

VERIFICATION OF PHYSICAL MODELLING OF STEEL DESULPHURIZATION IN THE PLANT CONDITIONS OF THE HOMOGENIZATION STATION

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Abstract

Steel treatment in the ladle in the secondary metallurgy units can be described as refining processes taking place between two non-mixable liquids representing metal and slag, namely under relative high temperatures. During refining processes, transition process appears between metal and slag which has an impact on increasing of micro-cleanness and mainly on steel desulphurization representing an important transfer process. Mentioned paper deals with verification of the results of desulphurization course of steel obtained by the model study in the physical model of the ladle with the help of plant experiments in the homogenization station (HS) with the inert gas. The homogenization station seems to be appropriate for the study of desulphurization because its primal aim is intensive homogenization of steel under the slag which has got a weak desulphurization effect. However, conditions during the whole experiment are constant because both chemical composition and slag temperature don't significantly change during the course of the whole process. Proper plant experiments were made in the 180 t ladle which served as a pattern for creation of the physical model in the geometric scale 1:9. The plant experiment was based on the methodology used at the physical modelling which consists in regular taking of metal and slag samples for evaluation of kinetics of the loss of sulphur in metal and the appropriate increase of sulphur content in slag. The goal of this paper was to obtain relevant information about transfer processes taking place in the interface slag - metal and to assess the rate and course of steel desulphurization in the physical model and in the ladle at the homogenization station.

Keywords: steel, slag, desulphurization, homogenization station, physical modelling

1. INTRODUCTION

Secondary metallurgy is an essential part of the modern steel production and it includes a whole range of types of refining treatment. Steel desulphurization, elimination of unwanted gases (hydrogen or nitrogen), controlled deoxidation and steel alloying, homogenisation of liquid steel, modification of inclusions, improvement of micro cleanness and overheating temperature modification of steel defined by a unit for continuous steel casting, etc. belong among them. These technological operations presenting steel refining are made 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, RH 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. Within the steel refining, more types of mass transfer exist: mass transfer between gas and liquid (adsorption and desorption of gas or reaction of gas - liquid), between liquid and liquid (reaction slag - metal), between solid particles and liquid (reaction with slag-making additions or lining) or between solid particles and gas (flotation of inclusions). Mass transfer slag - metal (or liquid - liquid) during the refining of liquid steel can be supported by creation of active (refining) slag and also by increasing of intensity of renewal of adequate interphase environment by the help of blowing of inert gases through porous bottom blocks situated in the bottom of the ladle furnace or through the nozzle submerged into the steel bath [3]. Study of mentioned processes is very time- and finance-

consuming, that's why physical or mathematical modelling is used which is subsequently verified by plant experiments [4, 5, 6].

Aim of this work was to obtain relevant information about transfer processes taking place in the interphase slag - metal and to assess the rate and course of steel desulphurization. Study of mentioned processes took place by the help of verification of results obtained from physical model of the ladle enriched with homogenization nozzle and by plant experiments realized in the homogenization station. Within the physical modelling, laboratory methodology was created which was modified for plant experiments.

2. CHARACTERISTICS OF PHYSICAL MODELLING AND PLANT EXPERIMENTS

Study of transfer processes in the ladle presenting homogenization station was initially made by the physical modelling. On the basis of results obtained in the physical model, verification by the help of plant experiments in the homogenization station was planned which was a pattern at the construction of the model of 180 t ladle. Proper experiments took place on the basis of prepared methodology for subsequent evaluation and verification of results.

2.1 Conditions of physical modelling of the homogenization station

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. The model mentioned in **Fig. 1** is located in the Laboratory



Fig. 1 Model of the ladle with top nozzle element and bottom stir element in a scale 1 : 9

of physical and numerical modelling at the Department of Metallurgy and Foundry, FMME, VSB - Technical University Ostrava. At research of transfer processes between slag and metal, more accurate methodology of modelling was created. Its basics came out from previous works made at the Department of Metallurgy [7]. Development of new methodology was to find more suitable model liquids which allow simulation of real system components (slag, metal bath, the monitored element, etc.) as well as the more precise measurement methodology.

