Представлені результати експериментальних досліджень процесу фазоутворення в системі $Fe^{2+}/Co^{2+}/O_2/H_2O$ в широкому діапазоні pH. Показано вплив присутності іонів Co^{2+}, величини pH вихідного розчину, температури і кількості окислювача на фазовий склад отриманих продуктів. Встановлено, що присутність іонів Co^{2+} прискорює процес окислення сполук Fe^{2+}

Ключові слова: сульфат заліза, гідроксид заліза, оксигідроксид, магнетит, каталітичне фазоутворення, кобальт (II), кисень

Представлены результаты экспериментальных исследований процесса фазообразования в системе $Fe^{2+}/Co^{2+}/O_2/H_2O$ в широком диапазоне pH. Показано влияние присутствия ионов Co^{2+}, величины pH исходного раствора, температуры и количества окислителя на фазовый состав полученных продуктов. Установлено, что присутствие ионов Co^{2+} увеличивает скорость процесса окисления соединений Fe^{2+}

Ключевые слова: сульфат железа, гидроксид железа, оксигидроксид, магнетит, каталитическое фазообразование, кобальт (II), кислород

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INVESTIGATION OF PHASE FORMATION IN THE SYSTEM $FE^{2+}/CO^{2+}/O_2/H_2O$

L. Frolova
PhD, Associate Professor*
E-mail: frolova_l.a@mail.ru
A. Derimova
Assistant*
E-mail: alena-derimova@rambler.ru
A. Khlopytskyi
PhD, Associate Professor*
E-mail: hapits@yandex.ua
Y. Galivets
PhD, Associate Professor*
E-mail: dnepr100500@ukr.net
M. Savchenko
PhD, Associate Professor*
E-mail: mashanew1@rambler.ru
*Department of Inorganic Materials Technology and Ecology
Ukrainian State University of Chemical Technology
Gagarina ave., 8, Dnipro, Ukraine, 49005

1. Introduction

Currently, ferrous salts are large-tonnage wastes of chemical and metallurgical industries. They are formed during steel etching, in preparing parts in the electroplating industry, in producing pigment titanium oxide and so on. In this connection, several processes need to transfer ferrous iron into trivalent state. This process is implemented in different ways: by the reagent oxidation, by intensification of the redox processes in aqueous solutions using high-energy external fields, by oxidation at elevated temperatures as well as oxidation by atmospheric oxygen. Investment ratio of this process leads to the accumulation of large quantities of waste ferrous chlorides and sulfates. Ideally, in many respects (the use of relatively low temperature, environmental friendliness and process time) the oxidant to be used is the oxygen of the air. The products of oxidation are oxide and oxyhydroxide compounds widely used in the industry.

The dispersed iron oxide compounds are widely used as magnet carriers, pigments, catalysts, sorbents [1–5]. Modification of the above by various cations results in changing the properties associated primarily with changes in the structure of the resulting substance. The cations used as modifiers are those of cobalt, nickel, copper, zinc, rare earths. Features of cobalt and iron compounds synthesis were studied by many authors [6–8]. Introduction of cobalt cations leads to anisotropy of the structure and shape. Small amounts of cobalt in the crystal lattice of iron oxide compounds result in a sharp change of many characteristics (color, coercive force, saturation magnetization). The most popular products in the studied system are α-oxyhydroxides having needlelike structure and ferrospinels possessing specific magnetic properties.

Therefore, the study of phase formation in the system $Fe^{2+}/Co^{2+}/O_2/H_2O$, as well as the study of the influence of the basic oxidative environment parameters on the phase composition of iron (III) oxides over a wide pH range, and obtaining precipitates with a given chemical composition appear to be urgent.

