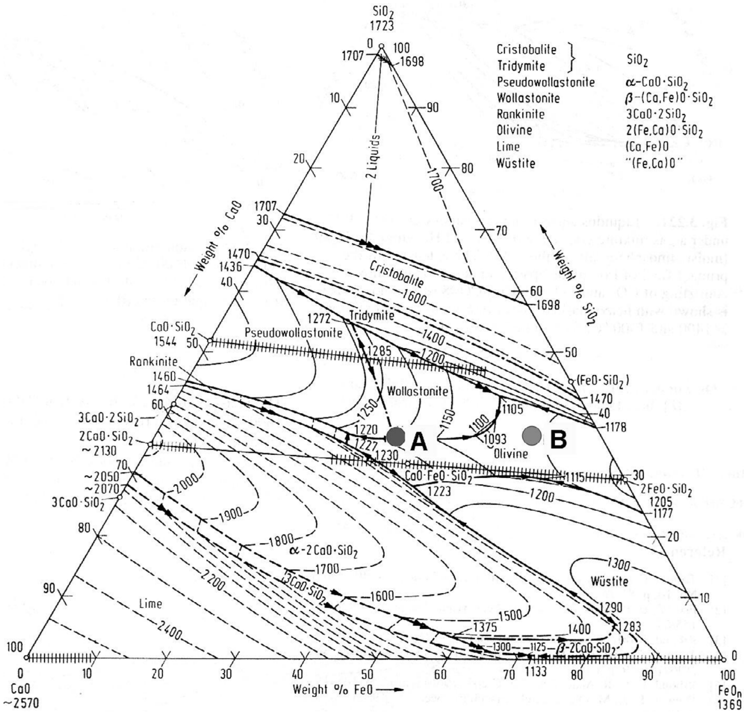

Figure 3: Ternary system FeO_n – CaO – SiO_2

Viscosity Measurement

The viscosity measurement is illustrated by schematically by a sketch in Figure 4. Determined slag in MgO crucible (O.D. 25.2 mm, height 125 mm) was placed in alumina reaction tube in a vertical electric furnace. The reaction tube was closed with both ends with water cooled brass caps. Upper cap has a hole for spindle axis and gas outlet. Lower cap has support for crucible with thermocouple touching the bottom and purified nitrogen inlet. Below and over the furnace the cylinders of kaowool are placed to minimize the vertical heat losses.

The slag was melted in nitrogen atmosphere and overheated to 1360-1380°C. When the temperature stabilized the MgO spindle (O.D. 25 mm and height 51.4 mm) with MgO axis 6.3 mm in diameter, extended by iron axis, was immersed in the slag.

The spindle was suspended on commercial Rotovisco HPL apparatus with stable rotation 5, 10, 20 50, 100 RPM and electronic measurements of torque. The viscometer signal, together with thermocouples signals, were connected to HYDRA data acquisition system and computer for data recording and the control of furnace temperature – linear ascending or descending.

The system was calibrated using in room temperature MgO crucible and spindle with glycerin and solutions glycerin-water.

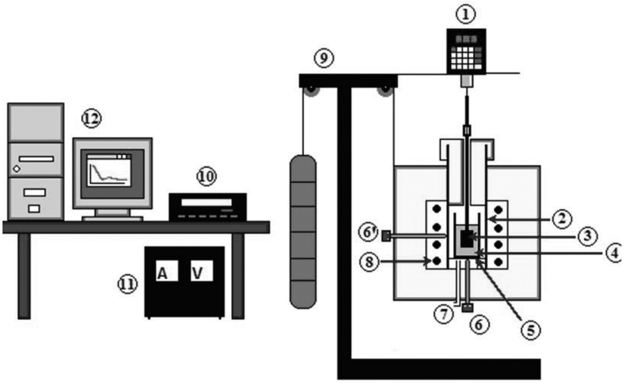

Figure 4: Experimental setup 1) Rotovisco, 2) Alumina tube, 3) MgO spindle, 4) MgO crucible, 5) Slag 6) Thermocouple 7) Nitrogen inlet, 8) Heating elements, 9) Stand, 10) Data acquisition, 11) Power supply, 12) Computer recording and temperature control system.

RESULTS AND DISCUSSION

The example of direct measurements results is presented in Figure 5. After stabilization of temperature the linearly descending temperature (4ºC/min) results in the increase of slag viscosity. The modeling of heat transfer showed that the delay in the decrease of bulk slag temperature against the measured temperature is about 1 min, what introduced the error of temperature determination approximately 4ºC. due to intensive slag stirring by spindle.

It can be seen the slow increase of viscosity in the range 1380-1270ºC and sudden increase at lower temperatures because the precipitation of a solid phase. Thus, the inflection point on the viscosity curve allows for estimation of a liquidus temperature.

