

COMPARISON OF STEEL DESULPHURISATION AT HOMOGENISATION STATION WITH PHYSICAL MODELLING RESULTS

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The paper deals with evaluation of relevant information about transfer processes taking place in the interface slag – metal and with the assessment of the rate and course of steel desulphurization. The study of mentioned processes took place with the verification of the results obtained by the plant experiments in the homogenization station using 180 t ladle and in the physical model of the ladle in the geometrical scale 1 : 9 supplemented by homogenization nozzle. Plant and physical experiments were based on similar methodology. Samples of metal and slag were taken in regular time intervals for following evaluation of kinetics of the sulphur loss in the metal and appropriate increase of sulphur content in the slag.

Key words: steel, slag, desulphurization, homogenization station, physical modeling

INTRODUCTION

Secondary metallurgy is an essential part of modern steel production and it includes a whole range of types of refining treatment that are realized in the ladle at various units of secondary metallurgy, such as homogenization station (HS), ladle furnace (LF or IR-UT) and vacuum station (VD, VOD or DH) [1 - 2].

Reactions taking place in the ladle during metal refining are often very complicated. These operations are made under relatively high temperature and the mass transfer between two unmixable liquids (slag and metal) plays an important role at decreasing of impurities content in the producing steel [3]. Study of mentioned processes is very time- and finance-consuming under the plant conditions, that's why physical or mathematical modelling is used which is subsequently verified by plant experiments [4 - 7].

The aim of this work was to obtain relevant information about transfer processes taking place in the interface slag – metal and to assess the rate and course of the steel desulphurization. The study of mentioned processes took place with the verification of results obtained by plant experiments realized in the homogenization station and by physical model of the ladle supplemented by homogenization nozzle. For plant and laboratory experiments, methodology was created applied for plant experiments and physical modelling. In the homogenization station and during modelling, samples were taken in regular time intervals for evaluation of kinetics of

steel desulphurization and increase of sulphur content in the slag.

CHARACTERISTICS OF PLANT EXPERIMENTS AND PHYSICAL MODELLING

Plant experiments aimed to results verification of the course of steel desulphurization took place under the conditions of the steel shop Třinecké železářny a. s. (TŽ, a.s.). Proper experiments were realized in the homogenization station where steel homogenization by the help of argon, namely by the top nozzle element 700 l/min and bottom stir element 400 l/min takes place. The intensive steel homogenization under the slag which has a weak desulphurization effect is a primary aim of this unit. However, conditions are the same for the whole experiment (chemical composition and slag temperature don't change significantly).

Altogether 16 verification heats at treatment of unalloyed construction steel grade S355J (ČSN EN 10025-2) was carried out. The whole experiment was planned for 18 min (1080 s). During steel treatment in the homogenization station, steel and slag samples were taken, whereas steel was taken in the intervals of 3 min and the slag at the beginning and at the end of the experiment. All the samples were subsequently subjected to analysis which concerned namely the content of sulphur. The samples of slag were subjected to analysis of basic elements and oxides.

Experiments studying transfer processes were carried out on the physical model designed in a geometric scale 1 : 9 in reference to the real 180 t operating ladle. Blowing of inert gas in the model and also in the real ladle after the calculation according to the Freude modified criteri-

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on met the requirements. In the real ladle, argon was blown through the bottom stir element with the intensity of 400 l/min and through the top nozzle element 700 l/min. The flow rate in the model corresponded after calculation 3,021 l/min through the bottom block and 5,290 l/min through the top nozzle element [8].

The simulation of transfer processes is based on the balance between the solubility of iodine in oil and water solution of potassium iodide. In general, it may concern any iodide that is water-soluble. The weak complex compound KI_3 results from such dissolution and because the slag-simulating liquid, which still contains some dissolved iodine, is applied to the KI_3 water solution, the system is in misbalance. In order for the proportion of distributed iodine between both phases to come near the equilibrium, the iodine transfer from "steel" to "slag" needs to take place. The intensity of such transfer depends, among others, on the stirring intensity of both phases and thus on the regime option for inert gas blowing. The process of iodine transfer from iodide solution into oil is described using the ionic equation, according to which the iodine bound in complex KI_3 compound is extracted with the oil, similar to the way the sulphur is transferred from a metal to a slag under the real conditions [9].

