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ENERGY SAVING EFFECT OF SLAG FOAMING BY CARBONATE ADDITIONS IN EAF PROCESS

EFEKT OSZCZĘDNOŚCI ENERGII PODCZAS PIENIENIA ŻUŻŁA PRZEZ DODATEK WĘGLANÓW W PROCESIE EAF

Slag foaming has been studied systematically for more than 50 years. The main reason for such interest is a big number of benefits of slag foaming technology in steelmaking, especially for the process in an electric arc furnaces (EAF). There are 2 types of reactions which can be used for slag foaming. The most famous one is the carbon oxidation by oxygen dissolved in metal. Another type of slag foaming reactions is a decomposition of carbonates or other substances, which can produce gas at high temperature. However, it can be concluded that the slag foaming with carbonates is not usual in steelmaking practice. The purpose of the present work is to study the energy effect of slag foaming caused by carbonates decomposition.

Keywords: slag foaming, EAF

Pienienie żużła badano systematycznie od ponad 50 lat. Głównym powodem takiego zainteresowania jest duża liczba korzyści technologii pienienia żużła w produkcji stali, zwłaszcza w odniesieniu do procesu w elektrycznych piecach łukowych (EAF). Są dwa rodzaje reakcji, które mogą być używane do pienienia żużła. Najbardziej znaną jest utlenianie węgla tlenem rozpuszczonym w metalu. Innym rodzajem reakcji jest rozkład węglanów lub innych substancji, które mogą wytworzyć gaz w wysokiej temperaturze. Jednak można stwierdzić, że pienienie żużła z węglanów zwykle nie jest w stosowane w praktyce. Celem niniejszej pracy jest analiza efektu energetycznego przy pienieniu żużła spowodowane przez rozkład węglanów.

1. Introduction

Slag foaming has been studied systematically for more than 50 years since Cooper and Kitchener introduced a new theory of slag foam stability [1-2]. In the recent 20 years a great attention has been paid to foam stability investigations, followed the concept of slag foaming index [3]. The main reason for such interest is a big number of benefits of slag foaming technology in steelmaking, especially for the process in an electric arc furnaces (EAF). The electric arc plasma has a temperature from 5000 to 20,000 K [4], and it is obvious that the good isolation of the arc by slag foam plays a key role in process efficiency. Fedina et al. [5] reported that if only half of the electric arc length is in slag, the part of energy, which is transferred from the arc to the liquid metal will be 31-42 %. However, if the arc is totally immersed into the slag, the metal bath will receive around 50 % of the arc power and the coefficient of energy usage will increase from 52-66 to 80-93 %. Finally, the energy saving effect of 10-30 kWh/ton was reported in the case of well-controlled slag foaming for 150 ton

electric arc furnace. Another report in the literature [6] indicates energy transfer efficiency improvements from 40% without a foaming slag to 60-90% efficiency when the slag is foamed.

Thus the energy balance of slag foaming is an important issue as besides the energy saving effect, the process of foam creation requires an additional heat for both gas producing reaction and gaseous products heating. Unfortunately, there are no systematic results on the influence of slag foam existence on the total energy balance.

There are 2 types of reactions which can be used for slag foaming. The most famous one is the carbon oxidation by oxygen dissolved in metal. This reaction is exothermic but it also requires an incubation period to start because of oxygen and carbon mass transfer stages. Sometimes this reaction is difficult to control and it can cause too vigorous foaming in oxygen blowing furnaces. Another type of slag foaming reactions is a decomposition of carbonates or other substances, which can produce gas at high temperature. These reactions don't have incubation period because they are limited only by heat

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transfer to a decomposed substance, which is usually much faster than mass transfer.

However, it can be concluded that the slag foaming with carbonates is not usual in steelmaking practice. On the one hand, it is traditionally believed that such reactions are not favorable for energy balance of the total process because they require an additional heat amount for the decomposition process. But, on the other hand, there is no available data on heat balance for slag foaming by carbonates decomposition.

The purpose of the present work is to study the energy effect of slag foaming caused by carbonates decomposition. The paper summarizes the results, presented in [7-8].

