

PRODUCING A WÜSTITE MELT BY THERMAL DECOMPOSITION OF HEMATITE PELLETS WITH ARGON PLASMA

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ABSTRACT

Reducing CO₂ emissions is of paramount importance, in order to address the issues of global warming. The negative contribution of Ukrainian metallurgists to atmospheric pollution over the past 20 years amounted to about 1 bln t of carbon dioxide by the year 2020. The solution can be found in the transition to the production of “green steel”, i.e. steel manufactured from direct hydrogen-based reduction iron. Under the conditions of applying plasma heating, high temperatures lead to a rapid melting of pellets, thermal decomposition of oxides occurs, and a reducing agent (hydrogen) is activated. Decomposition of oxides during the heating and melting process accelerates the overall process of pellet reduction to wüstite. And only in that moment, the use of hydrogen for reduction of iron and its deoxidation becomes justified. It was established that forming of a wüstite melt is possible without the use of a reducing agent during plasma melting in an argon atmosphere.

KEYWORDS: direct reduction, pellets, thermal decomposition, kinetics, magnetite melt, dilution with iron, wüstite

INTRODUCTION

Steelmaking is a large source of greenhouse gases. In 2022, 1.91 t of CO₂ were emitted per t of steel. The production of 1 t of steel, depending on the smelting method, emits 0.4–2.4 t of CO₂. The CO₂ emissions intensity and power consumption are calculated based on the weighted average steel production using different schemes: blast furnace — oxygen converter, blast furnace — electric arc furnace and direct reduced iron production in an arc furnace [1].

In 2023, the top 10 polluting countries increased their industrial emissions to a record 24.5 bln t of CO₂ compared to 23.9 bln t (+2.5 %) in 2022. The three major polluters were China, the United States and India, which together accounted for more than 53 % of all industrial emissions. China emitted a record 11.2 bln t of CO₂, which is an increase of 642 mln t compared to 2022 and the highest annual growth since 2011 [2, 3]. As for Ukraine, according to Ukrmetallurgprom, its metallurgical enterprises produced 6.19 mln t of steel in 2022, and 6.23 mln t in 2023. Experts predict that Ukrainian steelmakers will be able to increase steel production to 7–8 mln t. It should be noted that this forecast can be considered very optimistic, and the main reason here is the loss of a number of enterprises in Donetsk region, as well as the forced shutdown of a number of other enterprises [4, 5]. If we assume an average CO₂ emission of 1.4 t per t of steel, Ukrainian metallurgical plants will emit at least 8.7 mln t annually in 2022 and 2023, and over the 20 years from 2000 to 2020, 663.1 mln t of steel were smelted [6]

and, even according to underestimates, about 1 bln t of carbon dioxide were emitted. Such is Ukraine's negative contribution to air pollution.

Today, it is widely recognised that reducing CO₂ emissions is of paramount importance in combating global warming. The gas accumulated in the atmosphere absorbs and stores heat in the infrared range. A CO₂ concentration of one part per mln (1 ppm) is equivalent to adding approximately 7.8 Gt of carbon dioxide to the atmosphere [7].

Today, most blast furnaces in Europe are over 25 years old, and only a few of them have undergone modernization [2, 8]. This opens up the possibility of replacing some of the production capacities with a more updated steelmaking technology using direct reduction of iron ore pellets or ore with hydrogen, followed by smelting in various types of furnaces.

Transition to green steel production faces not only technological and design challenges. One of the most important areas of works to reduce carbon emissions is the production of hydrogen on a production scale, which is directly related to the development and launch of powerful electrolyzers and the generation of a significant amount of green electricity. According to estimates given in [2], electrolyzers will consume approximately 296 TWh of electricity per year. According to the online edition of “*Ekonomichna Pravda*”, electricity production in 2021 was 156.56 TWh [9] (156.56 bln kWh), which is half as much as the electricity consumption by electrolyzers.

Technologically, there are two ways of direct iron reduction from oxides by hydrogen. The first method,

which is the most developed and the one which uses existing production capacities, is the production of sponge iron using a hydrogen or a hydrogen-carbon environment. The use of natural gas or adding carbon to the hydrogen atmosphere have a positive effect on the reduction kinetics, but it does not completely eliminate carbon dioxide emissions. Reduction using ammonia as a reducing agent can give positive results, in particular, when reducing iron in the solid state [10, 11]. According to thermodynamic calculations, the degree of metallization is expected to improve significantly by increasing the amount of ammonia in the gas atmosphere, reaching 97 % when using 20 % of ammonia.

