Dissolution of iron electrodes during polarization with three-phase AC in hydrochloric and sulfuric acids solutions

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ABSTRACT

In present work the regularities of electrochemical dissolution of iron with the participation of industrial three-phase AC 50Hz in aqueous solutions of HCl and H_2SO_4 were studied the first time. The features of the dissolution of iron electrodes at polarization with alternating current in acid solution to form ions of iron (II) were studied and the influence of various factors was examined. Based on the study results a new and efficient method of synthesis of iron salts which are widely used as a coagulant in water treatment was proposed.

Keywords: Three-phase alternating current, current efficiency, iron, chloride iron, sulfate iron, polarization.

INTRODUCTION

This article examines ways of electrochemical obtaining chloride and ferric sulfate, which are used as coagulants in the treatment of contaminated water. In this regard, in this paper the patterns of electrochemical dissolution of iron electrode during polarization in industrial three-phase alternating current with a frequency of 50 Hz in solutions of hydrochloric acid and sulfuric acid were studied the first time. High efficiency and quality of an industrial alternating current polarization to obtain compounds of many sparingly metals are listed in earlier reports[1,2].

It is known that coagulation is a consolidation process of the colloidal and dispersed particles as a result of sticking, connection with one another depending on the values of their electrical charge.

Typically, many substances which pollute and stain natural water are in the form of colloids. The addition of coagulants lightens such water and increases the treatment efficiency. Water treatment plants mainly use compounds such as chlorides and sulfates of iron and aluminum[1,3].

Our research is devoted to the synthesis of ferric sulfate and chloride by electrolysis of waste iron at the polarization

with three-phase alternating current in solutions of hydrochloric and sulfuric acid, and is aimed at implementing the principle of non-waste technology. In addition, electrochemical methods are one of the important areas of clean sustainable technology. In this context, the synthesis of important metal compounds in different aquatic media using industrial AC gives the opportunity to solve many problems.

Standard electrode potentials of transition iron ions have negative value:

$$Fe - 2e \rightarrow Fe^{2+} \qquad E^0 = \ -0,44 \ B \ \dots(1)$$
$$Fe - 3e \rightarrow Fe^{3+} \qquad E^0 = \ -0,04 \ B \quad \dots(2)$$

However, under normal conditions an oxide film forming on its surface keeps the metal from being dissolved in water. Whereas in acids, for example in hydrochloric or sulfuric acid, iron dissolves significantly, but with a small rate[5]:

$$2Fe + 6HCl \rightarrow 2FeCl_3 + 3H_2 \qquad \dots\dots\dots(3)$$
$$Fe + H_2SO_4 = FeSO_4 + H_2 \qquad \dots\dots\dots(4)$$
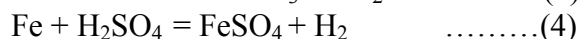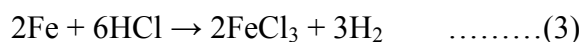
Our researches have shown that in 80 g/l hydrochloric acid at 25^0C the rate of chemical dissolution of the iron is 88 $g/(m^2 \cdot hour)$, and in 100 g/l sulfuric acid solution it is equal to $47g/(m^2 \cdot hour)$. Obviously, acidity of the solution plays a special role in iron dissolution. This is due to the participation of metal hydrocomplexes in electrode reactions.

Researches are done on the effect of the AC density, acid concentration, temperature and time of electrolysis for dissolution of iron electrodes during polarization by three-phase industrial alternating current at frequency 50 Hz in solutions of hydrochloric acid and sulfuric acid[3,4].

EXPERIMENTAL

Method

Experiments were conducted in an 200 ml electrolytic cell without stirring of the solution. Electrodes were made from iron plates. Solutions of hydrochloric acid and sulfuric acid were used as electrolytes. Three-phase alternating current obtained from special setup (three-phase transformer). Line current was regulated by a three-phase laboratory transformer (Fig. 1).

Current yield was calculated by the amplitude of the anode half-cycle of each phase weight change of iron electrodes before and after electrolysis.

In each phase of the anode half-cycle of AC, the iron on the electrode dissolves according to reactions (1) and (2) to form their ions.