2. Experimental part

Laboratory experiments

The laboratory studies of heat effects due to carbonate addition to slag bath were performed in a vertical tube furnace with a controlled temperature. The arrangement was based on a single thermocouple-thermoanalysis principle. Known amounts of the carbonate were added to slag melt and the temperature changes were recorded. The experiments had to be designed in such a way that a quantification of the enthalpy changes could be enabled with reasonable accuracy.

The carbonate addition experiments were carried out in a vertical furnace arrangement. An alumina reaction

tube (50 mm I.D., 60 mm O.D. and 1200 mm long) was positioned inside a vertical furnace equipped with super kanthal heating elements capable of attaining a maximum temperature of 1923 K. The furnace was controlled by a Eurotherm PID regulator to an accuracy of ± 2 K with a Pt-30 % Rh/Pt-6 % Rh thermocouple as the sensor. The experimental set up is shown in Figure 1a, and the detailed description of specially designed crucibles, made from ARMCO iron, and the experimental technique are given in [7].

In order to protect iron crucible, a purified argon gas was introduced into the furnace with a constant flow rate of 130 ml/min. It was important to have a homogeneous slag phase of low viscosity in order to monitor the temperature changes fast. The master slag of the following composition was chosen after systematic study of the composition-liquidus temperature dependencies for a number of slag systems [9-10]: CaO - 31%; SiO₂ - 31%; MgO - 7%; Al₂O₃ - 6%; FeO - 25%.

CaO, SiO₂, MgO and Al₂O₃ were obtained from Alfa Aesar company, while FeO was prepared *in-situ* by mixing Fe₂O₃ with Fe thoroughly and pressing them into a pellet. Argon gas, purity 99.999% was supplied by AGA gas, Stockholm.

The dolomite mineral (21% MgO, 29% CaO, 2.3% SiO₂, 0.44% Al₂O₃+FeO) was delivered by Dokshyt-sy mines in Belarus and limestone was provided by SSAB, Oxelösund, Sweden. The purity of the materials was established by XRD analysis. Both spherical and planar samples were prepared from natural materials (Fig. 1b-e).

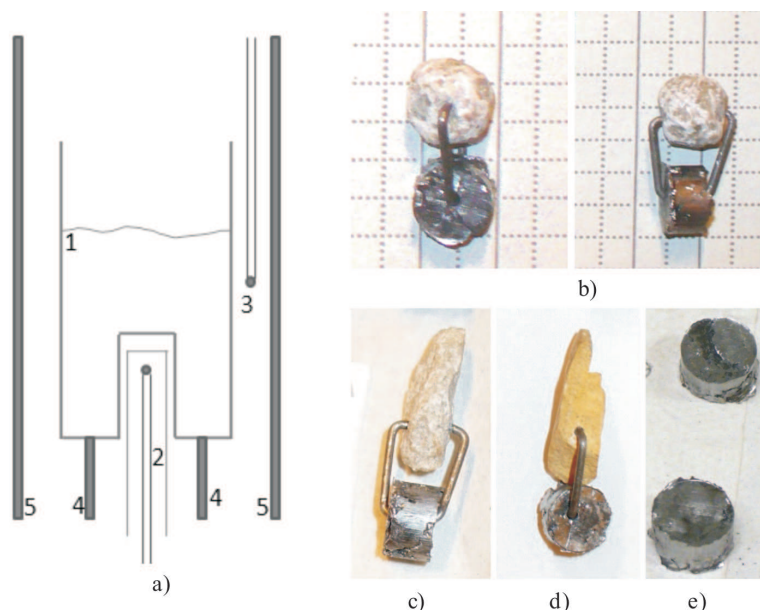


Fig. 1. The design of crucible (a) and the samples, used for the experiments (b-d). a: 1 – iron crucible with slag inside, 2 – inner thermocouple inside protective tube, 3 – outer thermocouple between crucible and furnace walls, 4 – crucible support tube, 5 – furnace walls. Samples: b – spherical limestone, c – plain limestone, d – plain dolomite, e – iron tablets

Preliminary experiments showed that the experimental results were not reproducible if the carbonates, which were lighter than the slag, floated on the slag surface. This was attributed to the heat transfer outside the slag phase because the endothermic heat of decomposition was taken partially from the furnace walls, but not fully from the slag in the crucible. In order to measure the total heat effect due to the decomposition of the sample and to get reproducible results, it was found necessary that the carbonate samples sunk to the bottom of the crucible as fast as possible. In order to facilitate this, the samples were tied to sinker tablets of pure iron using thin pure iron wires. The weight of the samples was in the range 1.3-1.8 gram for all of the experiments. Three decomposition temperatures were tested: 1623, 1673 and 1723 K.