The method of hydrogen reduction and production of iron in the form of a sponge is not perfect. Its main disadvantages are the long time of reduction and the need to use separate equipment for reduction and melting. It is possible to combine these two processes by using high-temperature hydrogen plasma as an energy source for reduction and melting.

STATE-OF-THE-ART OF THE ISSUE

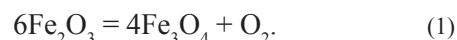
Plasma melting has a number of advantages over electric arc melting. The main advantage is that the process of iron reduction is intensified due to high plasma temperatures (hydrogen activation, acceleration of mass transfer, production of reduced iron in a liquid state and the possibility of melt alloying without intermediate production of iron ingots with their subsequent remelting). Also, an equally important advantage is a decrease in specific electricity consumption. For example, depending on various factors, its total specific power consumption for an electric arc furnace ranges between 500 and 700 kWh, and for a plasma arc furnace it is approximately from 350 to 550 kWh per 1 t of melted steel [12].

Hydrogen is an excellent reducing agent at both low and high temperatures. Moreover, when hydro-

gen molecules transfer into the plasma state, they can receive additional internal energy of oscillating and rotational motion, and transfer into atomic and ionised states. Free electrons, phot and other elementary particles are observed in the plasma. Their ratio depends on the plasma temperature, which can reach tens of thousands of degrees. However, the temperature of the liquid metal in plasma-arc melting is much lower and in the plasma plume action zone is about 3000–4000 K [13–15]. As a rule, excited molecules and atomic hydrogen interact with metal under real temperature conditions. Due to their high reactivity, the reduction of iron oxides occurs under much more favourable thermodynamic conditions than the reduction with hydrogen gas alone. PAM provides and improves the kinetic conditions for the interaction of hydrogen with oxides, which at solid state temperatures often determine the rate of reduction.

In the production of iron by direct reduction from oxides using hydrogen plasma, the first step is the melting of the charge (Fe_2O_3 hematite). Roughly in this period it is not necessary to use hydrogen as a reducing agent and the melting can be carried out in an inert gas (argon). This is associated with the following causes.

From the diagram of the Fe–O system shown in Figure 1 according to [16], it follows that at a temperature of 1730 K in an atmosphere of pure oxygen or at 1663 K in air, hematite dissociates with the formation of magnetite (Fe_3O_4) and oxygen, i.e., even before the melt is produced. The use of an inert atmosphere or vacuum accelerates this process, which occurs according to the reaction:



Thus, the oxygen content in the oxide decreases from 30.06 to 28.08 % at 1856 K. Hence, the primary reduction of the lower oxide from the higher oxide occurs without hydrogen consumption and without

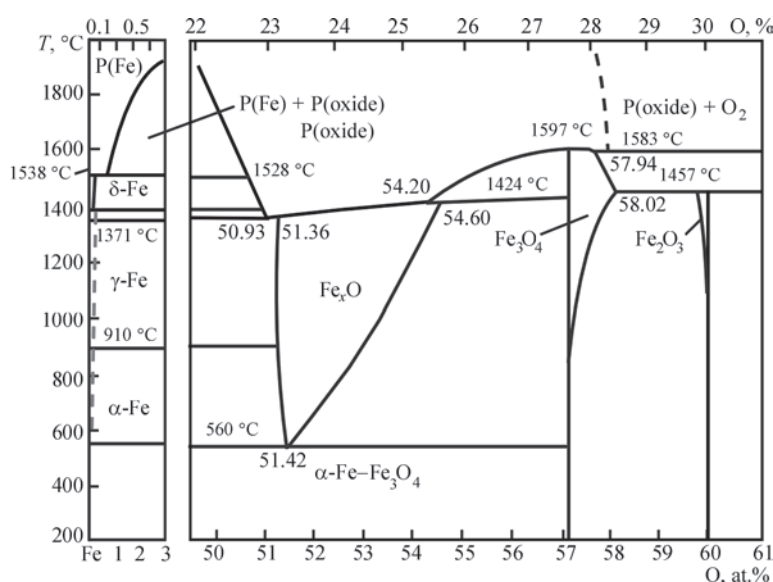
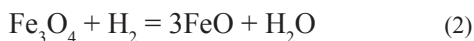


Figure 1. State diagram of the Fe–O system according to [16]

additional energy consumption directly for the reduction, since it coincides with the process of heating hematite to its melting point.