Whereas, in the cathode half cycle of AC hydrogen ions recover on the surface of iron electrodes:

$$2H^+ + 2e \rightarrow H_2$$
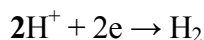
The results show that under optimal conditions in the anodic half cycle on the surface of the iron electrodes appears the formation reaction, generally of the divalent iron ion, as in the cathode half cycle hydrogen is produced as a gas[6,7].

RESULTS AND DISCUSSION

Fourier transform infrared spectral measurements

The effect of current density in the range of 500-2500 A/m^2 on the formation of iron ions(II) in hydrochloric acid and sulfuric acid solutions during electrolysis and the dissolution rate of the iron electrode was studied.

During polarization of iron electrode by three-phase AC in a hydrochloric acid solution the current output on production of iron ions (II) greatly increases with the

increase of the current density (Figure 2, curve 1). As it can be seen from Figure 2, at current densities of the electrodes 1000 A/m^2 and higher, the current output on dissolution of iron exceeds 100%. It was found that in the sulfuric acid solution the current output of the iron ions (II) decreases with increase of current density (Figure 2, curve 2). This phenomenon is explained by the fact that depending on the concentration increase of oxygen containing sulfate anion increases the possibility of iron oxide formation on the electrode surface.

In two acids, the increase of the current density increases the dissolution rate of iron electrode according to Faraday's law (Figure 3)

The effect of hydrochloric acid and sulfuric acid concentration on current output of iron dissolution and the dissolution rate of the iron electrode during the polarization of electrodes by three-phase alternating current was studied. As seen in Figure 4, with concentration increase of hydrochloric acid increases the output current and reaches a maximum value (105.9 %). Even when the current is stopped on the line intensive chemical self-dissolution of the iron electrode continues. Which is explained by the influence of active chloride ions. Therefore, at high concentrations of HCl solution, not only electrochemical but also a chemical dissolution of iron is going and the output current of the iron ions (II) exceeds one hundred percent.

Increasing the concentration of hydrochloric acid increases the dissolution rate of iron electrode (Figure 5, curve 1). When the concentration of sulfuric acid is increased up to 100g/l the iron dissolution rate increases to 1485 g/(m^2·hour). Further increase of the concentration of sulfuric acid leads to a decrease in the dissolution rate (Figure 5, curve 2). This is because of the possibility of iron oxide formation on the electrode surface due to the concentration increase of oxygen containing sulfate ion.

It is shown that during polarization by a three-phase AC of the iron electrode in a hydrochloric acid solution, the temperature change of the electrolyte does not affect the electrode processes.

Figures 6, 7 show that during the polarization by AC in acidic solutions the output by current of iron ion formation (II) and the dissolution rate initially increases and then decreases with the increase of electrolysis time. These dependences pass through a maximum. Reducing the current yield and the dissolution rate of iron over time can be explained by the gradual passivation of the electrode surface by the electrolysis products and the appearance of concentrative polarization.

After the electrolysis, the solution was evaporated, then cooled to obtain crystals of ferrous sulfate and chloride. X-ray phase analysis of the crystals obtained in hydrochloric acid solution showed the formation of $FeCl_2 \cdot 6H_2O$ compound (Figure 8).

All reflexes correspond to the phases of ferric chloride (II): 5,78 A^0; 4,37 A^0; 3,15 A^0; 2-9; 2,43 A^0.

Results of X-ray phase analysis of the crystals obtained in the sulfuric acid solution revealed the formation of a compound of $FeSO_4 \cdot 7H_2O$, i.e. ferrous sulfate heptahydrate (Figure 9), which by the common name is iron copperas.

All reflexes correspond to iron sulfate phases (II): 6,9 A^0; 5,48 A^0; 5,4 A^0; 4,5A^0; 4,0 A^0; 3,61 A^0; 3,40 A^0; 3,28 A^0; 3,23 A^0 and others, which belong to compound $FeSO_4 \cdot 4H_2O$ (ASTM 19-632).

Reflexes 4,92 A^0; 4,88 A^0; correspond to phase $FeSO_4 \cdot 7H_2O$ to compound (ASTM 19-632).

