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# Investigation of Surface Wettability of Hard Iron with the Slags of FeO-CaO-SiO2 and FeO-Al2O3-SiO2 Systems

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For a number of reduction technologies of ferrous production the period, during which the first ferrous slag phase coexists with a hard metallic phase of newly reduced iron, is a characteristic feature. The interaction of these phases highly influences the processes of metal saturation by carbon and other impurities, as well as processes of metal and slag separation into independent phases. Surface wettability of hard iron with the liquid ferrous slags of FeO-CaO-SiO2 and FeO-Al2O3-SiO2 systems at temperature 1100-1300 °C was investigated experimentally.

Keywords: IRON ORE REDUCTION, FIRST SLAG, IRON, WETTABILITY

## Introduction

Slag system FetO-CaO-$SiO_2$ is one of the most widespread and important processes in the steel industry, associated with iron ore reduction. However, such an important parameter as wettability by slags of the system of reduced iron, which defines the conditions of mass transfer between the metal phase and the environment when it is reduced by both solid fuel and gas, is still understudied. Views regarding the role of the first slag during the reduction process are rather contradictory. According to A.A. Baikov's scheme [1] reduction observes appearance of a liquid phase in the ore-coal pellet as an undesirable phenomenon that dramatically reduces specific surface area of contact between the oxide and the reducing gas. However, studies carried out previously at the National Metallurgical Academy of Ukraine, showed [2] that the appearance of the slag phase in the ore-coal pellet is accompanied by accelerated reduction of iron oxides due to the increased rate of diffusion.

Later, in the works of various authors, for example [3], it is shown that due to the development of the Marangoni effect during iron ore reduction in presence of the first slag phases, the transfer by means of surface-tension gradient ensures the development of much more intensive mass transfer than during the diffusive one.

Currently interest in the reduction processes involving ferriferrous slags has increased significantly, what is mostly due to the development of new reduction technologies for the production of iron (for example ITmk3 [4]), as evidenced by numerous studies of the mechanism of reduction in heterogeneous systems containing liquid (first slag), solid (just reduced iron, solid fuel) and gas phases [5].

Regularities of interfacial interaction in this heterogeneous system to a great extent determine the development of iron carbonization and its sulfur and silicon saturation. Thus, G.A. Volovik [6] established that, at the site from the burden level to the middle of the shaft the rise of the total sulfur content in agglomerate is observed, however later the reduced spongy iron is not saturated with sulfur, and only after the formation of hot metal sulfur content in it dramatically increases, reaching a maximum (0,3-0,4%) at the level of the tuyeres, and further reducing by the desulphurization of droplets in a slag layer. Similar results were obtained subsequent to the results of frozen blast furnaces dismantling for other impurities [7]: metal egress was observed after carbonization up to 0.8-1.0%, in the metal droplets from the furnace waist - 2.0% C, and from the bosh 4,0% C; in the area of viscous-plastic state metal contains less than 0,03% Si, after carbonization and beginning of metal egress the content of silicon reaches 0.2%, and in the area between the bosh and the waist 2% when smelting pig iron.

By means of studying the processes of softening and melting of iron ore materials during reduction and heat processing [8] it is shown that in conditions of viscous-plastic state under load gas-barrier material is formed, the outer part of which is enveloped by slag, from which much of the FeO is already reduced, while the internal layers contain the reduced metal sponge and slag with high iron content. The development of separation processes of metal and slag is determined by the conditions of formation fluid slag and subsequent carbonization and metal melting.

The role of processes, taking place between solid and molten state of materials, for the alternative reduction technologies of metal production is less studied, but it can be assumed that in this case, the regularities of mass transfer are largely determined by the interfacial interaction between solid metal and liquid slag phases.

A detailed analysis of literature sources indicates a lack of knowledge of wettability of hard iron with slags containing FeO. Practically the only published work, in which the experimental data on the wetting angle of hard iron by liquid ferrous slags were obtained, is an article by M. Hino et al [9], which investigates some parameters of the interaction of complex ferrous slags, corresponding the composition of first slags in conditions of Japanese blast furnaces maintenance. The data on the impact of FeO content on the wetting angle of the first slag FeO-2CaO.$SiO_2$.$Al2O_3$ (Gehlenite)-CaO.$SiO_2$ at a ratio of Gehlenite / (CaO.$SiO_2$ + Gehlenite) = 0.3 were obtained. It is established that the surface of iron is well wetted by such slags, the wetting angle of which is 10-30°, moreover a relatively high level of scatter of measurement readings in the general tendency to decrease the wetting angle with increasing FeO content in slag. However, the results provide only a limited understanding of the regularities of wetting in this system.

## Methodology

The objective of this paper is to study the characteristics of the interaction between the first liquid slag and solid metal phases in conditions of typical for both the blast process, and other reduction technologies of metal production.

