Slag foaming by carbonates addition: studies of enthalpy and kinetics

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Abstract: Slag foaming phenomena was studied by using calorimetric measures, X-Ray radiography technique and plant data analysis. The kinetics of slag foaming with limestone addition was observed using X-ray camera in a laboratory furnace at 1773 K for the 4 different fraction sizes from 3,0 to less than 0,3 mm. A model for description of limestone decomposition in a slag was proposed based on the assumption of heat transfer as the rate controlling mechanism. The results showed a good agreement between calculated gas evolution rates and experimentally observed changes in foam height for the biggest fraction of limestone (1-3 mm). However, as the fraction size decreases, the observed decomposition time becomes longer than predicted from the model and secondary peak of foam height becomes more evident. Additionally, industrial data from 100-ton EAF were statistically analyzed in order to see the energy effect of both limestone and dolomite addition. The results showed that during liquid bath, when slag foaming is possible and temperature is relatively high, the addition of Ca and Mg carbonates demands only 60-70% of the theoretical decomposition energy while the addition during scrap melting required almost full amount of energy. The results are in agreement with the previous stage of investigations, where special thermal analysis technique was used for the measurement of total heat balance of slag foaming by carbonate decomposition. The measured energy for dolomite and limestone decomposition was 20-40% less than theoretical values.

Key words: Slag foaming, foam model, heat transfer, limestone decomposition

1. Introduction

Slag foams have been studied for more than 50 years since a new theory of slag foam stability was introduced by Cooper and Kitchener [1-2]. During the past 20 years, a great deal of attention has been paid to foam stability investigations in EAF steelmaking [3]. In this process, thermal insulation of the arc by slag foam plays a key role in energy efficiency. As it was reported by Fedina [4], an energy saving effect of 10-30 kW/ton can be attributed to well-controlled slag foaming in the case of 150 ton electric arc furnace. Further, energy transfer efficiency up to 60-90 % with a foaming slag (efficiency is as low as 40 % without a foaming slag) have also been reported by Fruehan [5]. Richard and Swartz [6] presented a detailed description of the advantages of slag foaming with respect to the energy efficiency, refractory protection etc. The optimal way of foaming agent addition should depend on the reaction kinetic and fraction size of the agent. Carbonate decomposition can be used for slag foaming due to its simplicity, easy control and industrial availability of minerals. Regardless the obvious benefits of slag foam there are no systematic results on the kinetics of slag foaming and total energy balance of the process in the case of carbonates decomposition. The present investigation aims to fill up this knowledge gap.

2. Experimental

2.1 Sample preparation

The particles of natural limestone were sieved into four different fractions of sizes 1-3 mm, 0.5-1.0 mm, 0.3-0.5 mm and less than 0.3 mm. Each fraction was separated into portions of 1.25 g and then packed into a container made from thin paper. The containers were attached to a silica rod which was precisely introduced into furnace to provide a good contact between liquid slag and limestone particles. A schematic diagram of the experimental set up is presented in Figure 1.

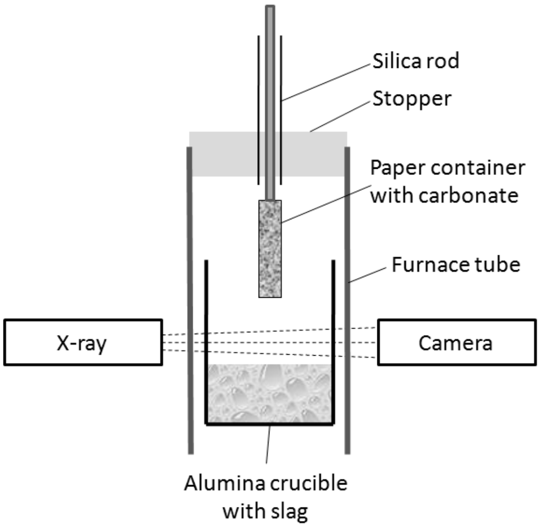


Fig. 1: Experimental set up for X -ray radiography observations

An alumina crucible of 36 mm i.d. and 60 mm height was used to hold the slag amount of 34.5 g. The following composition was used as the synthetic slag at 1773 K: Al_2O_3 – 20 %, MnO – 15 %, CaO – 32.5 %, SiO_2 – 32.5 %. It was found that no significant change in the kinetics of slag foaming could be detected even after 6 consequent additions to the same slag.