The formation of this compound is also shown by Mossbauer spectroscopy method (Chart, Figure 10).

Chart

Determination of the obtained compound by Mossbauer spectroscopy.

Sample	Is, мм/с	Qs, мм/с	S* отн., %	Sample formula
	1.26	3.22	100	$FeSO_4*7H_2O$

Thus, the results of the research made possible to obtain new information about the patterns of the iron electrochemical dissolution during the polarization by industrial three-phase alternating current.

An efficient synthesis method of inorganic iron salts (II) chloride ($FeCl_2 \cdot 6H_2O$) and sulfate ($FeSO_4 \cdot 7H_2O$), polarization of iron electrodes by three-phase alternating current in solutions of hydrochloric and sulfuric acids is proposed. Obtained salts have high purity and the compositions do correspond to the chemical formula, so no doubt to use them as chemical reagents.

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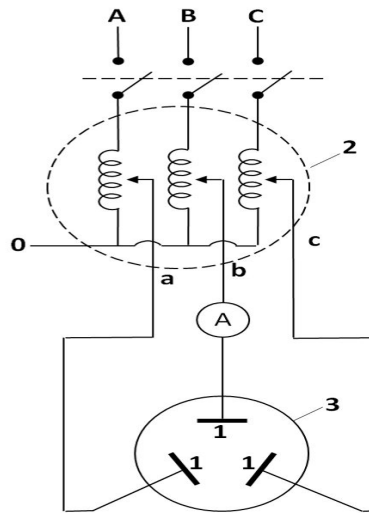
Fig. 1: Drawing of the setup for study of iron electrodes dissolution in the acidic medium during polarization by three-phase AC.

        1- Iron electrodes
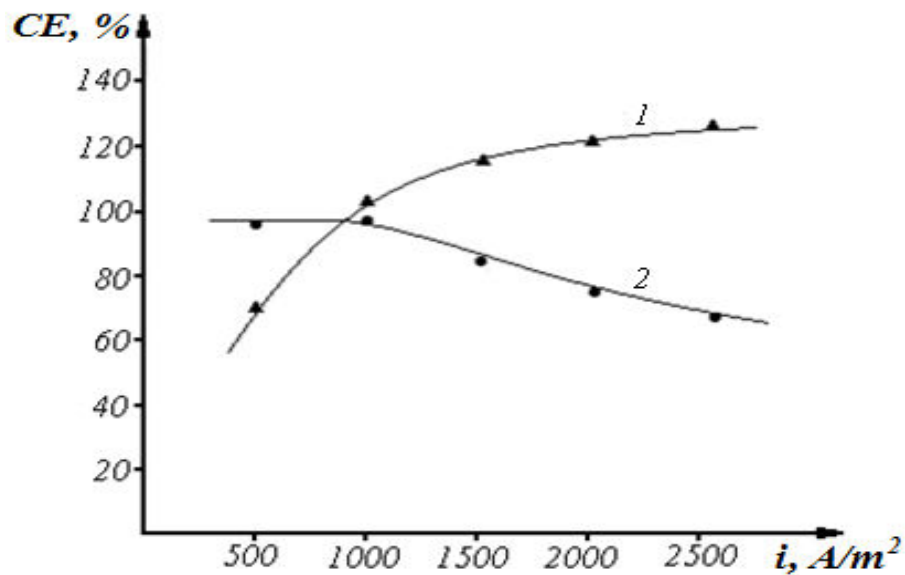   2- Three-phase laboratory transformer
        3- Electrolyzer