The purpose of the work is obtaining experimental data on the patterns of interfacial interactions in the hard iron - liquid ferrous slag system, which is the basis of rational choice of the iron ore material and technological conditions of reduction.

The wettability of iron surface with slags was researched by means of sessile drop method. The experimental setup is shown in Figure 1. The following components were used for the preparation of the slag mixture: $SiO_2$ (98,0%), CaO (97,5%) and FeO. Iron monoxide has been synthesized by using the following method. Metallic iron (powder, particle size -10 µm, purity 99.99%) and $Fe2O_3$ (analytical reagent grade, powder, particle size - 5 µm, 99.95%) were mixed in a stoichiometric ratio corresponding to the reaction $Fe_2O_3$ + Fe = 3FeO and the mixture was heated in a quartz flask in an inert atmosphere at a temperature of 1020-1050° C for 5 h. Then the content of the flask was hardened by immersion into water. Further synthetic slag of the chosen composition was formed by weight measuring, mixing thoroughly and grinding in a mortar the obtained ferrous product with $SiO_2$, CaO and $Al_2O_3$ (analytical grade reagents).

The compositions of the experimental slags were chosen taking into account the state diagram of the FeO-CaO-$SiO_2$ system, where the slag with a relatively low temperature of liquidus belong to the crystallization region of wollastonite, olivine and wustite. Liquidus surfaces in these crystallization regions are relatively plateau-like compared to the surrounding steeply rising liquidus tridymite surfaces and dicalcium silicate. Easily fusible silicates of the previously mentioned three crystallization regions are most similar in composition to the first slag, emerging in the final stages of iron ore material reduction in a blast furnace or other reduction aggregate. The compositions of the investigated slags are shown in **Table 1**.

**Table 1**. Chemical composition of slags

| Experiment № | $SiO_2$, % | CaO, % | CaO/$SiO_2$, % | FeO, % | $Al_2O_3$, % | Wetting angle, (θ) g. | Temperature, °C |
|---|---|---|---|---|---|---|---|
| 1 | 50,0 | 22,0 | 0,44 | 28,0 | 0 | 60,0 | 1200 |
| 2 | 43,0 | 29,0 | 0,67 | 28,0 | 0 | 50,0 | 1200 |
| 3 | 38,0 | 34,0 | 0,89 | 28,0 | 0 | 44,0 | 1200 |
| 4 | 43,0 | 11,0 | 0,26 | 46,0 | 0 | 38,5 | 1150 |
| 5 | 38,0 | 16,0 | 0,42 | 46,0 | 0 | 19,0 | 1150 |
| 6 | 26,0 | 28,0 | 1,08 | 46,0 | 0 | 9,0 | 1150 |
| 7 | 38,0 | 0,0 | 0,0 | 62,0 | 0 | 5,5 | 1250 |
| 8 | 32,0 | 6,0 | 0,19 | 62,0 | 0 | 8,5 | 1150 |
| 9 | 25,0 | 13,0 | 0,52 | 62,0 | 0 | 22,2 | 1100 |
| 10 | 28,5 | 0,33 | 0,01 | 52,7 | 11,33 | 18,0 | 1180 |

The slag is number 10 represents the point of the least refractory area of the corresponding three-component slag system.

Slags, investigated by M. Hino et al. [9], belong to a different slag system, in particular, their basicity was 1.08 and the content of $Al_2O_3$ 8,3-11,5%.

Slag sample 5 mm in diameter and weighing about 200 mg were placed on a substrate made of commercially pure iron (АРМКО iron) installed on a pedestal of lightweight chamot in isothermal furnace zone. Directly next to the sample was a platinum-rhodium thermocouple. Another thermocouple was under the reaction tube of the furnace to control the isothermal reaction region. During heating the reaction chamber was fed with commercially pure argon (99,99% Ar). The rate of heating of the samples was 10° C per minute. In order o obtain data about the contact wetting angle a digital camera was used. The contact wetting angle was determined for the melting temperature (liquid hemisphere formation) plus 20° C. Digital processing of images was performed using the free software ImageJ [10].

