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Regularities of solid-phase reduction of iron oxides under conditions of combined chemical-catalytic and energetic influence

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Закономірності твердофазного відновлення оксидів заліза в умовах комбінованого хіміко-каталітичного та енергетичного впливу

Abstract. Purpose. *The purpose of the work is a physicochemical analysis of the intensification of the process of solid-phase iron reduction under the conditions of the joint influence of catalytic additives and an electromagnetic field (EMF).* ***Methodology.*** *The experiments were conducted in an alternating magnetic field with a frequency from industrial to ultrasonic using the thermogravimetric method. The process of reduction of various iron ore materials was studied in the temperature range of 873-1373 K.* ***Results***. *The results of laboratory experiments indicate the influence of the electromagnetic field and intensifying catalytic additives on the process of solid-phase reduction of various iron ore materials. The non-additivity of the results of the joint influence of additives and an intensifying EMF is shown. The study of the influence of various process parameters on the rate and degree of reduction of iron ore materials is carried out.* ***Scientific novelty***. *The joint intensifying effect of catalytic additives and EMF on the process of solid-phase iron reduction is experimentally shown. A physicochemical justification of the non-additivity of the joint influence on the kinetics of the reduction process is proposed.* ***Practical significance***. *Intensification of the processes of solid-phase reduction of iron ore raw materials provides a significant increase in the productivity of direct iron production technologies - process intensification and process productivity.*

Keywords: *solid-phase reduction, intensification, kinetics, iron oxides, alternating electromagnetic field, mechanism, catalytic additive.*

Анотація. Мета. *Метою роботи є фізико-хімічний аналіз інтенсифікації процесу твердофазного відновлення заліза в умовах сумісного впливу каталітичних добавок та електромагнітного поля (ЕМП).* ***Методологія.*** *Експерименти проводились у змінному магнітному полі з частотою від промислової до ультразвукової за допомогою термогравіметричного методу. Процес відновлення різних залізорудних матеріалів вивчався в температурному діапазоні 873–1373 К.* ***Результати.*** *Результати лабораторних експериментів свідчать про вплив електромагнітного поля та інтенсифікуючих каталітичних добавок на процес твердофазного відновлення різних залізорудних матеріалів. Показано неадитивність результатів спільного впливу добавок та інтенсифікуючого ЕМП. Проведено дослідження впливу різних параметрів процесу на швидкість та ступінь відновлення залізорудних матеріалів.* ***Наукова новизна.*** *Експериментально показано спільний інтенсифікуючий вплив каталітичних добавок та ЕМП на процес твердофазного відновлення заліза. Запропоновано фізико-хімічне обґрунтування неадитивності спільного впливу на кінетику процесу відновлення.* ***Практичне значення.*** *Інтенсифікація процесів твердофазного відновлення залізорудної сировини забезпечує значне підвищення продуктивності технологій прямого отримання заліза – інтенсифікацію процесу та продуктивність процесу.*

Ключові слова: *твердофазне відновлення, інтенсифікація, кінетика, оксиди заліза, змінне електромагнітне поле, механізм, каталітична добавка.*

Introduction. The processes of solid-phase iron reduction are usually carried out at moderate temperatures (up to 1373 K) [1-4], which makes the productivity and efficiency of the units directly dependent on the rate of iron ore charge reduction and the possibility of its intensification. This, in turn, requires an in-depth study of the kinetic laws and mechanism of the recovery processes, as well as the identification of limiting links to scientifically select ways to accelerate the process.

Various chemical-catalytic and energy (physical) influences as possible regulators of physical and chemical processes are attracting the attention of researchers for a long time. Thanks to numerous studies, the most significant successes in this area have been achieved by using electromagnetic and corpuscular radiation [5-11] and alkali metal salts.

The possibility of targeted control of the concentration of electronic and structural defects in crystalline phases by introducing impurity ions and energetic influence on the reacting system opens new ways to intensify the reduction of metals from oxides. At the same time, the simultaneous effect of these methods on the solid-phase reduction of iron-containing materials appears to be of interest.