Metal bath was for its physical resemblance defined by criteria of similarity replaced by water, more precisely by a water solution of potassium triiodide which simulated molten steel with defined content of dissolved element such as sulphur under real conditions.

Liquid that should simulate the slag under the model conditions must meet following requirements:

- good extraction of iodine from water-based solution of iodine and its insolubility in water,
- lower density and higher viscosity in comparison with water,
- health harmlessness (must not be toxic), the stability in the oxidation environment,
- adequate interphase tension between water solution and this liquid.

After conducting many tests, the best conformity for one type of paraffin oil whose properties were in good agreement with all the required parameters was found. Paraffin oil is a non-polar solvent which is capable of extracting iodine from the water solution and in this way the "gross analogy" of desulphurization process is observed [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 (1), 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 paper [10].

2.2 Course of plant experiments in the homogenization station

Plant experiments aimed to results verification of the course of steel desulphurization took place under the conditions of the steel shop TŽ, a.s. Proper experiments were realized in the homogenization station mentioned



Fig. 2 Homogenisation station (HS) with the top nozzle element in the Fig. 2 where steel homogenization by the help of argon, namely by the top nozzle element ($700 \text{ l}\cdot\text{min}^{-1}$) and bottom stir element ($400 \text{ l}\cdot\text{min}^{-1}$) 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). Homogenization station seems to be appropriate for desulphurization study and for the subsequent verification with the results of physical modelling under the same marginal model conditions.

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). Due to lack of time the experiment was in some heats shortened to 15 min (900 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. Temperature of steel was also measured at each sample taking. 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 [11, 12].

3. EVALUATION OF OBTAINED RESULTS

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

3.1 Evaluation of results in physical modelling

As mentioned before, experimental methodology of plant experiments is based on model study to make both methodologies comparable. Samples of steel and water solution were taken in regular defined time intervals. Blowing of inert gas in the model and also in the real ladle after the calculation according to the Freude modified criterion met the requirements. In the real ladle, argon was blown through the bottom stir element with the intensity of 400 l·min⁻¹ and through the top nozzle element 700 l·min⁻¹. The flow rate in the model corresponded after calculation 3.021 l·min⁻¹ through the bottom block and 5.290 l·min⁻¹ through the top nozzle element.

Due to the impossibility of longer measurement, the length of plant experiments was in comparison with model study shorter. 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.

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 (2).

$$\tilde{c}_{[i]} = e^{-\frac{k_w A}{V} t} \quad (2)$$

where: $\tilde{c}_{[i]}$ - dimensionless iodine concentration in water solution, (-)

k_w - coefficient of mass transfer, (m·min⁻¹)

A - transfer surface, (m²)

V - volume of meltage, (m³)

t - time, (min)

It is obvious that the coefficient $k_w A$ is an expression of "steepness" of the exponential regression curve. The higher this value is, the faster the iodine transfer into the "slag" is. On the contrary, if the coefficient is close to zero, the transfer processes are slow and inadequate. For standardized experimental conditions of the model study, where the only variable is the intensity of blowing (Q_v) and the stir element positions (X_x , X_y , and X_z), the dependence of the $k_w A = f(Q_v, X_x, X_y, X_z)$ coefficient can be recorded.

Transfer rate of iodine into water solution can be observed because of the change of oil colour. With the increasing iodine concentration in oil, it changes the colour from transparent, through pink to dark violet. The course of iodine transfer from water solution into oil is given in **Fig. 3**.