2. Literature review and problem statement

Currently, there are a few basic processes of obtaining iron oxide compounds. Hydrophase process is considered to be a major one among them. The raw material for ferric oxide compounds production is traditionally ferrous salts, because of their cheapness. The variety of thermodynamically possible compounds obtained in oxidizing ferrous salt leads to poor reproducibility of the properties of the resulting products. Researches existing in this area are insufficient and controversial. In [9], the authors studied the process of iron cations oxidation by air at various pH. The authors of [10] give phase state diagrams corresponding to various oxidation conditions. It is found that at pH below 4 the concentration of Fe^{2+} cations dominates and the rate is pH independent. At pH>5, iron is much more easily oxidized. At pH 5 to 8, the concentration of trivalent iron increases dramatically. At pH values>8 the concentration no longer changes with the pH and oxidation rate doesn't depend on the pH.

The process of oxidation-hydrolytic co-precipitation (OHCP) in the presence of NO and SO_2 was described in detail. The mechanisms involved in the oxidation of ferrous ions to ferric ions with oxygen in the presence of low concentration nitrite ions were studied.

The effect of silicates seed crystals on the process of OHCP [11] was studied. This study evaluated the effect of silicic acid (at concentrations ranging from 5 to 40 mol % Si) on ferrihydrite deposition. It is found that the presence of iron oxy-hydroxide compounds significantly accelerates the rate of oxidation, which is explained by the catalytic action of both iron (II) cations [12], and of goethite [13]. The results are explained by solid phase recrystallization of iron (III) oxide, induced by the catalytic action of iron (II) cations. The iron oxides are treated as dynamic phases which change composition under the influence of variable redox conditions. It has been found [13] that the reaction of Fe (II) cations in an aqueous medium with oxides of Fe (III) is a complicated process involving sorption, electron transfer, and in some cases, the reductive dissolution and conversion of secondary products. To study the dynamics of these reactions, the authors measured the degree and rate of isotope exchange between an aqueous solution of Fe (II) and goethite using isotopes. These results require a revision of the existing models of iron cations oxidation.

A large number of works are devoted to the study of iron cations oxidation at low pH [14, 15]. However, the rate of oxidation is not the only factor affecting the phase composition of the precipitate. The composition of the resulting precipitate is largely dependent on the mode of conducting the oxidation process: additional cations and anions [16], the nature of the oxidizing agent [17], the rate of oxidation, temperature, pH of the onset of oxidation, the concentration and nature of the precipitating agent [18] and the initial solution of the salt, seed crystals [19]. The studies considering the formation of phases in the presence of cobalt haven't been found.

Chemical oxidation of Fe (II) to Fe (III) with the help of O_2 in the presence of ~~a~~ cobalt cations is a complex process involving the formation of metastable partially oxidized intermediates that are ultimately converted to various stable oxide compounds such as hydroxide, hematite, magnetite, goethite, lepidocrocite and cobalt ferrite. Although in many practical situations the nature of the final products is of more interest than the kinetics of oxidation, it is difficult to find in the literature a description of all the main stages and principles governing the kinetics of these reactions, and ultimately the regularities of phase formation.

3. The purpose and objectives of the study

The goal of the research was to study the effect of the mode of conducting oxidation of Fe^{2+} by atmospheric oxygen on the phase composition of the products obtained.

To achieve the goal the following tasks were set:

– calculation of the equilibrium concentrations of the components of the system $Fe^{2+}/Co^{2+}/O_2/H_2O$ over a wide pH range;

– determining the influence of Co^{2+} ions presence, the pH of the initial solution, the temperature and amount of oxidizing agent on the rate of Fe^{2+} oxidation;

– studying the features of producing iron (III) oxide compounds and determining their phase composition at various oxidation conditions.

4. Materials and methods of research

Aqueous solutions of iron (II) sulfate and cobalt sulfate in a concentration of 1–10 % weight percent have been used for the investigation. Selection of salts was caused by industrial application in the production of metal oxides. The initial concentration of sodium hydroxide was 1 mole/liter.

The concentration of iron in the solution was measured in three ways: by permanganate, bichromate and – in the case of joint presence of iron and cobalt salts – by weight method using α-nitroso β-naphthol.