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Research results and their analysis. Experimental studies of the kinetics of the process of solid-phase reduction of iron oxides under conditions of chemical catalytic and energy impact were performed using the thermogravimetric method, with the registration of changes in the mass of the sample and the composition of the waste gases.

Hematite was reduced at a high rate (Fig. 1), with ~ 95 % of the oxygen containing iron oxide being removed within 40 min. Increasing the temperature from 1073 to 1173 K accelerated only the first stage, the final stage of reduction proceeded somewhat slower, which is probably due to the increased difficulty of inner diffusion gas exchange due to sintering of iron crystals. The application of EMF slightly intensifies the process (Fig. 1).

The rate of magnetite reduction was lower, with ~90% of the oxygen bound to iron being removed within 40 min (Fig. 2). The transition from 1073 to 1173 K did not cause a significant inhibition at the final stage, which can be attributed to the slow sintering process of iron particles obtained from less active Fe_3O_4. The intensifying effect of EMF is approximately the same as in the case of Fe_2O_3 reduction.

The recovery of magnetite concentrate (MC) was slower, with the degree of recovery (ω_B) reaching 63 and 70% in 40 min at 1073 and 1173 K, respectively (Fig. 3). The nature of the effect of temperature on the process kinetics indicates that sintering and recrystallisation do not develop significantly during the experiment. The alternating EMF intensified approximately in the same way as for other iron ore materials (Fig. 3). A similar pattern was observed when the reacting system was chemically catalysed by the introduction of KCl into the charge (Figs. 1-3).

A more significant intensification of iron reduction was observed under the combined effect of EMF and potassium chloride (Fig. 1-3). Lithium chloride had the opposite effect in the process of indirect reduction. Adding it to the charge significantly inhibited the reaction, so that in the presence of 1% LiCl, ω_B decreased by 3-4% (Fig. 1-3). The inhibitory effect of lithium chloride was almost the same for all tested iron ore materials.

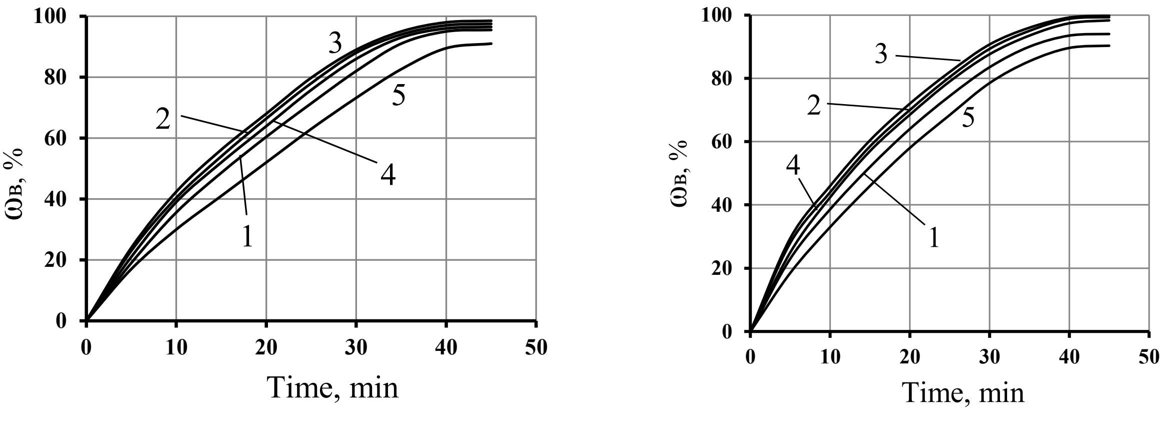
The same set of studies was used for the carbon-thermal reduction at 1373 K. Without catalytic influence, the complete carbon-thermal reduction of hematite was completed in 20 min, and of magnetite in 30 min. The last stage of the $FeO_{minO} \rightarrow Fe$ process was characterized by autocatalysis (Fig. 4), which is due to the catalytic intensification of the gasification step ($CO_2+C=2CO$) by metallic iron.