The temperature profiles were recorded continuously by a data logger before the samples were dropped inside and during the dissolution till the temperature reached constant value after completion of reaction. The experimental sequences were as follows: the experimental arrangement was calibrated three times by dropping pure iron tablets, followed by the experiments with 2 pieces of dolomite and 2 pieces of limestone. The number of experiments was restricted to 4 in one series in order to avoid drastic changes in slag properties that can have an impact on the experimental results. The typical temperature profile, measured after sample of limestone addition, is shown at Fig. 2 [7].

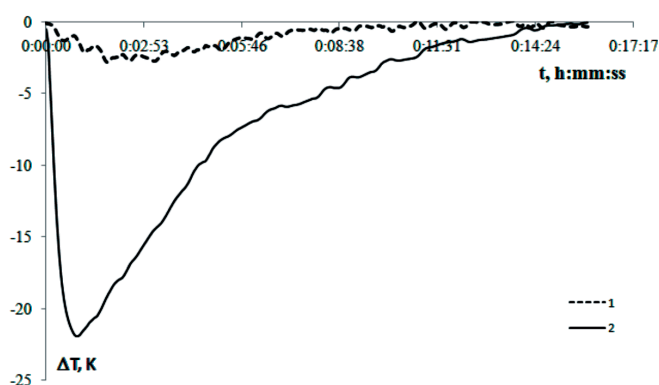


Fig. 2. Typical temperature profile, measured after sample of limestone addition

Plant heats 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. All the heats were conducted in a 100-ton EAF furnace with 75 MWh power supply (produced by Danieli ©). Most of the heats had approximately 1 hour tap-to-tap time and 90-95% steel scrap in a charge. During the investiga-

tion, statistical methods of data analysis were employed. After that the 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 detailed description of the normalization is given in [8].

As the relative time of carbonate addition in EAF can influence the energy consumption, all the heats were divided into groups, depending on the dimensionless time of carbonate addition (t_C), which was calculated for each heat as:

$$t_C = \frac{\sum_{i=1}^n Q_i^{carb} \cdot m_i^{carb}}{Q_{tot} \cdot m_{tot}^{carb}} \cdot 100\% \quad (1)$$

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_C characterizes the relative time of carbonate addition in relation to whole heat duration. 2 groups of the heats were analyzed: 1st – with early addition of carbonates ($t_C < 33\%$) and second – with later addition ($t_C > 50\%$).

3. Results and discussion

Calibration curves shape and peak position

The experimental profiles of slag temperature change after the addition of the calibration pieces of iron of the same mass showed different values of temperature drop as well as different initial slope of the curves. It was found that the temperature profiles are in agreement with the model of a spherical body heating from the initial temperature T_c to the outer temperature T_0 . The analytical solution of this task is considered in [11]. These authors propose the following equation for this problem:

$$T = T_0 + \frac{2RT_0}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{R} e^{-\frac{\kappa n^2 \pi^2 t}{R^2}} \quad (2)$$

where T - current temperature, T_0 - surface temperature, R - sphere radius, r - distance from the center, t – time, s; κ - thermal diffusivity coefficient, m^2/s .

$$\kappa = \frac{K}{\rho C_p} \quad (3)$$

where K – thermal conductivity, $W/(m \cdot K)$; ρ – slag density, kg/m^3 ; C_p – slag heat capacity, $J/(kg \cdot K)$.

By using the equations (2) and (3), one can obtain the description of temperature profile for any distance from the center of the sphere. Using the following boundary conditions (at $t=0$ and $r=0$ $T_c=T_0 - \Delta T_{max}$; at any t and $r=R$ $T=T_0$) together with data on slag heat conductivity, density and heat capacity, it is possible to estimate the change of temperature inside a sphere with time. The results of the comparison between calculated

and experimental temperature changes for the calibration experiments with iron tablets are shown at Fig. 3.

It is clear from Fig. 3 that a curve slope is varied depending on the distance to the center (i.e. fallen sample position). It means that only the curves of same slope should be compared during the analysis.