The obtained magnetite has the stoichiometric formula Fe_3O_4 , which can be written as $(\text{FeO} \cdot \text{Fe}_2\text{O}_3)$. The subsequent reaction already requires the presence of a reducing agent, in our case hydrogen, and can be written as:



or



Thermodynamic calculations show that reaction (3) occurs with a large negative change in free energy [17]. Since the plasma-arc furnace is a flow reactor, from which gaseous moisture is removed either by cleaning the gas phase during its recirculation or by continuous evacuation to the surrounding atmosphere, the reaction can proceed even until the oxide is completely used and reduced iron is obtained. The duration of the iron reduction from wüstite is determined by the kinetic characteristics of the reaction.

The next stage of iron reduction from the melt of wüstite can be described by the reaction:



Here, a fairly quick running of the reduction process is ending. Reaction:



is proceeding very slowly in the temperature range from melting to 3147 K. The change in the free energy of the reaction of iron reduction from the wüstite melt in

this temperature range has a small negative value: from -2454 to -3142 J/mol, and the logarithm of the equilibrium constant varies from 0.0568 to -0.0191 [14].

The next step is deoxidation of iron with hydrogen. It should be noted that hydrogen deoxidation is very slow according to the data presented in [18]. The final oxygen content of 0.001 % was reached after 0.5 h during deoxidation of the metal containing only 0.035 % of oxygen with carbon under melting conditions. Hydrogen treatment under the same conditions after 4 h led to a decrease in oxygen content of only 0.0015 %, i.e. it was more than 8 times slower.

Thus, before addressing the issue of overcoming the kinetic obstacles during deoxidation of iron melt, it is necessary to produce a melt of wüstite and then reduced iron with the maximum amount of dissolved oxygen at the lowest consumption. There are at least two methods of producing a wüstite melt. These are reduction of the oxide melt to FeO or dilution of the magnetite melt with iron, i.e. the reaction [19]:



The change in the free energy of the reaction (6) ranges from -32174 to -63752 J/mol at temperatures from melting to 3000 K. The equilibrium constant varies within 8–13 in the same temperature range.

The latter method is considered in this paper.

RESEARCH PROCEDURE

MELTING PROCESS

To produce oxide melts, plasma-arc melting was used, the equipment for which was developed at the E.O. Pat Electric Welding Institute [15]. It allows melting under the condition, when the entire surface of the liquid pool is covered with a plasma plume. The sealed chamber in which the melting is carried out is cooled by water, it has a plasma arc observation system, a plasmatron adjustment system and a gas pressure regulation and control system.

After the liquid pool is melted and held in the atmosphere of plasma-forming gas, the high-temperature state of the melt is fixed in a water-cooled metal mould. The equipment scheme is shown in Figure 2.

The melting procedure is as follows. A sample weighing 5.5–7.5 g is loaded into the melting chamber on a closed mould. A vacuum of 0.133 Pa is created in the chamber and then the chamber volume is filled with an inert plasma-forming gas (argon) to a pressure of 83.36–98.07 kPa. Subsequently, the plasmatron arc is ignited. The pellet sample is heated and melted, and then the melt is held under plasma heating. At the end of the holding time, the sample is rapidly crystallized in a copper water-cooled mould. 10 melts of pellets were performed with a holding time of 150 s and pro-