X-ray diagrams of oxy-hydroxides and oxides were obtained on diffractometer DRON-2.0 with K_{Co} radiation.

To study the kinetics of the redox reaction of the conversion of ferrous hydroxide to ferric compounds the value of alkali consumption in the process of oxidative hydrolytic precipitation or co-precipitation in the system $Fe^{2+}/Co^{2+}/O_2/H_2O$ was used. Neutralization mode can be done either by a single addition of alkali up to a predetermined pH value or by keeping alkali pH at a constant level using continuous dosing of small portions of alkali. In the first case, after the addition of alkali during the hydrolysis process and product formation, pH decreasing (pH-dynamic mode) is observed. In the latter case, pH value ranges throughout the process about a predetermined value (pH-static mode). The pH-static mode allows you to follow the dynamics of alkali absorption in the system and thus to judge the speed of oxidative hydrolytic co-precipitation.

Reactions of OHCP were performed at different temperatures in a thermostatic cell equipped with temperature-compensated electrode systems to measure and record the pH and the redox potential of the system and with stirrer having rotation speed of 300 rev/min. The cell was provided with an input device and that of recording the amount of bubbling air (gas meter CGT-400). Ferrous sulfate solution in the amount of 0.2 liter was placed into the cell. The pH was adjusted to the predetermined values by means of NaOH solution. When carrying out the experiments in the pH-static mode the neutralization pH was set and kept constant, the amount of alkali consumed being fixed. Pulse feeding of alkali in the pH-static area was performed by automatic titration unit. In preliminary experiments the rate of alkali pulse feeding convenient for measurement in the test area was set, being 0.03 ml/min. The effective rate of air bubbling (min^{-1}) was calculated using the formula:

$$\varpi_{ef} = \frac{W}{V_{ef}},$$

where W – air consumption, l/min; V_{ef} – effective volume of the suspension, l.

The effective volume of the suspension is calculated as follows:

$$V_{ef} = V_0 + 1/2\left(\sum_i \Delta V \Delta t\right) / \left(\sum_i \Delta t\right),$$

where V_0 – initial volume of the solution to be treated (l); ΔV_i – the amount of the i-th introduced reagent (l); Δt_i – time of introducing the i-th reagent (min).

Redox potential and pH were measured by ion meter and presented as dependences: pH (t), E (t), dE/dt (t).

Fig. 1 shows how the pH and the redox potential change in the system $Fe^{2+}/Co^{2+}/O_2/H_2O$ at pH-static mode.

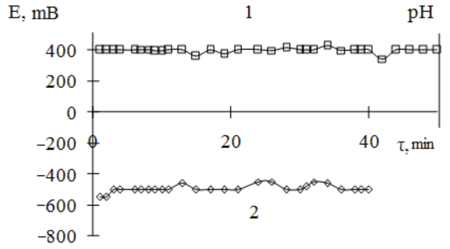

Fig. 1. Changing of pH (1) and the redox potential E (2) in the system $Fe^{2+}/Co^{2+}/O_2/H_2O$ at pH-static mode

No significant changes in pH and the redox potential with time makes it possible to assume that the formation of cobalt and iron oxyhydroxide compounds occurs constantly at adding new portions of alkali.

Fig. 2 shows how the pH and the redox potential change in the system $Fe(OH)_2$–$Co(OH)_2$–O_2–H_2O at pH-dynamic mode. There are several peaks on dE/dτ curve, allowing to determine the time of oxidation. Thus, it is possible to correlate oxidation time with the phase composition of the resulting product.