Then each experimental curve for carbonate sample addition was matched with a corresponding calibration one of the same slope in the same series. The examples of experimental and calibration curves, with corresponding initial slopes, for the experiments with limestone and dolomite are shown at the Fig. 4.

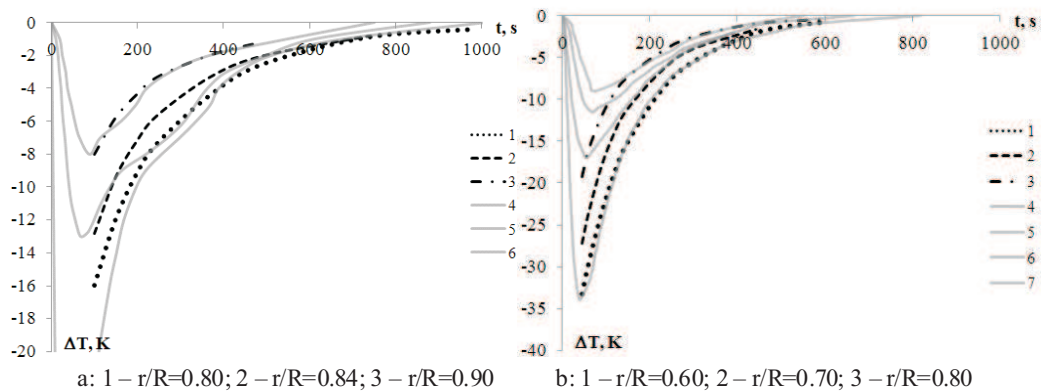


Fig. 3. The relation between calculated (1-3) and experimental (4-7) temperature profiles for calibration curves at (a) 1673 and (b) 1723 K. Slag properties: thermal conductivity: 0.15 at 1673 K and 0.25 Watt/(m·K) at 1723 K; density: 3000 kg/m^3 ; heat capacity: 1225 $J/(kg \cdot K)$, ΔT_{max} : 40 K, R : 0.01 m