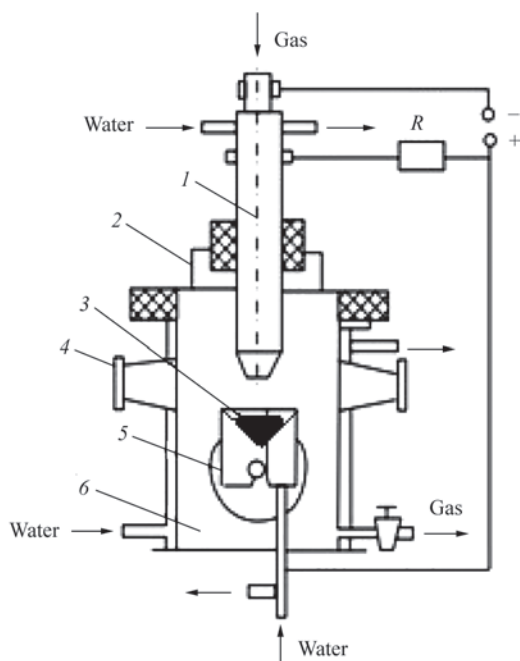


Figure 2. Scheme of the experimental plasma-arc installation [15]: 1 — plasmatron; 2 — cover; 3 — molten sample; 4 — observation device; 5 — opening mould; 6 — sealed chamber

Table 1. Initial data for melts and results obtained for dilution of the melt with iron

Calculation for the experiment								
Number of melting	1	2	3	4	5	6	7	8
Weight of Fe_3O_4 , g	4.021	2.913	2.673	3.244	3.826	3.826	3.821	3.101
Weight of iron, g	0	0.110	0.120	0.630	0.760	0.940	1.120	0.920
$\text{Fe}/\text{Fe}_3\text{O}_4$	0	0.038	0.045	0.194	0.199	0.246	0.293	0.297
Result of the experiment								
Weight of Fe_3O_4 , g	57.11	23.25 20.32	25.86 17.25	20.1 20.08	31.06 29.45	17.39 17.14	0 0	0 0
Weight of FeO , %	42.89	76.75 79.68	74.14 82.75	79.9 79.92	68.95 70.55	82.61 82.86	100 100	100 100

duced samples were averaged according to the chemical composition, which is given below:

Fe_3O_4 — 52.51 %, FeO — 24.01 %, Fe_2SiO_4 — 21.80 %, Fe_2O_3 — 1.42 %.

Thus, each subsequent experiment was carried out with the same material. The composition of iron silicide was converted to FeO and a mixture of the two components Fe_3O_4 and FeO , which amounted to 100 %, was the initial point. A certain amount of iron was added to the oxides, which was calculated in advance. The calculation data are shown in Table 1.

X-ray diffraction studies of the samples were carried out using a DRON UM-1 diffractometer in a monochromatic copper K_α radiation by the step scanning method ($U = 35$ kV; $I = 25$ mA, exposure time at a point is 5 s, step is 0.05° , output slits are 1×12 mm). The obtained X-ray patterns were decoded using PowderCell 2.4, a software for full-profile analysis of X-ray spectra from a mixture of polycrystalline phase components. The profiles of diffraction maxima were approximated by the Pseudo-Voigt function. The international crystallographic database PCPDFWIN (1973) was used for the calculations.

The examples of the obtained X-ray spectra of samples 2, 4, 6, and 8, respectively, are shown in Figure 3. After recalculation, the amount of magnetite and wüstite corresponds to the data in Table 1.

EXPERIMENTAL RESULTS AND DISCUSSION

In [19], the study of the kinetics of pellet decomposition was limited to 150 s for technical reasons. It was decided to extend the melting time to test the possibility of transferring the melt to a homogeneous state corresponding to the wüstite without dilution with iron.

The studies (Figure 4) have shown that with an increase in holding time, decomposition continues for at least 360 s.

The studies were carried out both with continuous holding of the melt for 360 s, as well as with periodic crystallization and subsequent heating. In other words, the sample was heated for 30 s until melting,

held for 60 s and crystallized. Then the cycle was repeated. The number of such cycles was 6. Thus, the sample was in the liquid state for 360 s and in the heating state for 180 s. The results for these two melting schemes were slightly different. Thus, when the melt