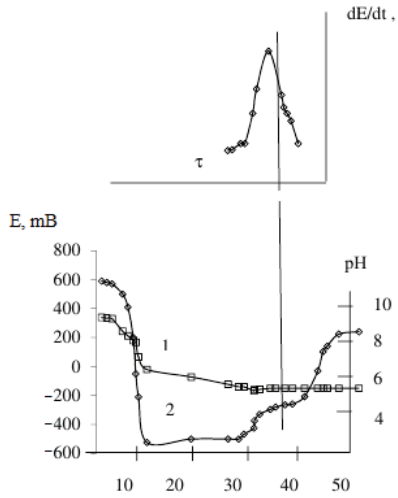

Fig. 2. Generalized dependence (1) — the redox potential (2) — dE/dτ on time for $Fe^{2+}/Co^{2+}/O_2/H_2O$ system

To determine the influence of the synthesis main parameters on the phase formation software package (SP) HYDRA-MEDUSA was used. SP is a combination of thermodynamic database and geochemical constants that enable to construct very easily many different types of chemical diagrams: Pourbaix diagram, mass proportions of thermodynamically possible phases, the solubility and others. The database makes it possible to create the input files for HYDRA-MEDUSA, which represent the windows interface with MS-DOS versions of the input devices and visualization program of the chemical equilibrium diagram. This software system allows calculating complete, metastable and intermediate chemical equilibria in the systems where an aqueous electrolyte solution, gas mixture, liquid and solid single- and multi-phases can be present simultaneously. SP includes a built-in system of intra matched bases of thermodynamic data and the bank of initial chemical compositions.

5. Research results of phase formation process in the system $Fe^{2+}/Co^{2+}/O_2/H_2O$

Fig. 3 shows the relationship between the calculated equilibrium concentrations of the system components and the pH in the oxidizing environment obtained by SP HYDRA-MEDUSA. At pH=3–1 hydrosulfate is formed, and further increasing of pH leads to the formation of magnetite with embedded cobalt cations, while at high pH values non-stoichiometric cobalt ferrite is formed.

The experimental results (Fig. 4) show that the phase composition of the product obtained depends largely on the pH of the solution. At pH-static mode, with increasing pH from 6 to 12 for the same synthesis parameters the following sequence of phase formation is recorded: γ-$Co_xFe_{1-x}OOH$–α-$Co_xFe_{1-x}OOH$–$Co_xFe_{3-x}O_4$. With further increase of the solution pH only $Co_xFe_{3-x}O_4$ is formed. At pH-dynamic mode, the sequence of phase formation is maintained (with no γ-modification). Dependency analysis shows that both in pH-static and pH-dynamic modes the conditions for obtaining non-stoichiometric cobalt ferrite are alike: range of pH=10–12, t=20–60 °C.

It was also found that depending on the synthesis parameters the modified ferric oxyhydroxide of α-modification, a mixed oxide of iron (II) and iron (III) or a binary mixture of α-$Co_xFe_{1-x}OOH$ and Fe_3O_4 can be the end product of ferrous hydroxide oxidation.

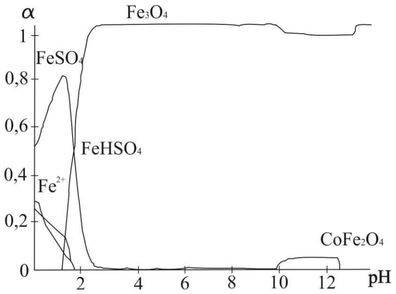

Fig. 3. The dependence of the calculated equilibrium concentrations of the components in $Fe^{2+}/Co^{2+}/O_2/H_2O$ system on the pH (C_{Fe2+}=0.5 M, C_{Co2+}=10 % by weight, the gaseous medium is air)