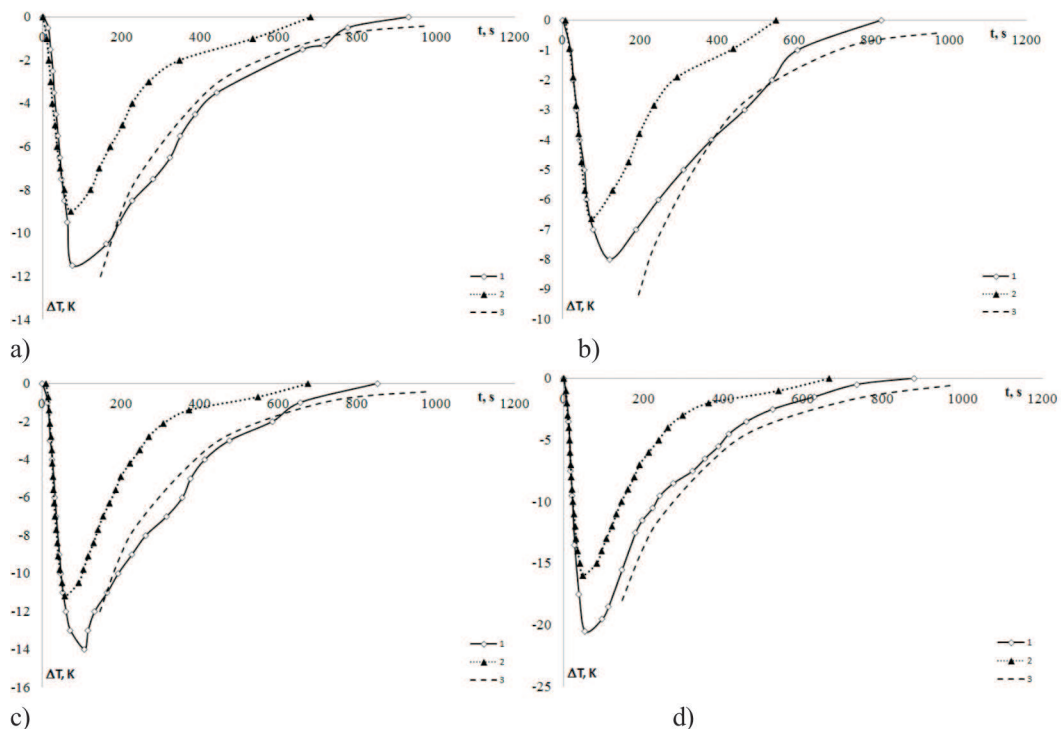


Fig. 4. The examples of calibration (1) and experimental (2) curves for dolomite and limestone at 1673 K. a – 1.6141 g of plain limestone; b – 1.7051 g of round limestone; c – 1.705 g of round dolomite; d – 1.4235 g of plain dolomite; dashed line (3) represents the temperature decrease according to equation (5) at $\Delta T=40$ K and $r=0.7-0.8$

Then the heat effects of dolomite and limestone decomposition were calculated in relation to “iron equivalent” by comparison of the areas above calibration and experimental curves according to the equation:

$$Q_{foam} = Q_{Fe} \cdot \frac{S_2 - S_1}{S_1} \quad (4)$$

where Q_{foam} – the heat effect of slag foaming (which corresponds to the endothermic heat due to the decomposition plus the heat insulation effect due to foam formation), Q_{Fe} – heat required for heating of calibration piece of iron to experimental temperature, S_1 – the area above the most suitable calibration curve, S_2 – the area above the experimental curve.

The amount of heat, required for iron to be heated, was calculated on the basis of equations (5) and (6) [12]:

$$H_{T_2} - H_{T_1} = \sum \int_{T_1}^{T_2} C_p dT + \sum \Delta H_{tr} \quad (5)$$

where HT – substance enthalpy at the temperature T, J/mol; CP – the heat capacity of the substance, J/K · mol; ΔH_{tr} – the enthalpy change for a phase transition, J/mol.

$$\int_{T_1}^{T_2} C_p dT = a(T_2 - T_1) + \frac{1}{2}b \cdot 10^{-3} \cdot (T_2^2 - T_1^2) + \frac{1}{3}c \cdot 10^{-6} \cdot (T_2^3 - T_1^3) - d \cdot 10^5 \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (6)$$

where a, b, c and d are the coefficients in heat capacity equation, J/mol.

The enthalpy changes for carbonates decomposition were calculated as:

$$\Delta_{dec}H = \sum_i n_i H_{f,prod}^0 - \sum_i n_i H_{f,init}^0 \quad (7)$$

where $\Delta_{dec}H$ – the enthalpy change for a decomposition process, J/mol; n_i – a stoichiometric coefficient in front of i-substance in the equation of decomposition process, $H_{f,prod}^0$ and $H_{f,init}^0$ – the standard enthalpy changes of the formation of products and initial substances, J/mol. As the heat capacity of the whole system increases with each additional sample, the determined heat effect values were corrected by taking into account the changes in the specific heat of the system.

The source data and more detailed description of the calculation are presented in [7].

Combination of foaming and endothermic enthalpy effects

In order to estimate the energy saving effect, the amount of heat, required for the process of both decomposition and heating of the products from 298 to 1673 K was calculated. The heat capacities were taken into account by using the equation (3). The calculations were also checked using commercial thermodynamic software. The calculated values of decomposition energies are presented in Table 1.

For further discussions, the calculations carried out by the authors based on the C_p values reported [12] are used. The measured and calculated total heats for the carbonates decomposition are presented in Table 2.

TABLE 1
The results of the calculations of the heat demand for the carbonates decomposition and products heating from 298 to 1673 K

Source of calculations	Dolomite energy demand, J/g			Limestone energy demand, J/g		
	ΔH_r^{298}	Products heating	Total	ΔH_r^{1127}	Products heating	Total
Thermocalc software	–	–	3203.3	–	–	3225.0
Calculations based on literature [12] data	1545.4	1568.3	3213.7	1569.1	1059.9 + 689.9	3318.9

TABLE 2

Calculated and measured heat effects of dolomite and limestone decomposition

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	492.7	689.8	15.0	21.0
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	492.7	689.8	14.5	20.4

The results showed that the experimental values of decomposition energies are in the range of 55-74% of the theoretical ones. Such differences are believed to be attributed to the energy saving effect of slag foaming on total energy balance.

It was found that the experiments at 1723 K resulted in a big scatter in the values. It can be concluded from observations that too vigorous decomposition and material blowing out were the reasons for some samples to have near-zero decomposition enthalpy effect.