Under these conditions, the catalytic effect of Fe_{Met} was not fully manifested, the process was relatively slow and was completed in 45 min. The chemical-catalytic and energy (EMF) effects had a positive effect on the rate of carbon-thermal reduction (Fig. 4, 5). Lithium chloride, which inhibited the gas reduction process, significantly accelerated the carbon-thermal reduction. The intensifiers were ranked by their effectiveness: EMP, 1% LiCl, 1% KCl, 1% KCl together with the field. Their effect is much higher than in gas reduction. For example, the presence of 1% KCl in the charge provided a relative acceleration of ~ 30%.

In the experiments with Fe_2O_3 and Fe_3O_4, these effects do not change the general appearance of the kinetic curves, however, during the carbon-thermal reduction of magnetite concentrate, catalytic additives led to a clearly expressed autocatalysis at the $FeO_{min\,O} \rightarrow Fe$ stage (Fig. 5).

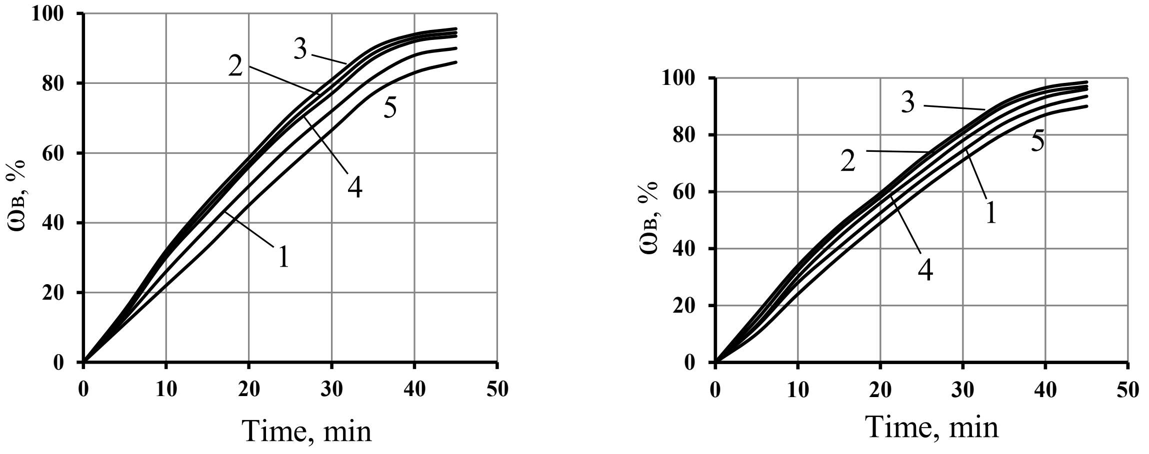
The complex reduction of iron ore materials was carried out by graphite together with CO at 1173 and 1273 K, proceeded at a high rate and complete oxygen removal was completed in 25 min at 1173 K and 16 min at 1273 K. The kinetic curves, as in the case of carbon-thermal reduction, were accompanied by the development of autocatalysis at the $FeO_{min\,O} \rightarrow Fe$ stage (Fig. 6).

During the reduction of magnetite concentrate, there were no clear kinks in the kinetic curve (Fig. 5), which may be due to the relatively poor contact between carbon and concentrate.