During the experiment, the water solution samples are drawn from a standardized sampling point at regular intervals, during which the content of iodine is determined. This analysis uses the titration method, which is based on the selective chemical reaction of iodine with sodium thiosulfate ($Na_2S_2O_3$) to form NaI and $Na_2S_4O_6$. During the titration process, the rest of the free iodine in the solution is identified using a starch solution, which together with iodine creates a weak blue complex, the destruction of which reliably indicates the quantitative behaviour of the reaction. The more detailed methodology, including the derivation of relations, through which the iodine content remaining in the sample is calculated, is given in the work [10].

For the graphical representation of the kinetic curves dimensionless concentration was used. The reason for usage of dimensionless concentration was to eliminate the fluctuation of the starting concentration and thus to prevent distorting of compared curves. Dimensionless concentration was defined by the experiment beginning when the dimensionless concentration reached the value 1 and by the balanced concentration of both components which surrounded the interval with zero. Balanced concentration was experimentally determined under laboratory conditions.

Measured values were processed using the regression and correlation analysis method, while the best fit, even in terms of the physical nature of the process, has shown to be an exponential dependence described in the equation (1).

$$\tilde{c}_{[i]} = \exp\left(-\frac{k_w \cdot A}{V} \cdot t\right) \quad (1)$$

where:

$\tilde{c}_{[i]}$... dimensionless iodine concentration in water solution / -

k_w ... coefficient of mass transfer / m/min

A ... transfer surface / m^2

V ... volume of meltage / m^3

t ... time / min

Due to the impossibility of longer measurement, the length of plant experiments was shorter in comparison with model study. Undercooling of the meltage was imminent and other complications connected with it. But this deficiency doesn't impede the comparison of kinetic of element transfer by the help of defining of kinetics curve decrease in no way.

RESULTS AND DISCUSSION

Evaluation of obtained results was realized in three following parts. At first, evaluation of plant experiment in the homogenization station aimed to the course of steel desulphurization and changes of chemical composition of slag in the ladle was made. Subsequently, evaluation of physical modelling aiming the study of transfer processes slag – metal (or liquid – liquid) was realized. Finally, verification of obtained results from physical modelling and plant experiments was carried out.

Course of transfer processes in the homogenization station was also evaluated by the help of analysis of steel desulphurization characteristics in the ladle. Proper results of steel desulphurization are given in Figure 1. It is evident from these results that decrease of sulphur content in steel is gradual and desulphurization efficiency increases with the homogenization period when intensive steel stirring in the ladle leads to the increase of reaction surface presenting interface metal – slag. It is also obvious from the results that average decrease of sulphur content by 0,010 wt. % in the time interval $\tau = 18$ min can be observed.

It is also evident from Figure 1 that established regression dependence expresses obtained results with a high determination coefficient relatively well. Values confirm the achievement of similar results at repeating even when experiments were carried out in demanding

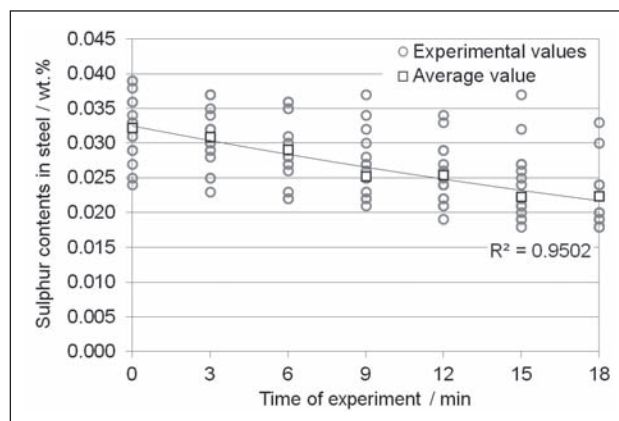


Figure 1 Desulphurization course in the homogenization station

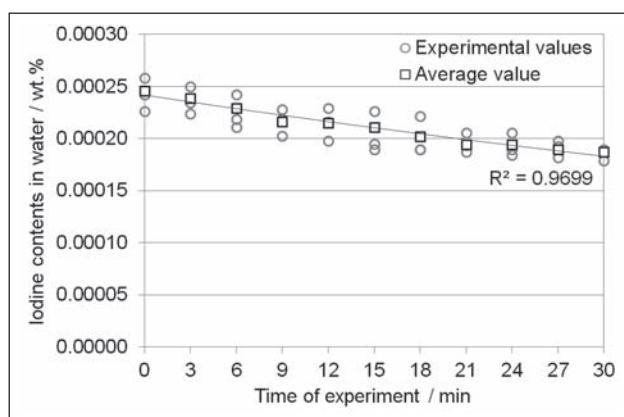


Figure 2 Course of iodine transfer from water solution into paraffin oil simulating steel desulphurization