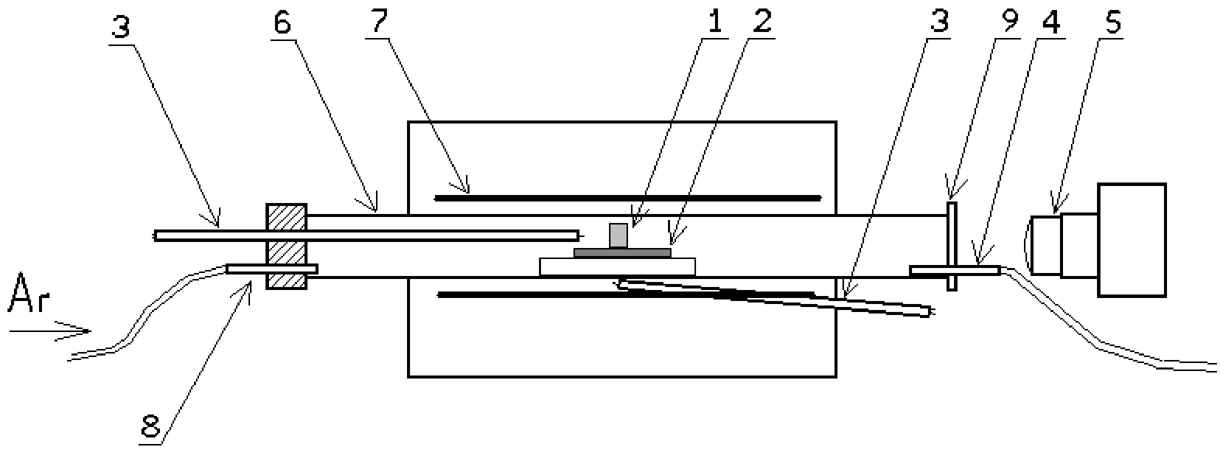


**Figure 1.** The scheme of the experimental unit: 1 –slag sample, 2 – iron base, 3 – thermocouples, 4 – gas disposal, 5 – camera, 6 –reaction tube, 7 – heating elements, 8 – gas input, 9 – quartz glass

**Results and Discussion**

The results of measurements of wetting angles are presented in the **Table 1**.

First of all, it is necessary to acknowledge good wettability of the iron surface with slags containing FeO. In general, the experimental results presented in **Figure 3** are in agreement with data on the effect of FeO content in slag on the wetting angle obtained by M. Hino et al [9], although in the present study higher values of contact wetting angle were obtained, due to different methodological approach to the measurement of this parameter: we determined the wetting angle when the furnace temperature was equal to the temperature of hemisphere emerging plus 20° C, while in study [9], the temperature measurement was fixed to 1350° C. Decrease of FeO content leads to the increase of the contact wetting angle (**Figure 2**). The effect of FeO content on the wetting angle is so dominant that the slag number 10, although it refers to a three-component system containing Al2O3, yet fits into the overall pattern of influence of the FetO content on the wetting angle.

The experimental data also allow estimating the influence of the basicity of slag on the iron wetting (**Figure 3**).

According to the results of multiple regression analysis, the following connection was obtained for the contact wetting angle:

$\theta$ = 98,02 - 15,19•CaO/SiO2 - 1,38•FeO, (R = 0,79),

where FeO, CaO, SiO2 – content of the corresponding components in slag, mass. % by weight.

Management of the slag composition,which provides the movement of the first slag phase from one crystallization region to another, can significantly reduce the influence of the basicity on the contact wetting angle. Thus, the slags 1-3 with 28% content of FeO are in the crystallization regions of wollastonite, and for them basicity is increasing with a decrease of $\theta$.

Slags 7-8, containing 62% FeO, are in the crystallization region of olivine and have approximately equal values of contact wetting angle, but slag 9, which at the same FeO content in