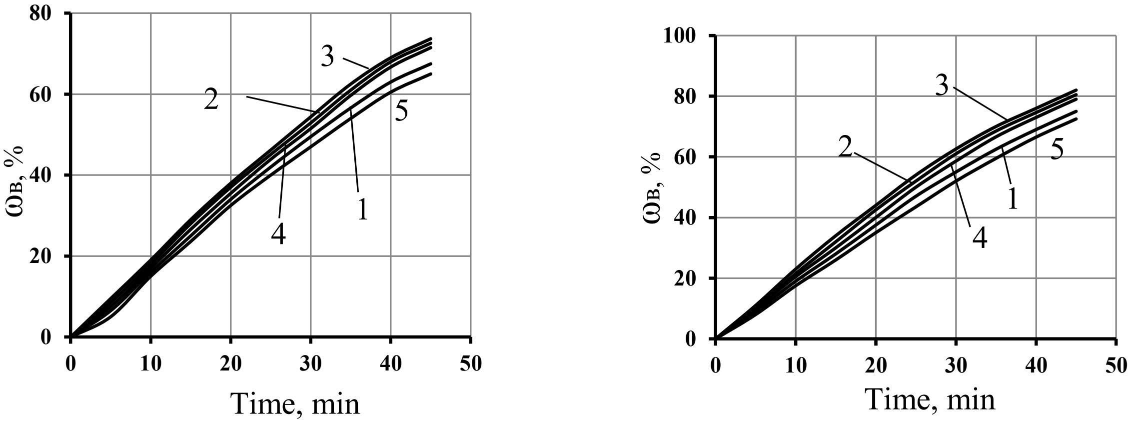
(a) (b)

Fig. 1. Kinetics of Fe_2O_3 reduction by carbon monoxide at a) 1073 K, b) 1173 K: 1 - no additive; 2 - 1% KCl; 3 - EMF + 1% KCl; 4 - EMF; 5 - 1% LiCl



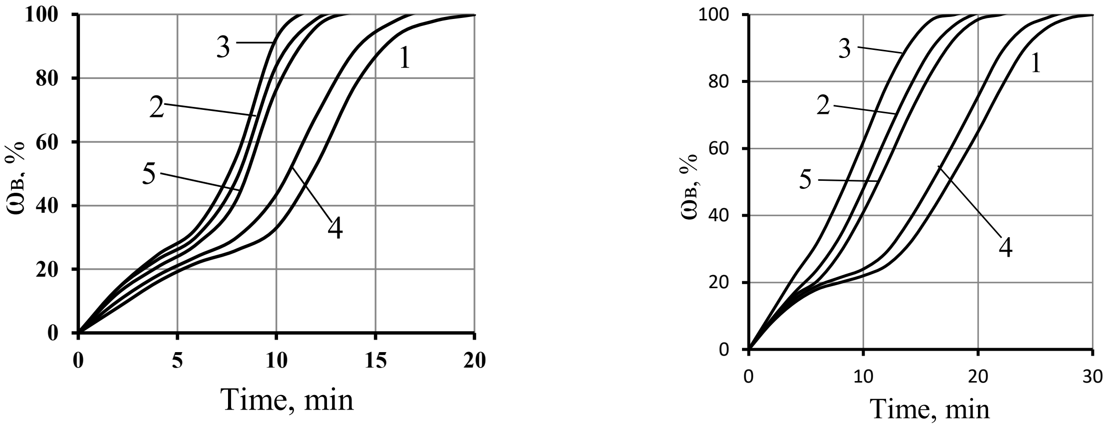
(a) (b)

Fig. 2. Kinetics of Fe_3O_4 reduction by carbon monoxide at a)1073 K, b)1173 K: 1 - no additive; 2 - 1% KCl; 3 - EMF + 1% KCl; 4 - EMF; 5 - 1% LiCl



(a) (b)

Fig. 3. Kinetics of MC reduction by carbon monoxide at a)1073 K, b)1173 K: 1 - no additive; 2 - 1% KCl; 3 - EMF + 1% KCl; 4 - EMF; 5 - 1% LiCl



(a) (b)

Fig. 4. Kinetics of carbon-thermal reduction at 1373 K a) Fe_2O_3 and б) Fe_3O_4: 1 - no additive; 2 - 1% KCl; 3 - EMF + 1% KCl; 4 - EMF; 5 - 1% LiCl.