Fig. 2: The effect of the current density in the electrodes on formation of iron ion by the current. 1-80 g/l HCl; 2 - 100 g/l H_2SO_4; τ = 0,5 hour.
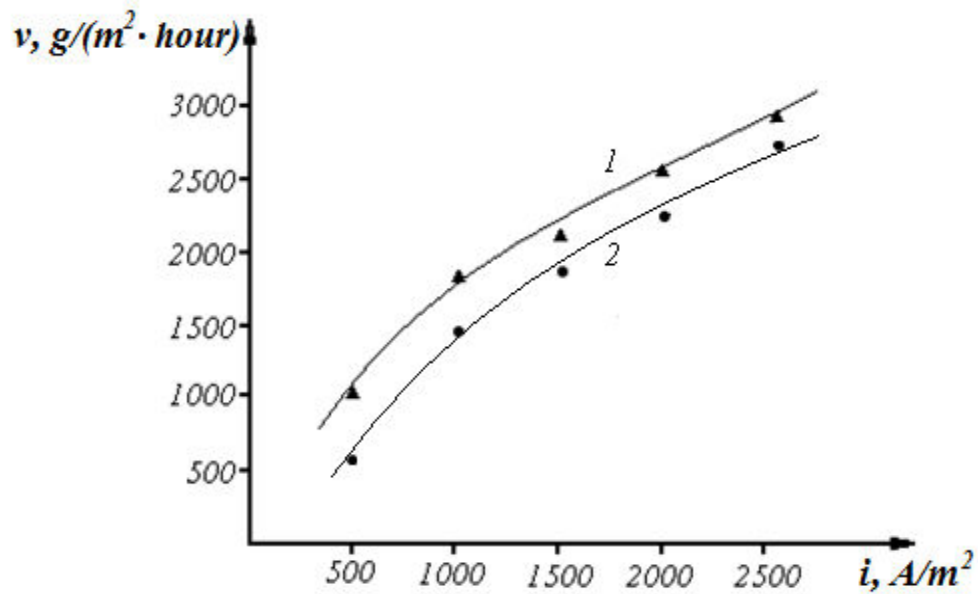
Fig. 3: Effect of the current density in the electrodes on the metal dissolution rate in the formation of iron ions (II). 1-80 g/l HCl; 2 - 100 g/l H_2SO_4; τ = 0,5 hour.
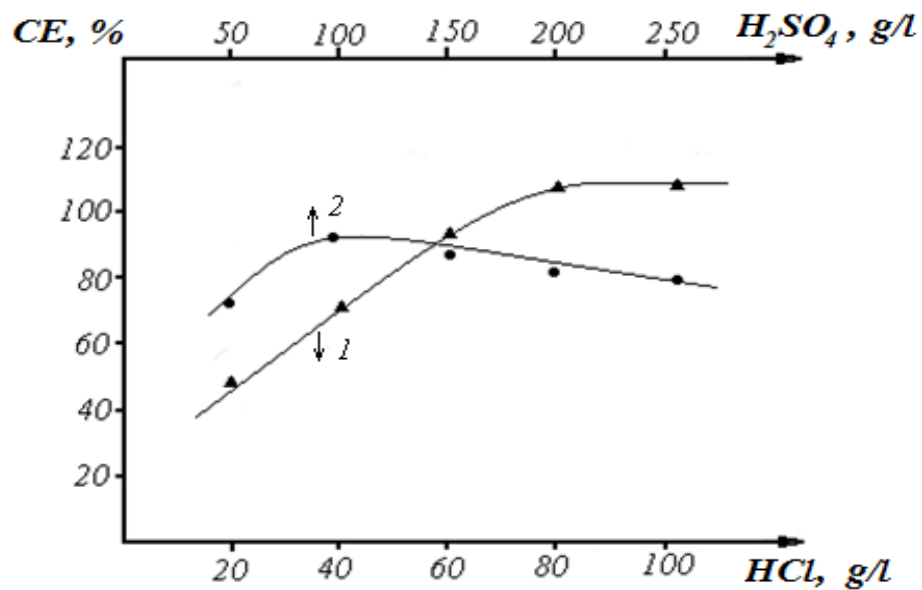
Fig. 4: Effect of hydrochloric (1) and sulfuric (2) acid concentration on the output current of iron ions (II). i = 1000A/m²; τ = 0,5 hour.
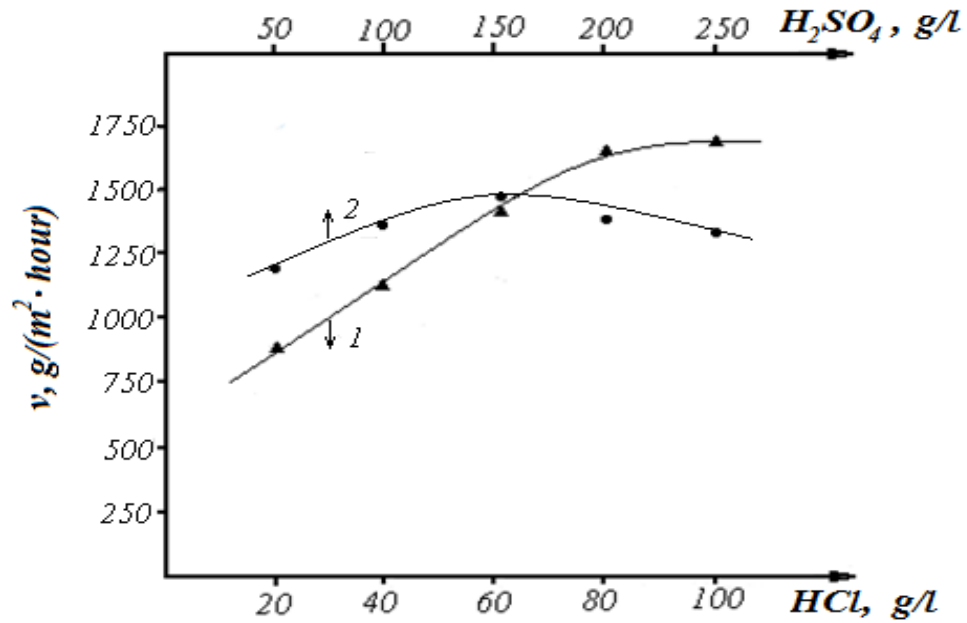
Fig. 5: Effect of hydrochloric (1) and sulfuric (2) acid concentration on dissolution rate of iron electrodes (II). i = 1000A/m^2; τ = 0,5 hour.
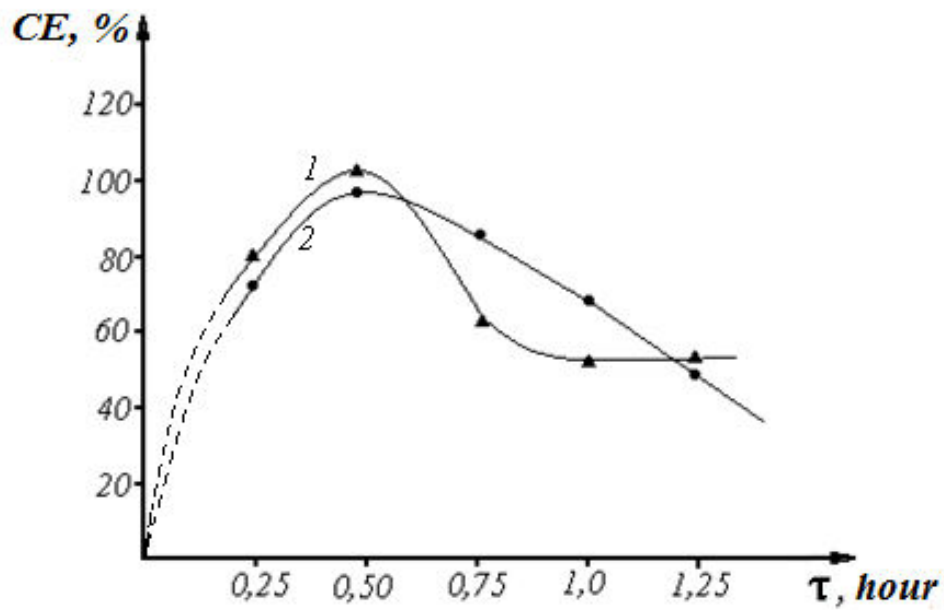