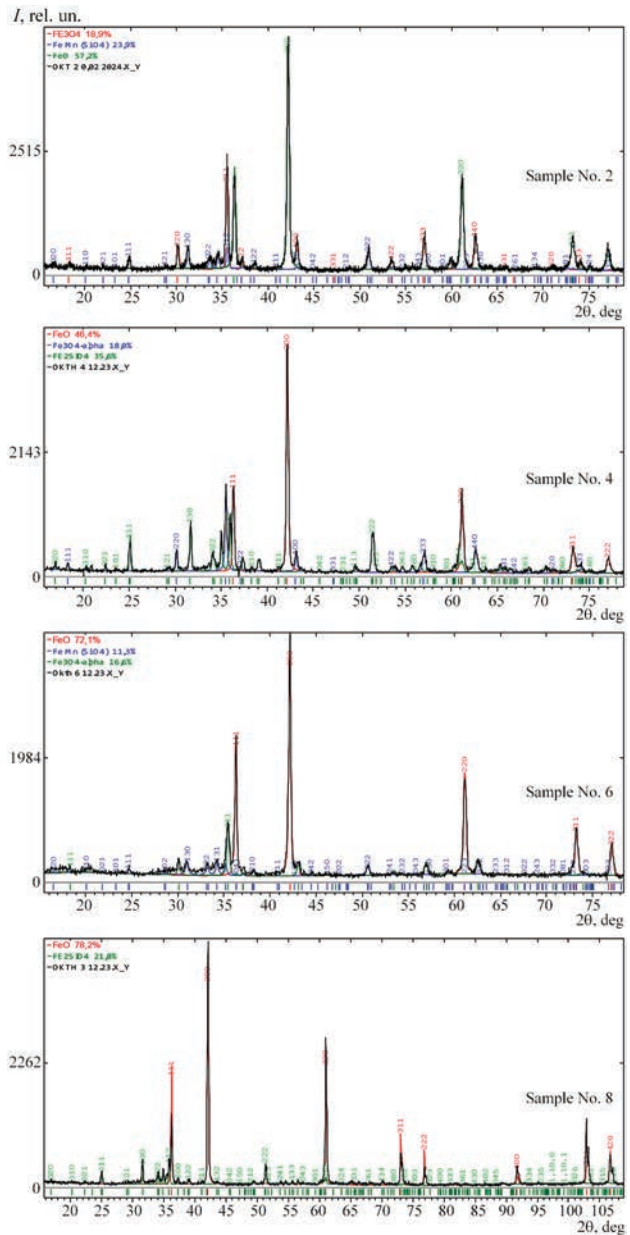


Figure 3. Examples of X-ray spectra of melt samples 2, 4, 6 and 8 (see Table 1)

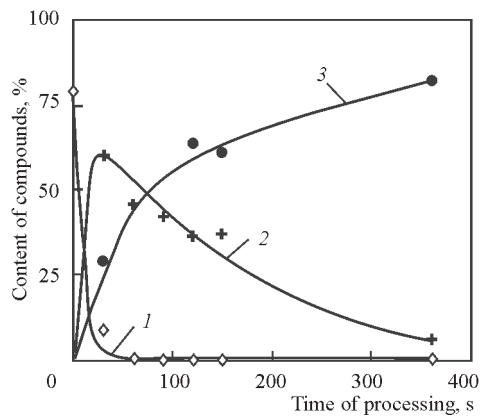


Figure 4. Change in the content of oxides in a rapidly crystallized melt after different holding times at PAM in an argon atmosphere: 1 — Fe_2O_3 ; 2 — Fe_3O_4 ; 3 — FeO

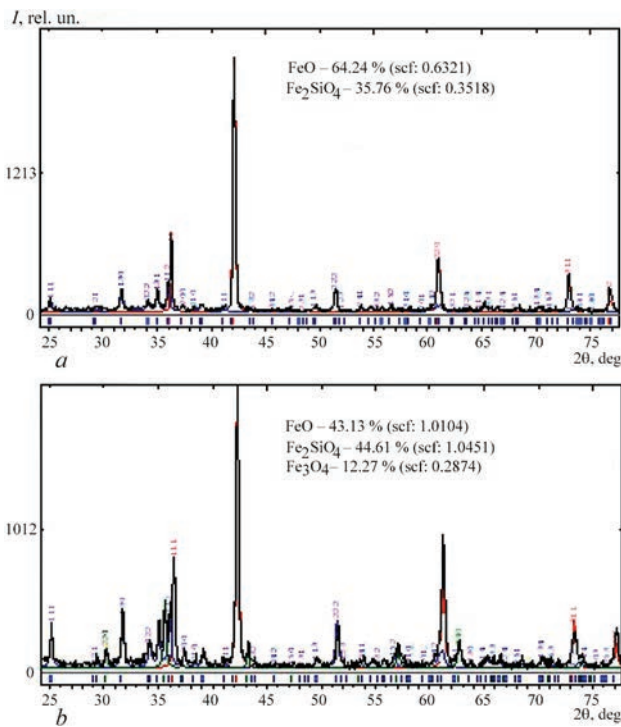


Figure 5. X-ray spectra of samples at step and continuous holding of the melt: *a* — 6 cycles of 60 s, *b* — 1 cycle of 360 s