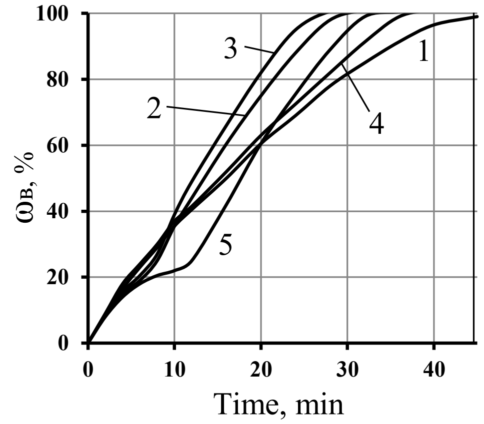
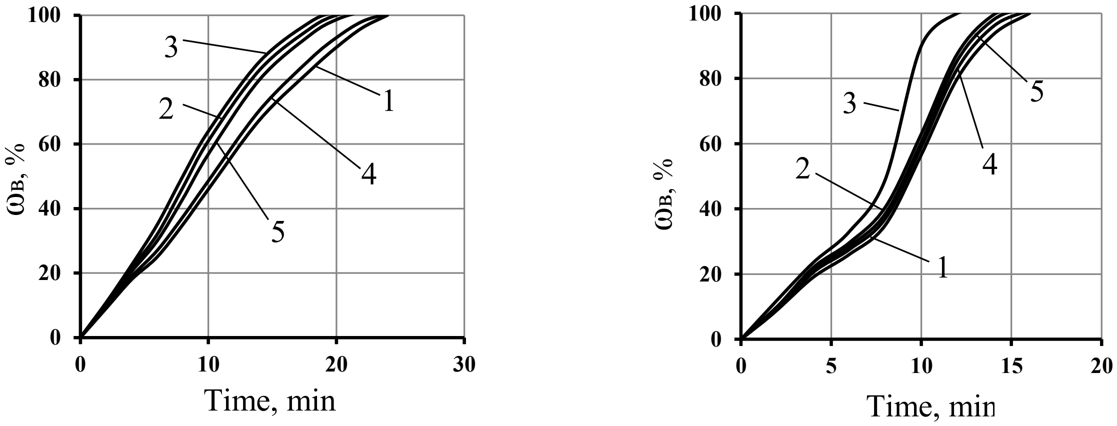


Fig. 5. Kinetics of MC reduction by carbon at 1373 K: 1 - no additive; 2 - 1% KCl; 3 - EMF + 1% KCl; 4 - EMF; 5 - 1% LiCl

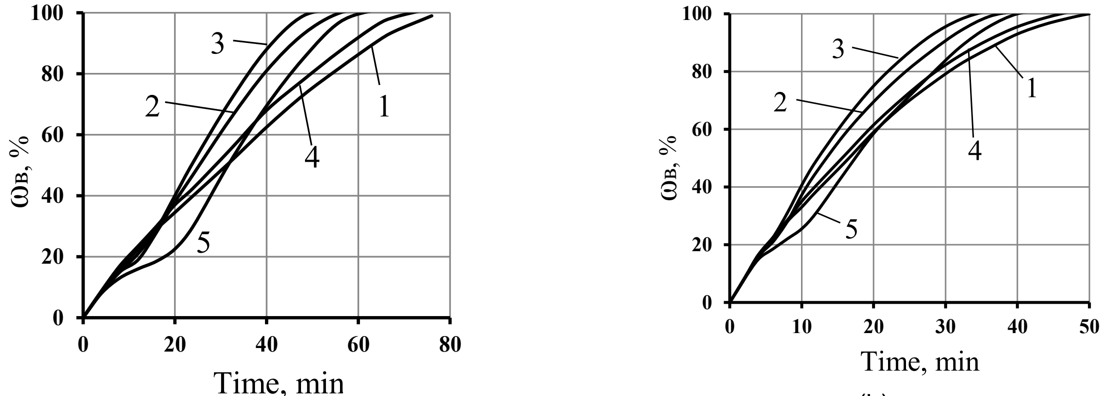


(a)

