

# Study of the process coprecipitation of Fe-Ni hydroxides for ferrite production

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## Introduction

Nickel ferrite has been the subject of research by scientists for many years. This is primarily due to the extremely wide range of its applications, covering such as high-density magnetic recording, computed tomography, magnetic resonance imaging contrast agents, targeted drug administration and hyperthermia, electronics, telecommunications and space equipment, environmental technologies, gas sensors, supercapacitors, etc.

The use of liquid-phase technologies for the production of nickel ferrites allows to change the structure, composition and, as a consequence, the functional properties of the final product. A hydrophase method is common, which includes the stage of coprecipitation of trivalent and divalent hydroxides followed by heat treatment at high temperatures. More promising is the technology based on co-precipitation of iron (II) and nickel (II) hydroxides. However, this process has not been studied enough.

## Experimental

The study of the co-precipitation process was carried out in a thermostatic reactor equipped with a stirrer, a thermometer. The constant temperature was maintained with the help of thermostat.

Potentiometric titration was performed in thermostat (1°C) by a pH meter-millivoltmeter pH-150. As the measuring electrode used glass brand ESL-15-11, as the reference electrode is a chloride silver electrode brand EVL-1G4, the error of measurements of pH was 0.02 units. The titration was performed as follows: from a burette with a split price of 0.02 ml was added a solution of NaOH to the original solution of FeSO<sub>4</sub> and NiSO<sub>4</sub>. To obtain comparable results and simplify the interpretation of the curves of the added volume of NaOH, led to a molar ratio of [OH<sup>-</sup> / Me<sup>2+</sup>].

Cyclic voltammograms (VBA) were obtained using the Potentiostat / Galvanostat Reference 3000 (Gamry) potentiostat in potentiodynamic mode at a potential deployment rate of 100 mV/s. The platinum of 2.0 cm<sup>2</sup> served as the working electrode. The auxiliary electrode was also platinum. Comparison electrode - a saturated chloride silver electrode brand EVL-1M1, connected to the cell by an electrolytic bridge.

## Results

The main parameter characterizing the hydrolysis process of inorganic salts of ferrous and nickel is the pH of these solutions. The pH of the initial solutions of salts varies depending on the concentration and nature of the hydrolyzing salts. In addition, the metastable nature of solutions of ferrous sulphate causes the artificially low pH of the original solution by adding sulphuric acid.

To determine the completeness of the deposition of hydroxides, depending on the pH, it is necessary to consider the effect of the acidity of the medium on the equilibrium in the selected systems. Thermodynamic analysis of the deposition and coprecipitation process was performed according to the technique [20].

In solution, the values of the product of solubility  $K_{sp}Fe(OH)_2=10^{-15.1}$ ,  $K_{sp}Ni(OH)_2 = 10^{-14.7}$ . The relationship between the concentration of metal ions and pH values can be expressed as:

$$[Fe^{2+}] = \frac{K_{sp}Fe(OH)_2}{[OH^-]^2} = \frac{10^{-15.1}}{10^{2pH-28}} = 10^{12.9-2pH} \quad (1)$$

$$[Co^{2+}] = \frac{K_{sp}Ni(OH)_2}{[OH^-]^2} = \frac{10^{-14.7}}{10^{2pH-28}} = 10^{13.3-2pH} \quad (2)$$

Thus, the molar particles of the individual forms are determined by the values of the stability constants of the corresponding degrees of equilibrium and the concentration of free OH groups. Knowing the value of the step constants of stability and specifying the concentration of H<sup>+</sup>, it is possible to determine the fractions of individual forms of hydroxocomplexes of metals (II) at different pH values of the solution. Then the total concentration of residual metal ions [Me]<sub>s</sub> and the total concentration of ligands [L]<sub>s</sub> in the system Me-OH-L can be calculated according to equation:

$$[e]_s = [Me] + [MeL] + \dots + [MeL_n] = [Me]\{1 + \sum_{i=1}^n \beta_i [L]^{i-1}\} \quad (3)$$

$$[L]_s = [L] + [MeL] + 2[MeL_2] + \dots + n[MeL_n] = [L]\{1 + [Me] \sum_{i=1}^n i \beta_i [L]^{i-1}\} \quad (4)$$

where L is the ligand, n is the coordination number, and  $\beta_n$  (n = 1, 2, ...) is the equilibrium constant in the ligands.

The total concentration of residual metal ions of [Me<sup>2+</sup>]<sub>s</sub> in the Me<sup>2+</sup>-NaOH-H<sub>2</sub>O system with different pH values can be calculated by formulas.

According to the results of these calculations, a graph of the distribution of hydroxyl compounds of ferrous and nickel, depending on the pH of the medium, was constructed (Fig. 1).