Fig. 6: Effect of the electrolysis time on current yield of iron dissolution. 1-80 g/l HCl; 2 - 100 g/l H$_2$SO$_4$; i = 1000A/m^2.
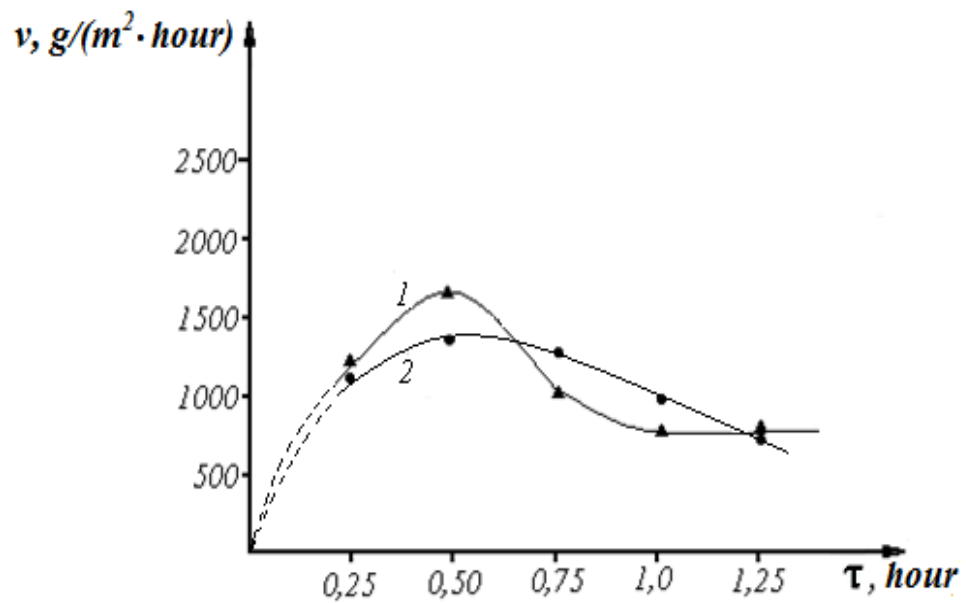
Fig. 7: Effect of electrolysis time on the dissolution rate of iron. 1-80 g/l HCl; 2 - 100 g/l H_2SO_4; i = 1000A/m^2.
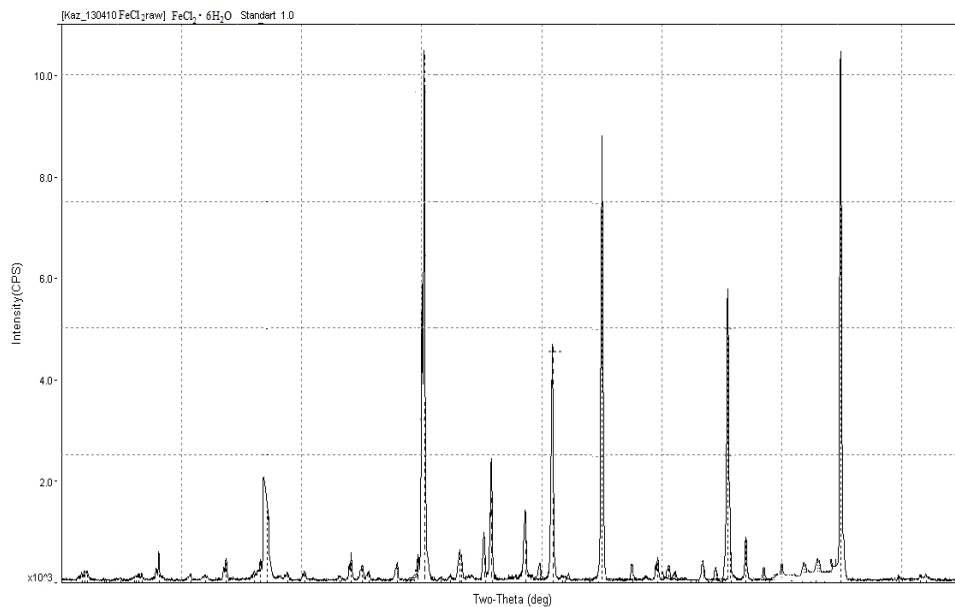