(b)

Fig. 6. Kinetics of complex reduction of Fe_2O_3 at a) 1173 K, b) 1273 K: 1 - no additive; 2 - 1% KCl; 3 - EMF + 1% KCl; 4 - EMF; 5 - 1% LiCl

The complex reduction of the magnetite concentrate was characterised by a monotonous decrease in the rate (Fig. 7), the reaction proceeded relatively slowly, the time for complete oxygen removal was 75 and 50 min for 1173 and 1273 K, respectively. The degree of influence of the intensifiers was characterised by the same sequence as in carbon thermal treatment (Figs. 6, 7). The kinetic curves did not undergo serious changes under the influence of the intensifiers. Only in the complex reduction of MC were signs of autocatalysis observed at the last stage if KCl and especially LiCl were introduced into the charge.



(a)

(b)

Fig. 7. Kinetics of complex reduction of MC at a) 1173 K, b) 1273 K: 1 - no additive; 2 - 1% KCl; 3 - EMF + 1% KCl; 4 - EMF; 5 - 1% LiCl

In addition to the industrial frequency EMF, the recovery of magnetite concentrate was studied under the application of ultrasonic exposure at 773 K in a hydrogen flow. This effect had a higher efficiency compared to the industrial frequency field.

Separately, a series of experiments was performed to study the joint intensifying effect on the process of direct iron reduction in the fluidised bed mode using conical and cylindrical reactors. The temperature and EMF parameters (frequency and intensity) were varied. Table 1 shows some of the experimental results.

The data shows that at 973 K, the effect of additives on the metallisation process occurring under conditions of periodic exposure to a magnetic field was approximately the same as in experiments without a field. At W_{H2} = 1 l/min, the value of the degree of metallisation (**α**) because of the introduction of 1% KCl increased significantly (from 46.5 to 63.0%). the reduction in the fluidised bed (W_{H2} = 2 l/min) was almost doubled. However, at 873 K, additives under these conditions did not produce the expected effect. Moreover, the process even slowed down, which was reflected in a decrease in the amount of metallised iron from 72% to 62.5%.

Table 1. Concentrate metallisation in hydrogen flow under different external influences (conical reactor), τ = 40 min, EMF: f = 0.5 Hz, H = 400 Oe

T, K	W_{H2}, l/min	Degree of metallisation (α), %		
		No additives and EMF	EMF	1 % KCl + EMF
873	2	46,4	72,2	62,5
973	1	47,5	46,5	63,0
973	2	49,1	55,2	100

The high values of α observed when the field was applied in a conical reactor in the absence of additives are explained by the specific conditions of the charge particle movement, which was accompanied by alternating cycles of ‘deposition’ and ‘swelling’ of the concentrate layer. With such a layer organisation, particle sintering is difficult and does not significantly affect the process of oxygen removal from the oxide lattice. The weakening of this effect in the presence of salts is difficult to attribute to the influence of their layer structure and the nature of particle movement. Probably, other reasons underlie the observed patterns.

Similar patterns were found in the cylindrical reactor (Table 2).

Table 2. Concentrate metallization under different external influences (cylindrical reactor), τ = 40 min; EMF: f = 0.5 Hz, H = 400 Oe

T, K	W_{H2}, l/min	Degree of metallisation (α), %		
		No additives and EMF	EMF	1 % KCl + EMF
873	2	42,2	41,6	70,5
973	1	43,5	46,8	93,0
973	2	44,2	45,2	100

At 973 K, KCl additives during the metallisation of the concentrate in a magnetic field had a significant accelerating effect, contributing to an increase in α from 45-47% to 93-100%. However, in contrast to previous experiments, the positive effect of the additives at a temperature decrease from 973 to 873 K was preserved, albeit in a weaker form: the α values increased from 41.6 to 70.5%.