In acidic solutions, metals exist in the form of double charge cations. As the pH increases from 0 to 5, Fe(OH)<sup>+</sup> and Ni(OH)<sup>+</sup> hydroxocomplexes prevail in the solution, and the precipitate of Ni(OH)<sub>2</sub> is formed when the pH is increased to 8-9. Sedimentation of ferrous hydroxide begins at pH=9, complete precipitation is achieved at pH = 10.5. At pH = 11.7, the dissolution of nickel (II) hydroxide begins, with the formation of Ni(OH)<sub>2</sub>

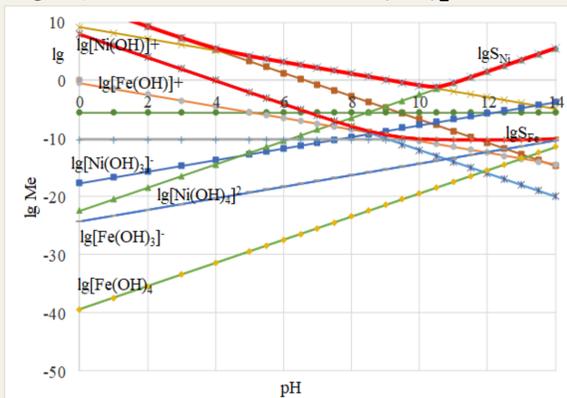


Figure 1: Dependence of the logarithm of the concentration of ions and hydroxocomplexes of Fe (II) and Ni (II) on pH

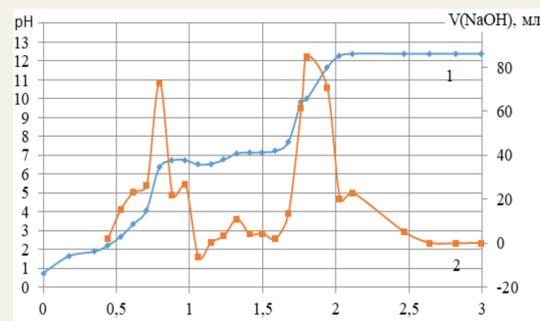


Figure 2: Potentiometric titration curves of Ni<sup>2+</sup> -Fe<sup>2+</sup> -SO<sub>4</sub><sup>2-</sup> -H<sub>2</sub>O solutions, 1: 2 molar ratio, integral form (1), differential form (2)

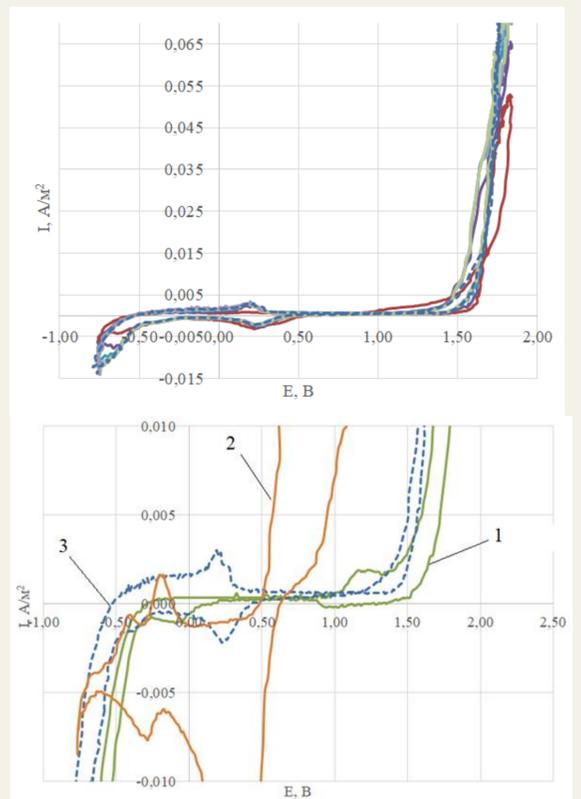


Figure 3. CVA solutions of a- Ni<sup>2+</sup>- Fe<sup>2+</sup>- SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O(a) five cycles and b- Ni<sup>2+</sup>- SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O (1) Fe<sup>2+</sup>-SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O (2) i Ni<sup>2+</sup>- Fe<sup>2+</sup>-SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O (3) five cycles per mol the ratio [OH<sup>-</sup>/M<sup>2+</sup>]= 1

Analysis of Figures 3 shows that at a molar ratio of  $n = [OH^-]/[M^{2+}] = 1$  solutions of Ni<sup>2+</sup>- Fe<sup>2+</sup>-SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O systems, the course of the curves practically does not change for cycles 1-5, that is, the speed of electrode processes is much greater than the speed destruction of polynuclear hydroxocomplexes. This is due to the stability of the particles. The peak of the anode branch of the curve in the potential range 1.3-1.6 V has a symmetric peak in the cathode region. The cathodic recovery wavelength at potentials 0.25-0.3 V on the cathodic branch of the CVA practically does not change with increasing number of cycles. This may be due to the reduction together with Ni<sup>2+</sup> ions of Fe<sup>2+</sup> ions, which can also bind to biodiesel complexes. The slight increase in the peaks indicates that in this case stable biodernal polyhydroxocomplexes are formed. It should also be noted that the forward and reverse course of the cathodic sections of the CVA do not coincide with each other, indicating a significant impact of the gradual release of cations from the formed polyhydrocomplexes. Analyzing results, it can be assumed that in both cases aquatic complexes are formed in the initial stages of deposition, and further increases in pH result in the formation of intermediates. The final product of deposition is polyhydroxocomplexes of ferum and nickel. Since the ions of nickel and ferum are in solution in the form of aquacomplexes  $[Ni(H_2O)_5] - O - Fe(H_2O)_5]^{2+}$ .

## Conclusion

The work proposes the use of potentiometric titration and cyclic voltammetry to study the coprecipitation of ferrous (II) and nickel(II) polyhydroxides. To evaluate the coprecipitation process, the analysis of integral and differential dependence of pH on the ratio [OH<sup>-</sup>/M<sup>2+</sup>]=1 is proposed.

## Contact information

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