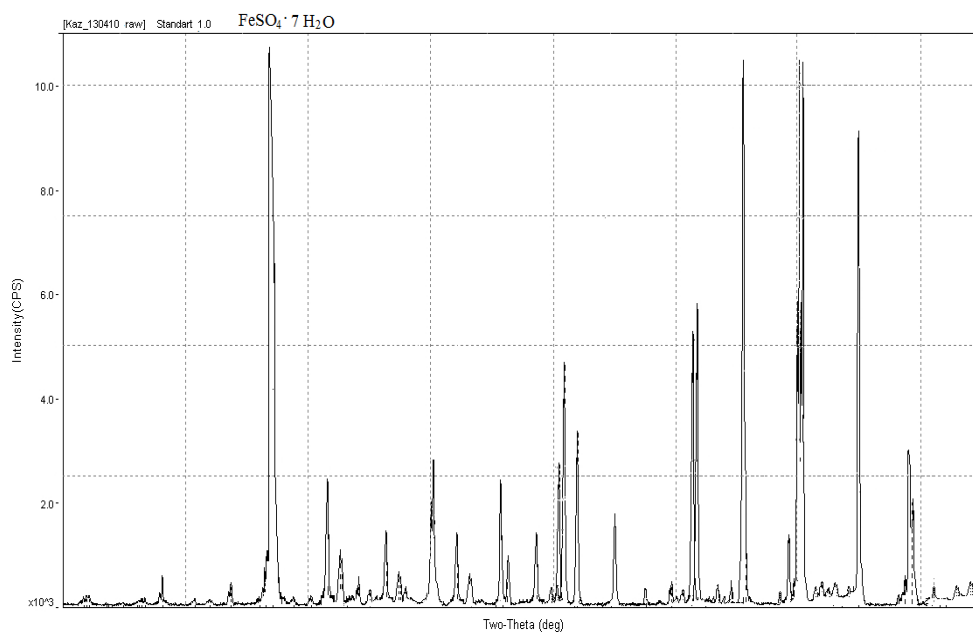**Fig. 8:** The results of X-ray phase analysis (XRF) of $FeCl_2 \cdot 6H_2O$ produced by electrolysis.