It should be noted that the efficiency of salt introduction at 873 K was significantly lower than the observed acceleration of processes without the field. Tables 3 and 4 compare the results of the metallisation of the concentrate with KCl additives under the conditions of field application and without it.

As can be seen from the tables, the combined use of EMF and catalytic additives has a positive effect on the process only at 973 K. In experiments with a stationary bed (W_{H2} = 1 l/min), the total accelerating effect exceeded that observed under the conditions of separate action of salts and field, which was reflected in the increase in α from 63.1% and 46.8% to 93% (cylindrical reactor) and from 55.0% and 46.5% to 63.0% (conical reactor).

In the fluidised bed, similar ratios were obtained in experiments lasting 30 min: the **α** values increased under the combined effect of the field and catalytic additives in the conical reactor to 100% compared to 95.5% (1% KCl without the field) and 55.2% (in the field without additives, τ = 40 min), and in the cylindrical reactor - to 100% compared to 98 and 45.2%, respectively.

Table 3. Concentrate metallization in the layer at different methods of process intensification (cylindrical reactor), τ = 40 min; EMF, f=50 Hz, H=400 Oe

T, K	W_{H2}, l/min	Degree of metallisation (α), %		
		No additives and EMF	EMF	1 % KCl + EMF
873	2	42,2	95,0	70,5
973	1	43,5	63,1	93,0
973	2	44,2	100	100

Table 4. Concentrate metallization in the layer at different methods of process intensification (conical reactor), τ = 40 min; EMF, f=0.5 Hz, H=400 Oe

T, K	W_{H2}, l/min	Degree of metallisation (α), %		
		No additives and EMF	EMF	1 % KCl + EMF
873	2	46,4	80,0	62,5
973	1	47,5	55,0	63,0
973	2	49,1	98,0	100

At 873 K, a significant weakening of the catalytic effect was observed when a magnetic field was applied along the course (Tables 3 and 4). This trend was observed both in the pulsed magnetic field and in the field of industrial frequency. The reduction of the accelerating effect of the additives was manifested in a decrease in the degree of metallisation in the field by 22-25%.

In a special series of experiments, the effectiveness of the magnetic field on the catalytic activity of salts was evaluated depending on the frequency and intensity of the magnetic field. The obtained values of the degree of metallisation are presented in Table 5 (numerator); the denominator shows the results of concentrate metallisation in the presence of salts, but without a field.

Table 5. Degree of concentrate metallization in a magnetic field of different frequency and intensity (W_{H2} = 2 l/min; 1% KCl; τ = 40 min)

T, K	Reactor type	EMF		α, %
		f, Hz	H, Oe	
873	conical	0.5	200	40.6/80.0
873	conical	0.5	400	62.5/80.0
873	conical	50	400	55.0/80.0
973	conical	0.5	200	100/96.0
973	conical	0.5	400	100/98.0
873	cylindrical	50	200	57.5/95.0
873	cylindrical	50	400	70.5/95.0
973	cylindrical	50	400	100/100
973	cylindrical	50	200	100/100

Experiments with the variation of field parameters (frequency and intensity) confirmed the above correlations.

It is well known that the solid-phase reduction process is complex, which is determined by the closely interconnected links of diffusion, crystal-chemical and carbon gasification reactions. In this context, the mechanism of both energetic and chemical-catalytic influence on the reacting system should be considered.

The presented results of the experiments allow us to draw certain conclusions about the mechanism of joint chemical-catalytic and energy intensifying influence on the processes of solid-phase iron reduction. It should be noted that direct experiments have shown a certain disagreement between the total effect of the sum of influences on the rate of reduction of iron oxides, i.e., there is a non-additivity. Moreover, there was a mutual levelling of the chemical-catalytic and energy effects when they were used together. The intensifying effect of the joint action of the additive and EMF differed depending on the type of process and field frequency and was the smallest compared to the separate variants. All the above makes it very difficult to analyse the mechanism of the joint effect of intensifiers on the iron reduction process.