2.2 Measurement

The X-ray radiographic experiments were conducted on Philips BV-26 imaging system. Furnace assembly (Thermal Technology Inc.), with a maximum temperature of 2300 K, was equipped with graphite heating elements. The furnace was fitted with an alumina reaction tube. The temperature of the furnace was controlled by a Eurotherm temperature regulator within ± 2 K. There were two parallel ports in the furnace assembly with quartz windows that allow the passage and detection of X-rays. The imaging system consisted of a CCD camera with digital noise reduction. The process was continuously recorded on video, after which the single screenshots were analyzed. The image acquisition card enabled the recording of the X-ray image at a maximum rate of 30 frames per second. The cross section of the foam layer was used to recalculate the average foam thickness in a crucible which was assumed to be a representative characteristic of real amount of foam. A detailed description of the apparatus is presented in earlier reports from the present division [7].

2.3 Industrial data analysis

To find out the influence of limestone and dolomite on the energy demand in 100-ton EAF, the heat reports with raw plant data of more than 8000 heats, conducted at Belarusian Steel Works in 2008, were collected. After that, filtering was performed to fetch only the heats with a certain range of other important parameters, which can have influence on energy demand (all heats without technical time-breaks, charge mass – 120 ± 3 ton, two basket scrap charge, etc.). To clarify the influence of carbonates among more than 100 parameters on energy consumption, all the heats were normalized to the middle values of parameters. The normalization includes the elimination of the “noise” influence of the parameters with the known impact to the energy demand. The values of the most important impacts were assumed based on the EAF heat balance calculations and long-time observations on BMZ. As the relative time of carbonate addition in EAF can influence the energy consumptions, the parameter t_Q, describing the dimensionless time of carbonate addition, was calculated for each heat as:

$$t_Q = \frac{\sum_{i=1}^{n} Q_i^{carb} \cdot m_i^{carb}}{Q_{tot} \cdot m_{tot}^{carb}} \cdot 100\% \tag{1}$$

where Q_i^{carb} – integral energy consumption by the moment of addition of i portion of carbonate, J; m_i^{carb} – mass of i portion of carbonate added, kg; Q_{tot} – total energy consumption for a heat, J; m_{tot}^{carb} – total mass of carbonate, added during a heat, kg. The parameter t_Q characterizes the relative time of carbonate addition in relation to whole heat duration. Then all the heats were divided into 2 group: first – with early addition of carbonates (t_Q < 33 %) and second – with later addition (t_Q > 50 %).

3. Results

3.1 Radiographic observations

It was found from the radiographic observations of slag foaming, that the decomposition time for the different fractions of limestone did not vary much with particle size. To get an idea about how decomposition time should vary with fraction size, temperature and material properties, a simplified model was implemented. It is assumed that the rate of limestone decomposition in the slag is governed by the heat transfer from the slag and then through the shell of undissolved CaO. In this case, the heat transfer from bulk slag to spherical surface of particle can be calculated as [8]:

$$Q_{sl} = 4\pi R K_2 (T_f - T_{surf})(t_2 - t_1) \tag{2}$$

where T_{surf} – the surface temperature of $CaO/CaCO_3$ granule, K; T_f – temperature of the surrounding slag foam, K; K_2 – thermal conductivity of slag (0,15 $W \cdot m^{-1} \cdot K^{-1}$); t – time, s; R – sphere diameter, m. Then, the heat transfer within the CaO shell can be described as [8]:

$$Q_{sp} = \frac{4\pi K_{CaO}^{eff} (T_{surf} - T_{dec})(t_2 - t_1)}{(\frac{1}{r} - \frac{1}{R})} \tag{3}$$