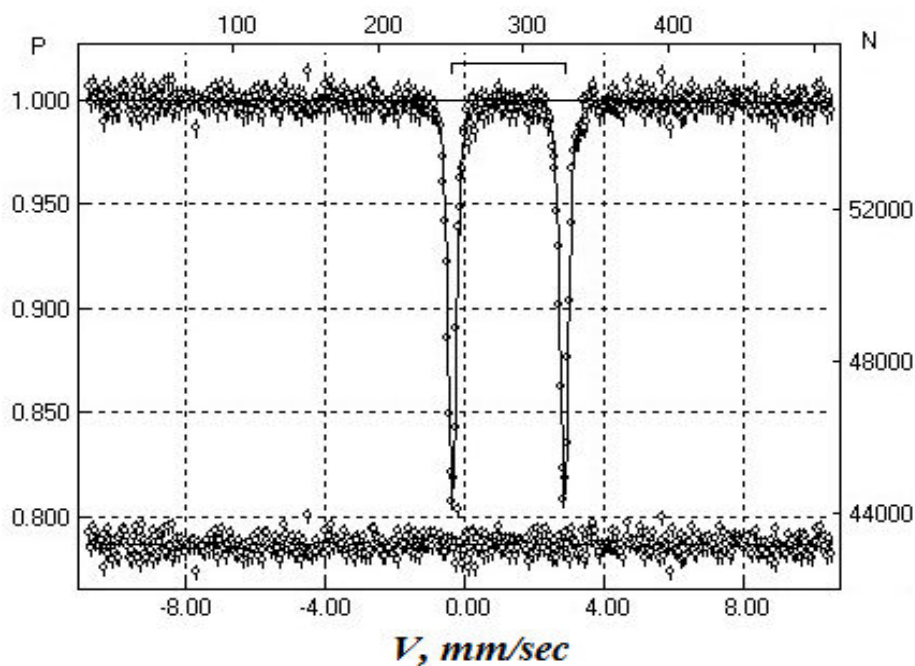**Fig. 9:** The results of X-ray phase analysis (XRF) of $FeSO_4 \cdot 7H_2O$ produced by electrolysis.

Fig. 10: Mossbauer spectroscopy analysis results of the compound obtained by electrolysis in sulfuric acid solution ($FeSO_4 \cdot 7H_2O$).