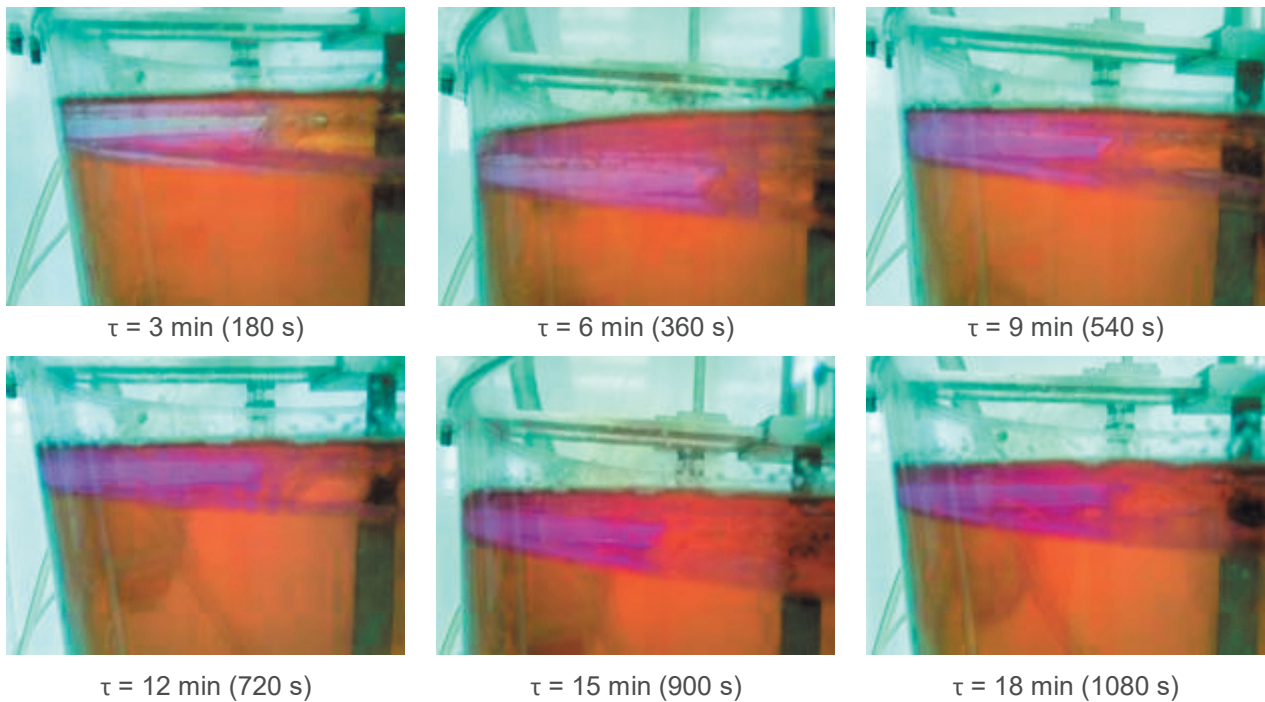


Fig. 3 Visual iodine transfer from its water solution into paraffin oil during experiment

Model experiment of combined blowing was carried out in a triple execution. All values, including average values, are shown in **Fig. 4**.

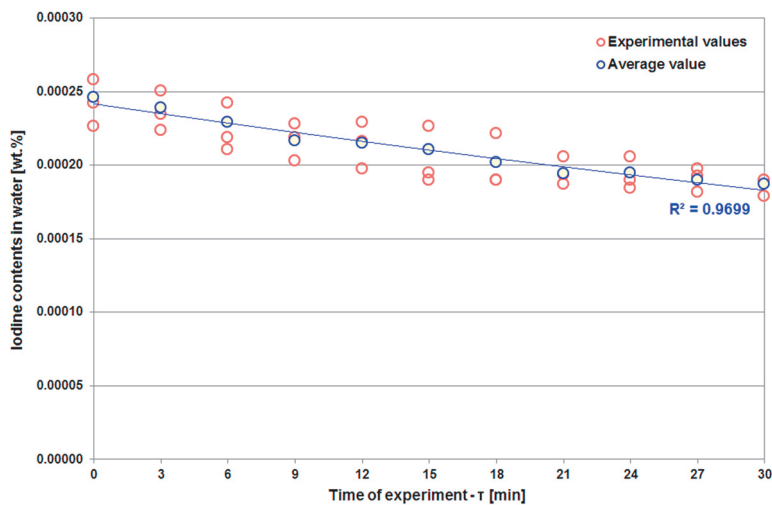


Fig. 4 Course of iodine transfer from water solution into paraffin oil simulating steel desulphurization