Plant trials results

As it was found from the analysis of the data during the plant investigation, both raw dolomite and limestone

lead to increase in energy demand in an EAF. However, the effect is different depending on relative time for carbonate addition. If carbonate is added during early stage of heat (when $t_c < 33\%$), when the specific energy consumption is around 2 times higher compare to the addition of carbonates into EAF at the later stage (Fig. 5). In the case of later addition (when $t_c > 50\%$), the heat effects for limestone and dolomite (2255 and 2264 kJ/kg respectively, Fig. 5c and 5d) are quite close to the values, determined during laboratory experiments, described earlier. That means the saving of at least 30% of energy, required for carbonate decomposition, when carbonates are added at the later stage of a heat (liquid steel bath) in an EAF.

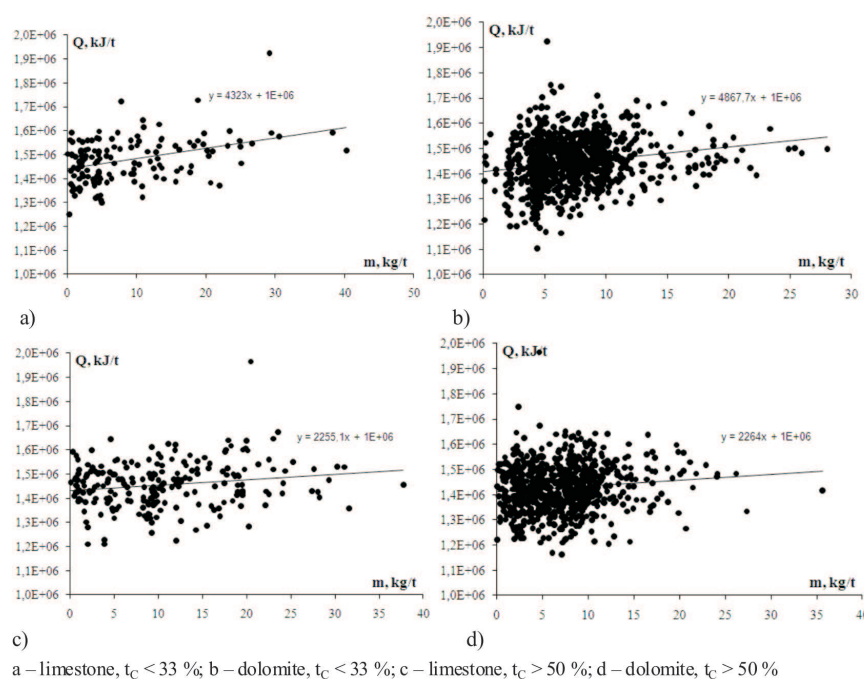


Fig. 5. Dolomite and limestone influence on the energy demand per liquid steel ton in EAF with different addition time

4. Conclusions

1. A modified thermal analysis technique was proposed for studying the heat effect of the slag foaming with carbonates addition. It is based on the observation of the temperature changes. The method enables the study of the full decomposition inside the slag. The technique was tested on the dolomite and limestone decomposition in the temperature range of 1623-1723 K with a slag of the composition: CaO – 31%; SiO₂ – 31%; MgO – 7%; Al₂O₃ – 6%; FeO – 25%. The lower temperature limit of the measurement is limited by poor heat conductivity of the slag, while the upper limit is caused by very high speed of decomposition of the carbonates, which can result in partial slag splashing and/or unreacted carbonate particles blowing out of the crucible.

2. The heat effects of dolomite and limestone decompositions were determined at 1623 and 1673 K. It was found that the decomposition energy for dolomite and limestone for the studied slag composition is in the range 55-74% of theoretical values, which is attributed to the energy saving effect of slag foaming. No influence of sample shape on decomposition energy was found both for limestone and dolomite at 1623 and 1673 K. There is no appreciable influence of carbonate type as well. However, the shape of the sample can influence on the temperature changes profile.

3. The energy consumption for limestone and raw dolomite additions were studied in 100-ton EAF. It was found that, in the case of carbonate addition to liquid steel bath, the heat effects for limestone and dolomite (2255 and 2264 kJ/kg respectively) were 70% of the theoretical values. Carbonate additions along with scrap charging was found to result in larger energy losses.

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