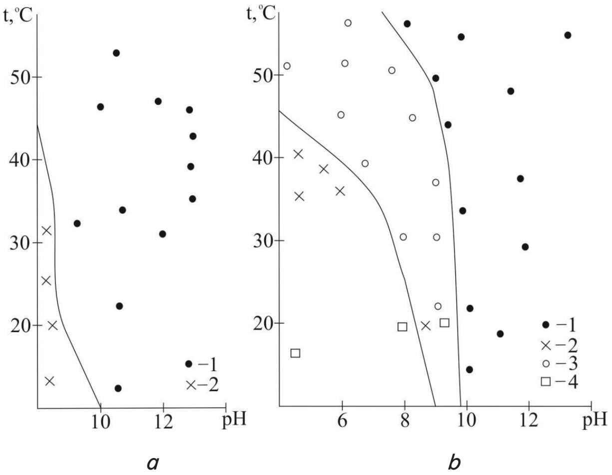

Fig. 4. The dependence of the phase composition of the resulting precipitate in $Fe^{2+}/Co^{2+}/O_2/H_2O$ system on the temperature and pH of the solution (*a* — pH-dynamic mode, *b* — pH — static mode): 1 — $Co_xFe_{3-x}O_4$, 2 — α-$Co_xFe_{1-x}OOH$, 3 — α-$Co_xFe_{1-x}OOH$ + Fe_3O_4 , 4 — γ-$Co_xFe_{1-x}OOH$

To determine the regularities of change in the phase composition of iron oxide compounds obtained while changing the temperature and air flow rate the studies were conducted at pH=9, within the temperature range of 20–60 °C and air flow rate of 4–10 min^{-1}. The process end was determined according to the data on the changes of the system's redox potential.

During the experiments the kinetics of alkali absorption in the oxidation process in $Fe^{2+}/Co^{2+}/O_2/H_2O$ system was also studied. The pH-static mode, which allows to follow the dynamics of alkali absorption in the system and thus to draw conclusions about the rate of OHCP in the studied system, was chosen as a mode of neutralization. In the course of the experiment, it was found that characteristic extremes (Fig. 2) are observed on the differential curve of the redox potential change during OHCP. With this, the first extreme corresponds to the onset of intermediate product formation, the second one – to the formation of the final product. The time interval between these extremes – the time of intermediate conversion to the final product of the reaction – can serve as the kinetic characteristic of the intermediate product conversion. The end of the oxidation process is the record of the potential jump, the system pH varying monotonically with time. To describe the kinetics of OHCP two values were introduced, namely the average rate of alkali absorption V□=dV_{OH-}/dt, which is defined as the ratio between the amount of the absorbed alkali and the time of the pH-static mode, and the value of the alkali maximum absorption rate. The dependence between the instantaneous rate of alkali absorption V and W is extreme in nature (Fig. 5), and at the same time, with increasing amplitude values $V_{мах}$ the curves maxima move along the time axis to the left. The latter can be explained by the fact that at a certain stage of the intermediates transformation the number of free H^+ cations is great and alkali absorption rate is maximal in this area. Accordingly, the shift of the maxima on the V□ – t curve to the left with the increase of W value represents an increase in the intermediates conversion rate.

In the second series of experiments the dependence of time change for the alkali absorption average rate at different content of cobalt in the system (Fig. 6, 7) was investigated.

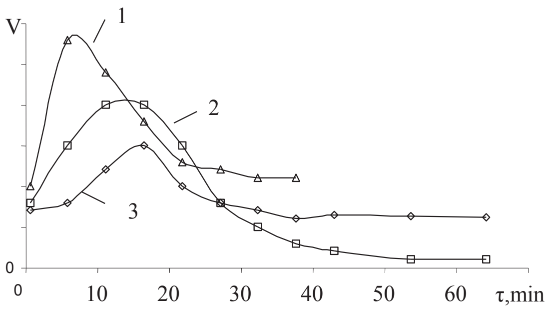

Fig. 5. Dependence of alkali absorption rate with time under different effective air speeds W, min^{-1}: 1 — 10, 2 — 8; 3 — 6

According to experimental data, with the decrease in the proportion of cobalt in the system the process time increases. As can be seen from Fig. 7, the average rate of alkali consumption is independent of the cobalt content in the system at the air flow rate 6–10 min^{-1}. The principal difference between the amount of alkali consumed for curve 1 in Fig. 7 can be explained by the fact that at low oxidation rate catalytic action of cations Co^{3+} is not manifested, so the average speed of alkali consumption increases.