Values of concentration content are given in absolute weight concentrations because of the possibility of difference comparison between graphs in absolute and relative quantities. Within the study of transfer processes, balanced dimensionless transfer coefficient (Ls) with the value 10 was defined.

It is obvious from **Fig. 4** 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 in the chapter dealing with results comparison.

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3.2 Evaluation of plant experiments

Series of experimental heats was carried out in the homogenization station. They were focused on the course of steel desulphurization, namely within the study of transfer processes in the interphase metal - slag. A weak desulphurization effect is achieved in this unit intended for intensive steel homogenization under the slag. However, conditions are during the whole experiment the same because chemical composition and its temperature don't change significantly.

Proper desulphurization effect in the homogenization station reached the desulphurization degree 29 %. Partial or full slag melting connected with the partial steel desulphurization happens during inert gases blowing through the top nozzle element and bottom stir element. During steel homogenization in the ladle, mixing and dissolving of particular components with the creation of oxides mixture showing generally lower temperature than pure oxides happens.

Influence of inert gases blowing on slag dissolving in the ladle is evident from **Fig. 5**. It can be seen during the arrival to the homogenization station ($\tau = 0$ min) that slag in the ladle is partially dissolved and it can't significantly participate in the steel desulphurization. A part of slag, which is in contact with steel in the interphase metal - slag, participates active in the steel desulphurization. However, slag surface presenting the interphase slag - atmosphere is not completely dissolved. At departure from homogenization station ($\tau = 18$ min) the slag in the ladle is dissolved. This liquid slag can significantly participate in desulphurization and refining of steel.

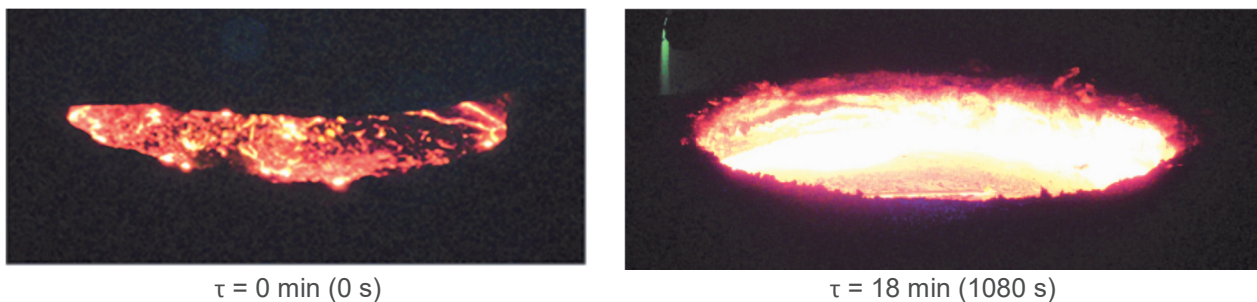


Fig. 5 Illustration of slag pictures in ladle at the beginning and at the end of treatment in the homogenization station