is held continuously for 6 min under plasma heating, the wüstite content grows to 74.6 %, and magnetite decreases to 12.3 % (Figure 5, *b*). The rest of content is SiO_2 . During the step heating and crystallization, it is possible to remove oxygen from the solid oxide system and the melt due to the additional time spent on repeated heating, and magnetite disappears (Figure 5, *a*). Thus, we obtain a melt of wüstite, although with a certain increase in power consumption.

The main negative conclusion is a significant decrease in the rate of decomposition of the Fe_3O_4 melt to FeO with an increase in the holding time of the oxide melt in the liquid state, even at PAM. Especially if we take into account the size factor when changing from small laboratory weighed portions to real industrial metal masses.

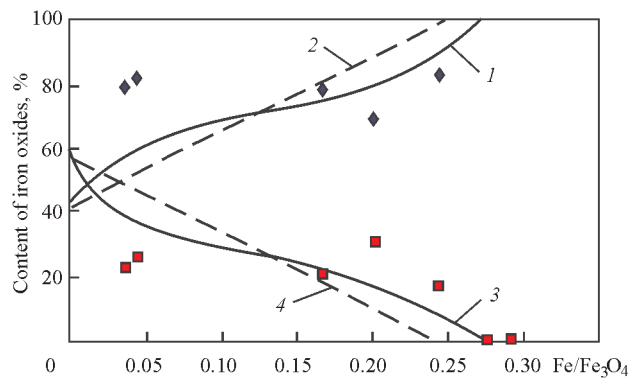


Figure 6. Change in the composition of the oxide melt depending on the amount of iron added to the magnetite melt: 1, 2 — wüstite content; 3, 4 — magnetite content; 1, 3 — experiment; 2, 4 — theoretical calculation

As for the other method, the theoretical calculation for the initial values of the components of reaction (6) (see Table 1) showed that when iron is added to the magnetite melt, the dependence of the content of iron oxides on the amount of iron, with respect to the $\text{Fe}/\text{Fe}_3\text{O}_4$ ratio, is linear (Figure 6) and is described by the following equations.

Change in FeO content (theoretical):

$$(\text{FeO}) = 237 \frac{\text{Fe}}{\text{Fe}_3\text{O}_4} + 42.9.$$

Change in Fe_3O_4 content (theoretical):

$$(\text{Fe}_3\text{O}_4) = -237 \frac{\text{Fe}}{\text{Fe}_3\text{O}_4} + 57.1.$$

The $\text{Fe}/\text{Fe}_3\text{O}_4$ ratio being 0.241, this means that all magnetite, according to reaction (6), is converted to wüstite.

The difference between the theoretical and experimental dependences is most probably associated with the use of small weighing portions of material during the experiments. However, the final difference between the theoretical value of the ratio of the initial reaction components being 0.241 and the experimental value being 0.293 is 0.052 or approximately 20 % in absolute values, which can be considered acceptable.

CONCLUSIONS

1. It was found that at continuous holding of the melt in argon plasma under experimental conditions for 360 s, the content of wüstite grows to 74.6 %, and magnetite decreases to 12.3 %. After 6 cycles of periodic crystallization of the melt and subsequent melting with a holding time of 60 s, magnetite completely disappears and a melt of wüstite FeO_{max} is formed.

2. A significant decrease in the rate of decomposition of liquid Fe_3O_4 to FeO with an increase in the time of continuous holding of the oxide melt in the liquid state even at plasma-arc heating is observed.

3. When adding iron to the magnetite melt, the theoretical dependence of the iron oxide content on

the $\text{Fe}/\text{Fe}_3\text{O}_4$ ratio is described by linear dependences. The experimental values differ from the theoretical ones by 20 %, but allow using this method to produce a wüstite melt.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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