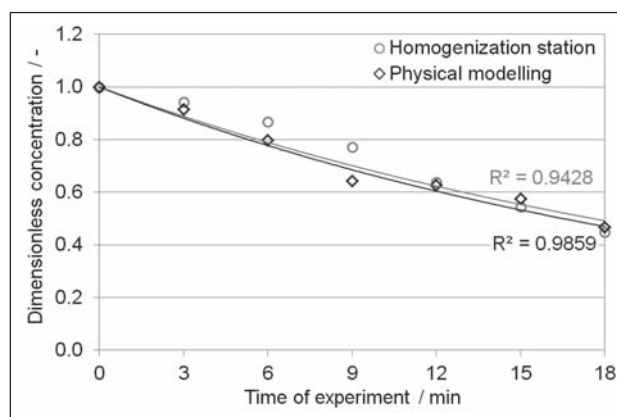


Figure 3 Comparison of kinetic curves of homologous experiment for model and real apparatus

plant conditions. There are evident specific extreme values in Figure 1 which are probably caused by penetration of ladle (oxidation) slag into the ladle. This penetration can cause the modification of chemical composition of slag which manifests in worsening of conditions of steel desulphurization and transfer processes in the interface metal – slag. Within the study of transfer processes in the homogenization station, balanced dimensionless transfer coefficient (L_s) that reached the value of 60, was defined.

Model experiment of combined blowing was carried out in a triple execution. All values, including average values, are shown in Figure 2. Values of concentration content are given in absolute weight concentrations because of the possibility of difference comparison between graphs in absolute and relative quantities.

It is obvious from Figure 2 that discovered regression dependence expresses measured results with high determination coefficient relatively well. Because the iodine contents in water solution and sulphur contents in the steel are in the absolute values incomparable, dimensionless values of concentrations will be presented below. Within the study of transfer processes, balanced dimensionless transfer coefficient (L_s) with the value 10 was defined.

Although the difference of equilibrium distribution coefficient is relatively noticeable at both systems (for model it reaches L_s ca 10 and for real apparatus ca 60), disproportion is compensated with an increased proportion of slag volume to the metal volume for a model. This problem is solved with the conversion criterion K .

$$K = \frac{V_s \cdot \rho_s \cdot L_s}{V_1 \cdot \rho_1} \quad (3)$$

where:

V_s ... slag volume / m^3

ρ_s ... slag density / kg/m^3

L_s ... balanced dimensionless transfer coefficient / -

V_1 ... metal volume / m^3

ρ_1 ... metal density / kg/m^3

Proportion of values for this criterion for model and real apparatus has the value near 1. In this way, total “desulphurization” capacity of slag is proportionally

the same and it isn't necessary to solve it with other calculation.

Experiments results are given into one graph presenting Figure 3. Results of concentration decrease were calculated into dimensionless values and interspersed with kinetic exponential curves that it was easier to compare each other. Average values were used for results verification of physical modelling and plant experiments. In case of plant experiments, analysis of results and melting paper was carried out. Heats with non-standard conditions (such as penetration of ladle slag, etc.) were eliminated.

High conformity between the results obtained during experiments in the real apparatus (homogenization station) and in its reduced model is obvious at the first sight when the curves for model and the real apparatus cover almost each other. Differences between curves are minimal and because more calculations aren't necessary according to the criterion K , it is possible to consider the setting of physical model as credible and qualified for modelling of real processes.

CONCLUSIONS

Within the plant and laboratory experiments, verification of plant experiments made in the homogenization station and model results was carried out. Within the verification, first plant experiments were carried out and then physical modelling according to the conditions applied for plant experiments was realized. It was a combined blowing with both top nozzle element and bottom stir element at the same time. Resulting kinetic curves from plant experiments and physical modelling in the homogenization station were almost the same. It is possible to state that the setting of physical model can be consider as credible and qualified for modelling of real processes in the ladle.

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