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 **Fig. 6**. It is

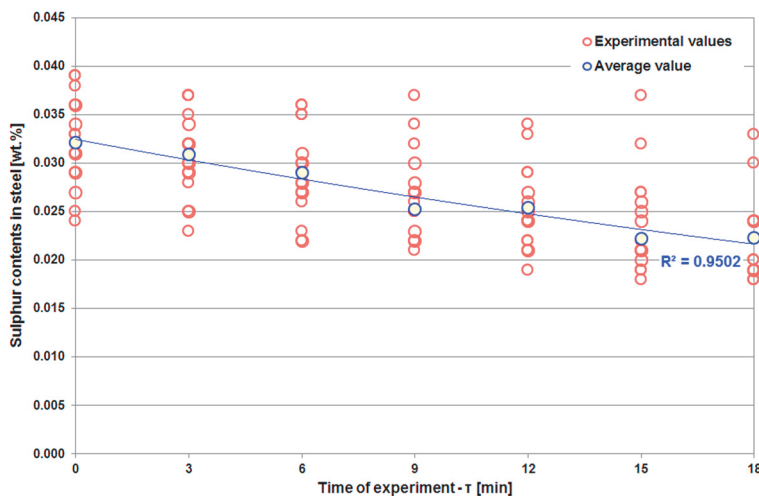


Fig. 6 Desulphurization course in the homogenization station

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 interphase 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 **Fig. 6** 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 plant conditions. There are evident specific extreme values in **Fig. 6** 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 interphase 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.

3.3 Comparison of results of physical modelling with plant experiments

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 .

$$K = \frac{V_s \cdot \rho_s \cdot L_s}{V_l \cdot \rho_l} \quad (3)$$

where: V_s - slag volume, (m³)
 ρ_s - slag density, (m³)
 L_s - balanced dimensionless transfer coefficient, (1)
 V_l - metal volume, (m³)
 ρ_l - metal density, (m³)

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 **Fig. 7**. Results of concentration decrease were

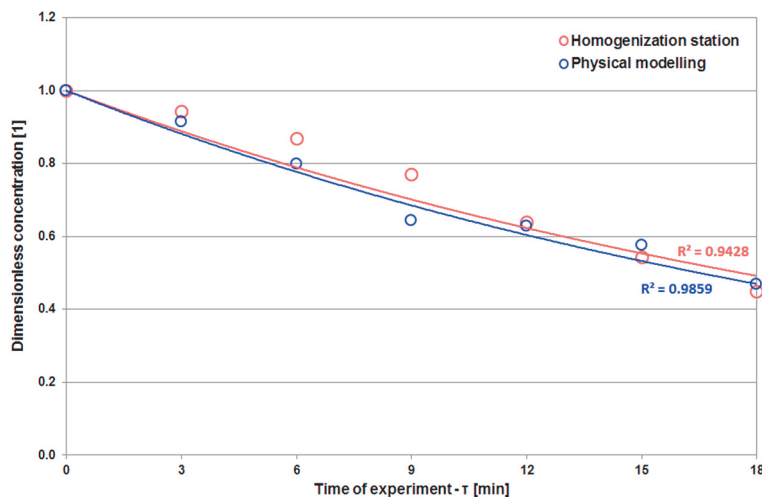


Fig. 7 Comparison of kinetic curves of homologous experiment for model and real apparatus

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 laboratory and plant experiments, verification of model results and plant experiments made in the homogenization station was carried out. Proper verification consisted in realization of laboratory experiments in the physical model of the ladle in the geometrical scale 1 : 9 enriched with top nozzle element and bottom

stir element. Subsequently, plant experiments in the 180 t ladle during steel treatment in the homogenization station used for intensive temperature and chemical homogenization with the possibility of weak steel desulphurization were carried out. Plant experiments proceeded from the methodology used by physical modelling consisting in regular taking of samples of metal and slag for evaluation of kinetics of sulphur decrease in metal and adequate increase of sulphur content in slag. Within the verification, first physical modelling was carried out and then experiments under beginning and marginal conditions proceeding from physical modelling were made. It was a combined blowing with both top nozzle element and bottom stir element at the same time. Resulting kinetic curves from physical modelling and plant experiments 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.

ACKNOWLEDGEMENTS

This paper was created in the Project No. LO1203 "Regional Materials Science and Technology Centre - Feasibility Program" funded by Ministry of Education, Youth and Sports of the Czech Republic and financial support project No. SP 2014/61 and SP2014/62.

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