The catalytic effect of alkali metal salts is widely reported in scientific publications and in our research results [12,13]. Based on the fundamental concepts of heterogeneous catalysis, solid state physics, and the theory of chemisorption on the surface of semiconductors, the mechanism of additives' action was developed through the influence on the adsorption-chemical link and diffusion of iron ions in the crystal lattice [14]. The influence of catalytic additives on the adsorption-chemical link is realised through changes in the structural and electronic defects of oxide crystals and, as a result, the adsorption capacity of the oxide surface. The diffusion processes are affected by the potential difference between the oxide surface and the volume formed during the chemisorption of gases [15,16].

It should be noted that the energy effect affected the indirect reduction and gasification steps. Iron, Fe_3O_4, and Fe_2O_3-γ are typical ferromagnets characterised by magnetostriction: size change when magnetised, and this effect plays a significant role in the reduction of iron oxides under alternating magnetic fields, facilitating inner diffusion gas exchange and crystal-chemical transformations.

Along with the diffusion transport of gases, electromagnetic effects, due to the magnetostriction effect, accelerate the crystal-chemical transformation step. The continuous movement of particles forming crystals in an alternating EMF increases their mobility, which leads to an increase in the rate of ion diffusion through the crystal lattice and facilitates phase transformations.

There are other ways in which an alternating field can affect the indirect reduction of iron oxides. For example, a change in the linear dimensions of ferromagnetic phases due to magnetostriction causes elastic stresses of different signs in them, which affects the rate of ion movement through the crystal lattice [14]. These stresses can also be transmitted to nonferromagnetic materials (FeO) that are in close contact with ferromagnets within the same grain. Consequently, the solid-phase diffusion of ions throughout the grain is accelerated. This is confirmed by the intensification of NiO reduction by hydrogen when an alternating field is applied to the reacting system.

It is known that an external electric field affects the activity of a semiconductor [17], which is associated with a change in the concentration of electrons and holes, which affects the adsorption capacity of the crystal surface. The activity of semiconductors also changes under the influence of EMFs. Chemisorption on the surface of oxides separates the charge into surface and bulk charges, creating an electric field that regulates the transfer of ions in the solid phase. The EMF imposed on the reacting system affects the mobile electric charge (Lorentz force) and can have a favourable effect on solid-phase diffusion processes and crystal transformations in general

Lastly, carbon gasification is also affected by EMFs. It is likely that the field affects the destruction of carbon-oxygen complexes on the carbon surface, which is accompanied by the release of CO into the gas phase and thus intensifies the carbon-thermal and complex reduction of iron oxides.

Thus, the mechanisms of influence of catalytic additives and EMFs on the recovery process are quite similar. The non-additivity of the joint effect of these intensifiers may be due to mutual ‘competition’. It is known that the catalytic effect of alkali metal salts is attenuated as the weight of the additive increases. This is also true for the power of the EMF. In this case, when the intensifiers act together, the maximum effect is achieved at a lower level compared to the sum of the effects. In the case of carbon-thermal and complex iron reduction, the non-additivity can also be caused by the physicochemical patterns of the intensifying effect on the carbon gasification reaction. Probably, the field affects the process of destruction of carbon-oxygen complexes on the carbon surface, which is accompanied by their release into the gas phase and thus intensifies the carbon-thermal and complex reduction of iron oxides. In this context, the mechanism of both energetic and chemical-catalytic influence on the reacting system should be considered.

An increase in the speed of each of the links should contribute to the intensification of the process, but the maximum effect can be obtained by accelerating the combination of these reactions.

Conclusions

The fact of the non-additivity of the joint effect of a catalytic additive and an intensifying EMF on the rate of the direct iron reduction process has been experimentally established. A physicochemical model of the mechanism of joint effect of intensifiers on the reduction process has been proposed. The effect of the frequency and intensity of the EMF on the intensification of the solid-phase reduction of iron ore materials was experimentally confirmed.

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