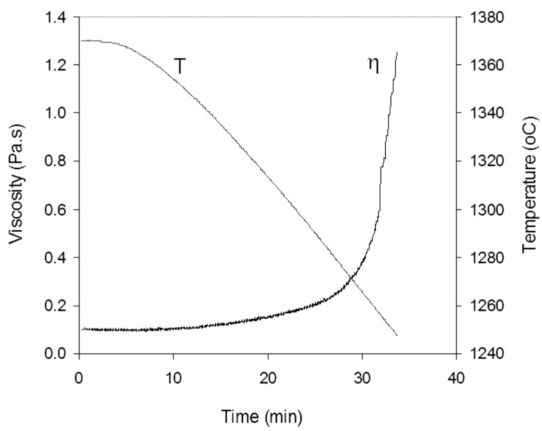

Figure 5: Continuous measurement of slag viscosity with descending slag temperature. Slag B1

The Temperature Dependence of Slag Viscosity

The comparison of the dependence of viscosity on temperature for low iron slag (A1) and high iron slag (B1) are illustrated by diagram in Figure 6. The liquidus temperature of slag A1 is about 1270ºC and slag B1 about 1220ºC respectively. Above 1280ºC both slags present similar viscosity approximately 0.15-0.20 Pa.s (1.5-2.0 poise).

It means that high and low iron olivine slags above 1280°C are fully operational and the slag/blister separation should proceeds without any problems. The high iron slag means the lower fluxes addition and smaller amount of produced converting slag.

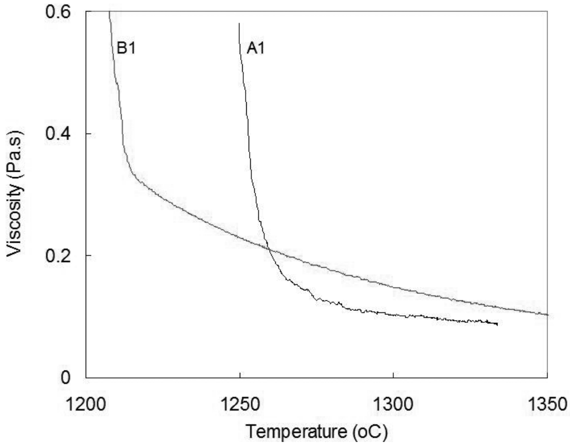

Figure 6: Slag viscosity as a function of temperature A1 – 36% FeO, 30% CaO, 34% SiO_2; B1 - 56% FeO, 10% CaO, 34% SiO_2

Effect of Alumina on the Slag Viscosity

The results shown in Figure 7 represents low iron slag with various addition of alumina. The addition of 5% Al_2O_3 does not effect slag viscosity at high temperature but lowers the liquidus temperature from 1270 to 1220°C (A1 and A2). Further increase of alumina content causes the decrease of viscosity and above 10% the increase of the viscosity. In order to show the effect of alumina addition the same results are shown in Figure 8 as viscosity versus alumina content for various slag temperatures.

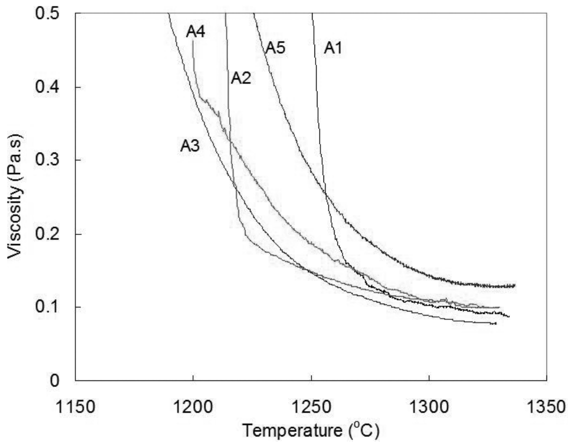

Figure 7: Viscosity of A slag versus temperature. A1-0%, A2-5%, A3-10%, A4-15%, A5-18% Al_2O_3

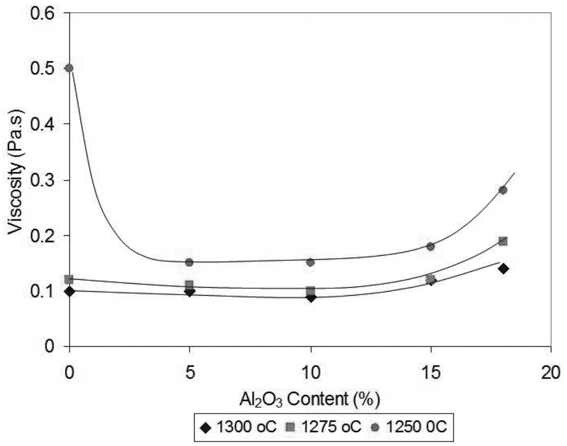

Figure 8: Viscosity of synthetic slag as a function of Al_2O_3 content

Using inflection points the estimated liquidus temperature is shown in Figure 9 as a function of alumina content.