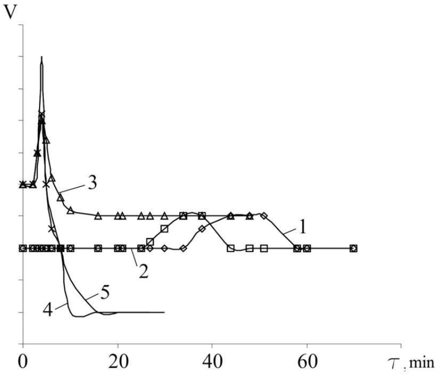

Fig. 6. Dependence of absorbed alkali volume versus time for different cobalt content in the solution: 1 — 0 % Co, 2 — 1 % Co, 3 — 2 % Co, 4 — 5 % Co, 5 — 10 % Co

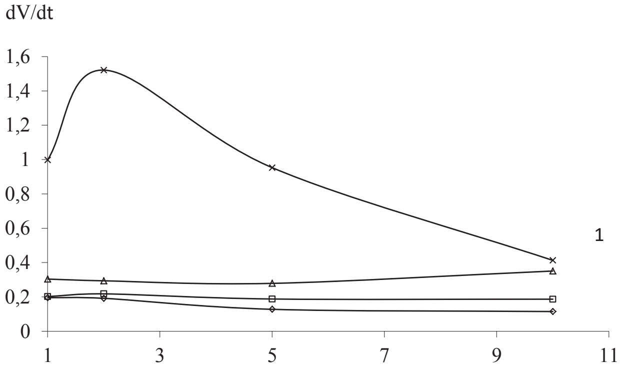

Fig. 7. Dependence of the alkali average absorption rate versus content of cobalt in the system W, min^{-1}: 1 — 4; 2 — 6; 3 — 8; 4 — 10

6. Discussion of the research results on the effect of oxidation conditions on the phase formation processes

From the theoretical and experimental data it follows that the rate of oxidation of iron (II) cations as well as phase composition of the products depend mainly on the pH values, the content of metal cations and air flow rate.

According to experimental data, with the decrease in the proportion of cobalt in the system the process time increases. The dependence of the duration of the oxidation process on cobalt content in the system at different air flow rates (Fig. 5, 6) may be due to heterogeneous redox processes. It is known that in systems containing additional metal cations, the process rate can be repeatedly increased. This is explained by the following reactions:

$Fe^{2+}–e=Fe^{3+}$,

$Me^{3+}+e=Me^{2+}$,

$Me^{2+}–e=Me^{3+}$.

Also, an additional cation is the catalyst not changing in the oxidation process. Polyvalent cations can act as catalyst cations.

According to the experimental data obtained, the presence of cobalt cations has a catalytic effect on the oxidation of Fe^{2+} ions. This is due to the fact that the air oxidation of bivalent cobalt Co (II) at low pH hardly takes place and at pH=8–10 oxidation occurs slowly to form $Co(OH)_3$ hydroxide. In the case of intensive bubbling the oxidation of Co (II) proceeds considerably faster to form Co (III) compounds. The degree of oxidation of +3 is unstable for cobalt, so cobalt (III) compounds exhibit their oxidizing properties and are reduced to the divalent state, oxidizing iron compounds.

7. Conclusions

1. It is found that in the system $Fe^{2+}/Co^{2+}/O_2/H_2O$ with constant cobalt content, the alkali consumption rate and the rate of product formation increase with increasing effective air flow rate. At constant rate of oxidation the oxidation time is reduced with the increase of cobalt content in the system.

2. The phase composition of the resulting compounds is determined by the mode of OHCP (dynamic or static). In the pH-static mode the range of obtaining α-$Co_xFe_{1-x}OOH$ is much wider than in the pH-dynamic mode. Formation of $Co_xFe_{3-x}O_4$ spinel structure occurs at high pH and slow oxidation process.

3. In the presence of cobalt ions 3+, the rate of iron 2+ compounds oxidation by atmospheric oxygen increases, because of their catalytic action.

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