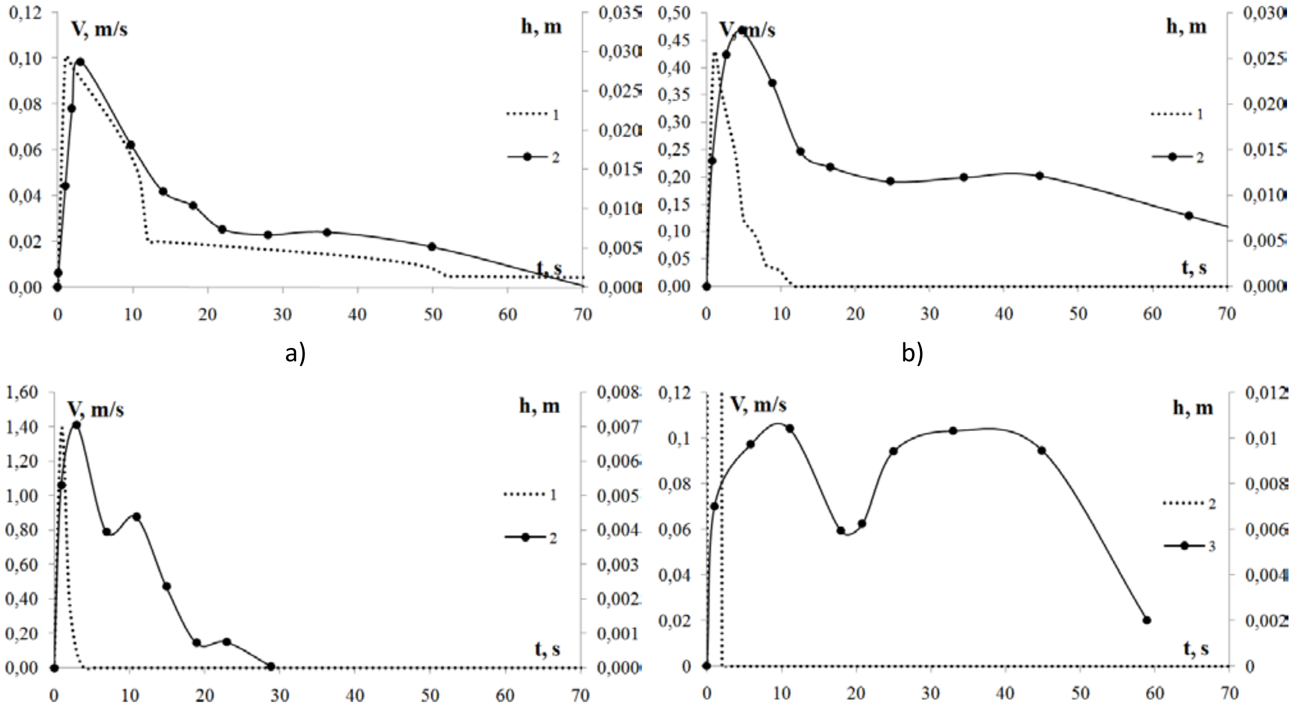
The decomposition temperature T_{dec} was assumed to be 1171 K. The influence of CaO porosity on the effective thermal conductivity (K_{CaO}^{eff}) can be estimated by using Maxwell-Eucken expression taken from the publication of Lin and Ford [9]:

$$K_{CaO}^{eff} = K_{CaO} \frac{1-P}{1+\beta P} \tag{4}$$

where P – estimated porosity (which is admittedly approximate); β – a pore shape factor, which was taken as 2/3 for randomly dispersed cylindrical pores. The porosity was calculated as the ratio:

$$P = \frac{\rho_b - \rho_e}{\rho_b} \tag{5}$$

where ρ_b – bulk density of the material; ρ_e – density, determined experimentally. Assuming that $Q_{sl} = Q_{sp} = Q_{dec}$, and that the heat of limestone decomposition (Q_{dec}) includes both change in reaction enthalpy and heating of the substances, it is possible to find intermediate temperature T_{surf} and thus the amount of heat transferred inside the particle for each time interval. The calculations were repeated for each 1 second interval to recalculate the temperature of the surrounding slag, CaO shell thickness and decomposition rates. The experimental foam height changes, recalculated from recorded video frames, are shown at Fig. 2 together with the gas evolution profiles, predicted for each fraction from the model. Each fraction was approximated by a mixture of particles of 3 sharply-defined sizes (minimum, average and maximum, each is 33% by mass). This caused some discontinuities in the model curves.



a)

b)

c)

d)

Fig. 2 – Superficial gas flowrate, calculated from the model (1), in comparison with the experimental foam height changes (2): a – 1-3 mm fraction; b – 0,5-1 mm; c – 0,3-0,5 mm; d – 0,3-0,12 mm

3.2 Industrial data analysis

The diagram on Fig. 3 shows an example of correlations between energy demand (kJ/ton) and carbonate consumption (kg/ton) for the studied heats with earlier and later additions of the carbonates. The angle coefficient at the trend line represents the specific heat effect of carbonate decomposition. The foaming can happen only if carbonates are added to the molten slag at the later stage of scrap melting ($t_Q > 50$ %).

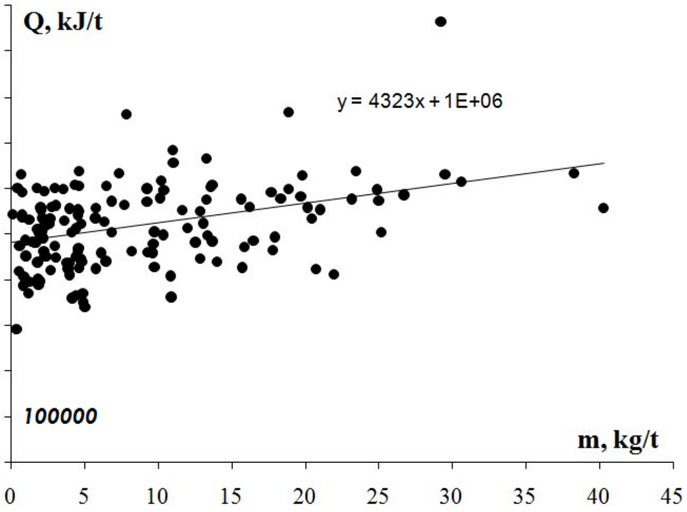


Fig. 3. The influence of limestone on the energy demand per liquid steel ton in the case of earlier addition ($t_Q < 33$ %) into EAF

The same angle coefficients were determined for the cases of early and late additions of limestone and dolomite. The results are presented in Table 1.