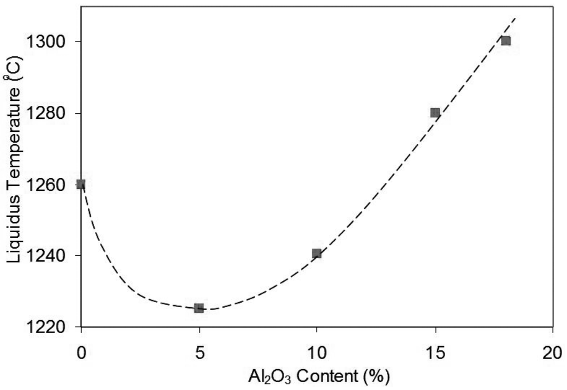

Figure 9: Estimated liquidus temperature as a function of alumina content

The effect of alumina addition to high iron slag is presented in Figure 10 as slag viscosity versus temperature. The addition of 5-10% of alumina results in the decrease of liquidus temperature and the viscosity. However, the addition of 15% Al_2O_3 increases the liquidus temperature approximately 80°C and the viscosity at lower temperatures.

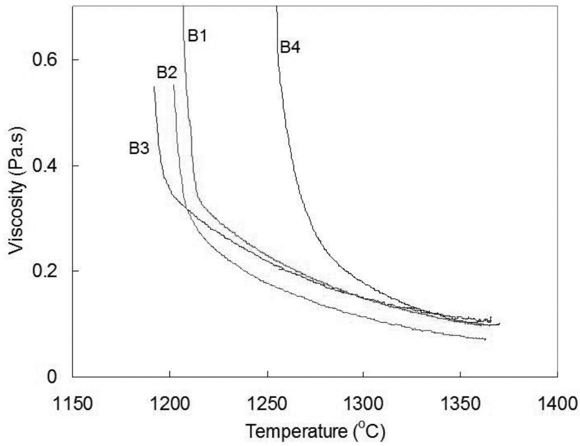

Figure 10: Viscosity of B slag versus temperature.
B1-0%, B2-5%, B3-10%, B4-15% Al_2O_3

In the same manner as before the effect of alumina addition on slag viscosity for high iron slag is shown in Figure 11. The addition from 5 to 10% of Al_2O_3 in temperature over 1250°C forms fully operational slag.

The solubility of Cu_2O in olivine slag [2] depends strongly on CaO/SiO_2 ratio and SiO_2/Fe ratio. For slag B1 the solubility is about 5%, at oxygen partial pressure 10^{-6}.

The addition of 5% Cu_2O into slag B3 (Table 1) decreases about 25% slag viscosity (Figure 12). Further increase of Cu_2O to 10% did not change significantly the viscosity. At the crucible bottom was found the slag layer enriched in Cu_2O, what is in agreement with work [2].

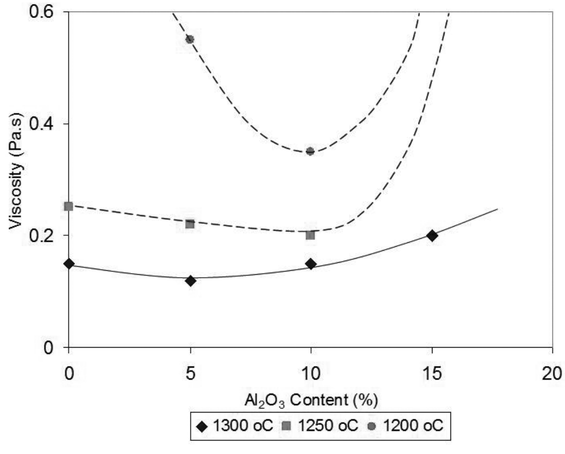

Figure 11: Viscosity of synthetic slag as a function of Al_2O_3 content

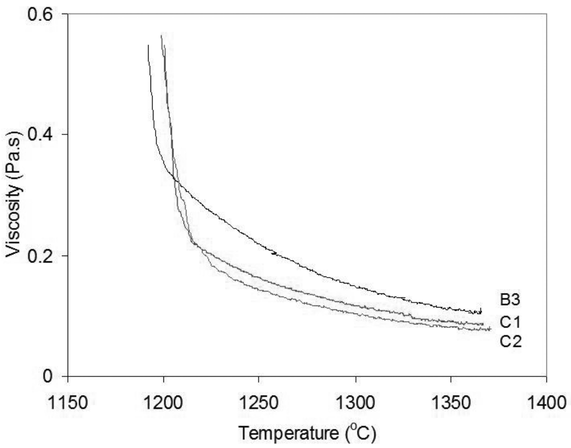

Figure 12: Viscosity of C slag versus temperature. B3-0%, C2-5%, C3-10% Cu_2O

CONCLUSIONS

The viscosity of alumino-olivine slags decreases with the increase of alumina addition up to 10% and increases with higher alumina content. Additionally alumina content causes the decrease of a liquidus temperature. Particularly, the high iron slags (50-55% FeO) are very attractive due to smaller converting slag amount.

In the range of typical converting temperatures 1250-1300ºC the slag viscosity is in the range 0.1-0.25 Pa.s (1.-0-2.5 poise) making slag fully operational and ensuring the effective separation of slag and blister copper. The expected Cu_2O content from 5 to 7% in converting slag due low solubility lowers additionally the slag viscosity and makes copper recovery easier by recycling into smelting unit or slag cleaning furnace.

The use of the mix of fluxes: quartz, clay, lime or limestone, is feasible in proposed continuous converting process, allowing for formation of preliminary slag and consumption of cheap fluxes.

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