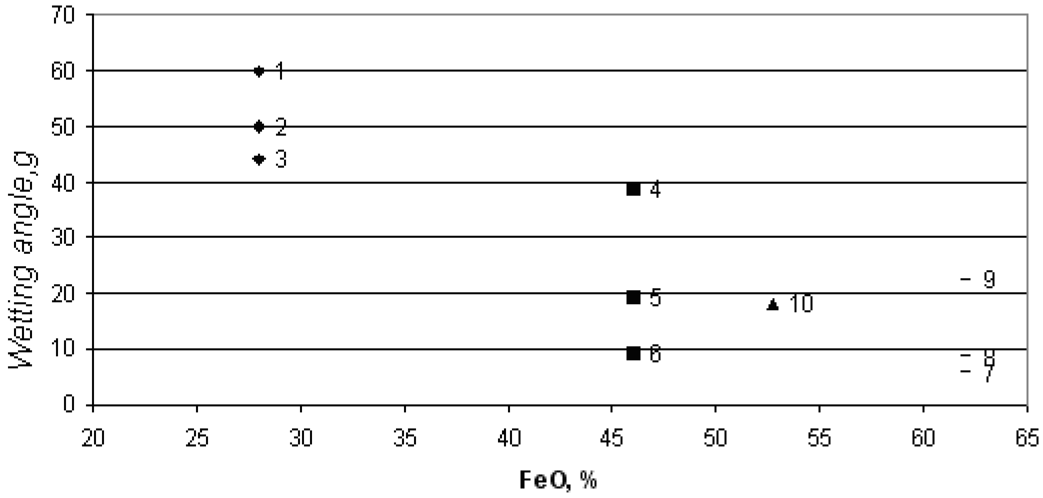


**Figure 2.** Dependence of the contact wetting angle of iron surface with slag on FeO content

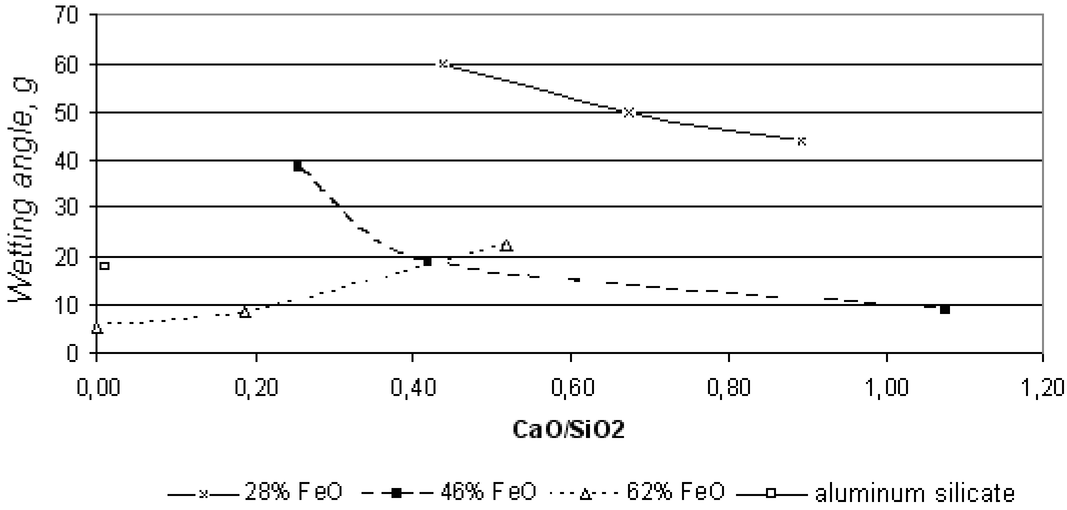


**Figure 3**. Dependence of the contact wetting angle of iron surface with slag on the ratio $CaO/SiO_2$ with different FeO

the crystallization region of wustite, obtained higher values of θ. This explains the inverse dependence of the angle θ from the basicity for slags with FeO content of 62%. Among the slags belonging to the group of 46% FeO, points 4 and 5 are in the area of the eutectic line of intersection of the planes of crystallization of olivine and wollastonite, moreover slag 4 is close to the ternary eutectic point on the border of the crystallization of tridymite, wollastonite and olivine. Unlike the plateau-like areas of wollastonite and olivine, tridymite area is characterized by a significant gradient of the liquidus surface. In this regard, it is not surprising that a relatively small increase in the basicity of the transition from point 4 to point 5 is accompanied by a sharp decrease in contact wetting angle. At the same time, a very substantial increase in the basicity of the transition from point 5 to point 6, which lies in the crystallization region of olivine, much less effect on the magnitude of the contact wetting angle, what is connected with the movement of crystallization of wustite into a plateau-like region. Since the conditions of wetting just reduced iron with the first slag have a significant impact on the regularities of carbonization of the metal and its saturation with sulfur, the results of this study suggest the possibility of management of these processes by selecting the rational structure of iron ore material and the reduction mode.

### Conclusions

The surface wettability of hard iron surface with first ferrous slag was studied and the following regularities of changing the contact wetting angle depending on FeO content and the ratio of $CaO/SiO_2$ were established:

1. Iron is good wetted by $FeO\text{-}CaO\text{-}SiO_2$ slag for all compositions that exist in the liquid state at temperatures below 1250°C. The model of changing the wetting angle of the iron surface for $FeO\text{-}CaO\text{-}SiO_2$ slags was obtained.
2. The increase of FeO content leads to a decrease of contact wetting angle.
3. Improving wettability and increasing basicity are observed for slags belonging to the same crystallization region.
4. Slag from the eutectic region of three-phase slag diagram $FeO\text{-}SiO_2\text{-}Al2O_3$ also wets the surface of iron well; moreover the effect of FeO content on the wettability is of defining value.

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### Исследование смачиваемости поверхности твердого железа шлаками систем FeO-CaO-SiO2 и FeO-Al2O3-SiO2

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Для целого ряда восстановительных технологий производства черных металлов характерным является наличие периода, в котором первичная железистая шлаковая фаза сосуществует с твердой металлической фазой свежевосстановленного железа. Взаимодействие этих фаз оказывает значительное влияние на развитие процессов насыщения металла углеродом и другими примесями, а также разделения металла и шлака в самостоятельные фазы. Экспериментально исследована смачиваемость поверхности твердого железа жидкими железистыми шлаками систем $FeO\text{-}CaO\text{-}SiO_2$ и $FeO\text{-}Al_2O_3\text{-}SiO_2$ в диапазоне температур 1100-1300°C.