Table 1. Energy effect of carbonates decomposition (kJ/kg) depending on time of addition into EAF

Carbonate	Time of addition	
	t < 33 %	t > 50 %
Dolomite	4868	2264
Limestone	4323	2255

4. Discussion

4.1 Radiographic observations

As it is seen from the results on Fig. 2a, the agreement between predicted gas flow rate and experimental profile of the foam height is good only for biggest fraction of limestone (1-3 mm). As the fraction size decreases the agreement becomes less and less. One possible explanation could be an influence of the foam formation on limestone powder decomposition. When the first portion of carbonate decomposes and produces foam, the rest of limestone can be lifted up together with the foam formed. Smaller fractions of carbonate have more chances to be removed into slag foam as they have higher specific area. Bigger particles will mostly stay in the liquid as they are too heavy to be lifted together with foam. As the carbonate material became entrapped into foam, the heat transfer from the slag to decomposed particles decreased considerably and the surrounding space is cooling down. This should lead to decrease in decomposition reaction rate or even to temporary “conservation” of the particles inside foam. As soon as the foam destroyed, the particles get into slag and decomposition reaction can start again. Such mechanism can explain the observed oscillations in foam height, which are especially evident for smaller fractions (Fig. 2, c and d).

4.2 Industrial data analysis

It is clear from the energy effects found (Table 1), that if the carbonates are added during the early stage of heat (if $t_Q < 33$ %), when the specific energy consumption is nearly 2 times higher as compared to the later stage of addition ($t_Q > 50$ %). In the last case, the heat effects for limestone and dolomite decomposition (2255 and 2264 kJ/kg respectively) are close to the values determined during laboratory experiments described in the previous part of the investigation (Table 2). The detailed description of special designed unit and experimental procedure can be found in [10]. This would mean the saving of at least 30 % of energy required for the carbonates decomposition, in the case of the later addition of the materials on liquid steel bath in an EAF. According to theoretical estimations (Table 2), the decomposition energy for dolomite and limestone should be in the range of 3400 kJ/kg. In the case of EAF the energy efficiency is around 70% due to heat losses with cooling water, outgoing gases and radiation. In such case, the effect of carbonates addition should be around 4860 kJ/kg which is more close to experimentally observed energy effects (Fig. 3and Table 1).

Table 2. Calculated and measured heat effects of dolomite and limestone decomposition [10]

Substance	T, K	Calculated dolomite decomposition energy, kJ/kg	Measured heat of carbonates decomposition, kJ/kg		Measured heat of carbonates decomposition, % from calculated values	
			Min	Max	From	To
Dolomite	1623	3146.6	1731.9	2187.6	55.0	69.5
	1673	3213.7	1801.6	2370.5	56.1	73.8
	1723	3281.5	-	-	-	-
Limestone	1623	3251.7	2005.3	2278.8	61.7	70.1
	1673	3318.9	1896.4	2180.9	57.1	65.7
	1723	3386.9	-	-	-	-

5. Conclusions

The kinetics of slag foaming with limestone addition was studied using X-ray radiography technique for the 4 different fraction sizes of carbonates from 3,0 to less than 0,3 mm. A model of limestone decomposition in a slag was constructed based on the assumption of heat transfer as the rate controlling mechanism. A good agreement between calculated gas evolution rates and experimentally observed foam height changes could be observed in the case of the biggest fraction of limestone (1-3 mm). For the smaller fractions the observed decomposition time was much longer than predicted from the model and secondary peak of foam height was found on the foaming curves. The differences can be caused by entrapment of decomposed particles into slag foam and slow down of the reaction.

Industrial data from 100-ton EAF were statistically analyzed in order to see the energy effect of both limestone and dolomite addition. The results showed that during liquid bath, when slag foaming is possible and temperature is relatively high, the addition of both carbonates demands only 60-70% of the theoretical decomposition energy while the addition during scrap melting required almost full amount of energy. The results are in agreement with the previous stage of investigations, where special thermal analysis technique was used for the measurement of total heat balance of slag foaming by carbonate decomposition. The measured energy for dolomite and limestone decomposition was 20-40% smaller than theoretical values.

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