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# PHASE TRANSFORMATION OF HEMATITE TO MAGNETITE UNDER MICROWAVE TREATMENT

*Phase transformations of natural and synthetic hematite in aqueous Fe (II)-containing medium under the influence of microwave radiation at a temperature range from room temperature to 260 °C and pressure of 6 MPa were investigated. The saturation magnetization of all initial samples was less than 1 $A \cdot m^2/kg$, while the saturation magnetization of the samples after phase transformations increases significantly (i.e., up to 27 $A \cdot m^2/kg$). It was shown by X-ray diffraction that all samples were transformed into magnetite. Thermomagnetic curves were measured for the treated samples and Curie temperatures were determined. Curie temperatures of the samples of natural hematite were determined as 560 °C and for synthetic hematite as 559 °C that are close to the Curie temperature of pure magnetite (580 °C). The relatively high saturation magnetization of obtained magnetic particles makes them promising for different applications (adsorbents of radioactive waste, carriers for magnetic drug targeting, etc.). The results of this investigation could also be useful for developing new technologies for production of iron ore concentrates from the hematite-containing waste of mining and processing plants.*

***Keywords:*** *hematite, magnetite, phase transformation, Fe (II)-containing solution, X-ray diffraction, magnetometry, thermomagnetic analysis.*

**Introduction**. Nowadays, deposits of high-grade iron ores and iron ores, which can be easily enriched (e.g. magnetite quartzite), are almost exhausted. That is why there is an increasing necessity of the creation of new technologies for iron ore concentrates production from low-grade oxidized iron ores (e.g. hematite quartzite) and iron-containing tailings.

Hematite ($\alpha$-$Fe_2O_3$) is one of the oldest known iron minerals. It is widespread in soils and rocks. The mineral is thermodynamically extremely stable at ambient temperature and usually is the final product of other iron oxides and hydroxides transformation. Hematite is antiferromagnetic, the Curie temperature of the mineral is 675 °C [1]. It is an important pigment, the main mineral of low-grade

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oxidized iron ores and waste of mining and processing plants.

Mainly, all methods of hematite transformation to magnetite in aqueous medium are based on the chemical method of magnetite synthesis. The main method of magnetite obtaining is a precipitation of mixed Fe(II)/Fe(III) solution in alkaline medium [2, 6, 8, 9]. The authors [3, 5, 7, 10, 11] investigated the influence of pressure, temperature and microwave radiation on the processes of magnetite production. For example, in the work [3], magnetite nanoparticles were obtained by precipitation of iron (II) sulfate in water medium by sodium hydroxide at pH ~11. After that, the precipitate was heated under the influence of microwave radiation for 10 min. As a result of the reaction, nanoparticles with the crystal size of 17 nm were obtained and their crystal lattice contains various hydroxocomplexes. The effect of microwave treatment of hematite iron ore samples was investigated by the authors [11]. The transformation was performed using a microwave oven with a maximum power of 900 W. Samples of iron ore were processed in oven at different duration and power levels without any other reagents. As a result, the content of reduced iron in the samples increased from 39.5% to 97.9% after microwave irradiation. In the other work [12], fine-grained ore particles were used as the source of Fe (III). The iron ore particles were dissolved in hydrochloric acid, and then the alkali was added. The solution was heated for 3 h in temperature range 90-110 ºC. As a result, magnetite nanoparticles with relatively high crystallinity were obtained.

Despite of the existence of many methods of transformation of the structure and magnetic properties of hematite into magnetite, the mechanisms of such transformations have not been studied enough, and the search of the most optimal methods of hematite to magnetite transformation continues. In our studies, we combine the method of synthesis of magnetic particles, methods of transformation of weakly magnetic minerals into strongly magnetic ones with minimization of the number of transformation stages. We believe that this will allow us to achieve the maximum conversion with minimal costs.

This work aimed to investigate phase transformations of synthetic hematite and natural hematite from oxidized iron ore from Kryvyi Rih basin, into magnetite in aqueous Fe (II)-containing medium under the influence of microwave radiation, increased pressure, and temperature.

**Materials and methods.** *Initial materials*. Samples of synthetic hematite were obtained after heating of synthetic lepidocrocite at 650 ºC for 2 hours. As a result, synthetic hematite was formed. Hematite ore was mined in the northern part of the quarry of the Ingulets Mining and Processing Plant. Samples of natural hematite were obtained by grinding of hematite ore up to <70 μm.

*Methods*. Mineral composition of the initial and transformed samples was determined by the method of X-ray diffraction (XRD) using diffractometer DRON-3M, $Co_{K\alpha}$ radiation ($\lambda$ = 0.178892 nm). The scan range of the samples was from 0 to 70 2θ, scan speed = 0.5 2θ per min. Qualitative X-ray diffraction analysis was performed by most intensive reflexes for each phase. The XRD phase diagnostics was performed using [4] by detected d-spacing. Cards for quartz: 89-8934; cards for magnetite: 89-0951; cards for hematite: 89-8104.

Magnetic characteristics before and after transformations were determined using a magnetometer with an Hall sensor. An external magnetic field of magnetometer varied in the range of 0 to ±0.45 T. Nickel carbonyl with saturation magnetization at room temperature of 54.4 $A \cdot m^2/kg$, was used as the reference sample.

Curie temperature of obtained samples was determined by thermomagnetic analysis using laboratory-built facility allowing automatic registration of sample magnetization as a function of temperature. The temperature range of sample heating was from room temperature to 650 ºC. The rate of sample heating/cooling was 65º/minute.

*The procedure of hematite transformation*. Investigations of synthetic and natural hematite transformation were carried-out at five temperature points: 100 ºC, 120 ºC, 160 ºC, 200 ºC and 260 ºC. Namely, 5 ml of 10% solution of ferrous sulfate was added to 1 g of initial hematite sample. After that, the reaction was started by adding 24 ml of 3M ammonia. The pH of solution was about 12. The solution was incubated at defined temperature and increased pressure (6 MPa) using Microwave Reaction System (Anton Paar Multiwave PRO) for 30 min. The obtained samples were washed three times with distilled water and dried in a thermostat at 90 ºC for 1 h.

**Results and discussion.** *X-Ray Diffraction*.

The initial synthetic sample consists mainly of hematite: the characteristic peaks (d-spacing) of hematite in XRD pattern are (Å) (Fig. 1, *a*): 3.382, 2.704, 2.251, 2.211, 1.848, 1.700, 1.602, 1.488, 1.458. Transformed samples consist of both hema-

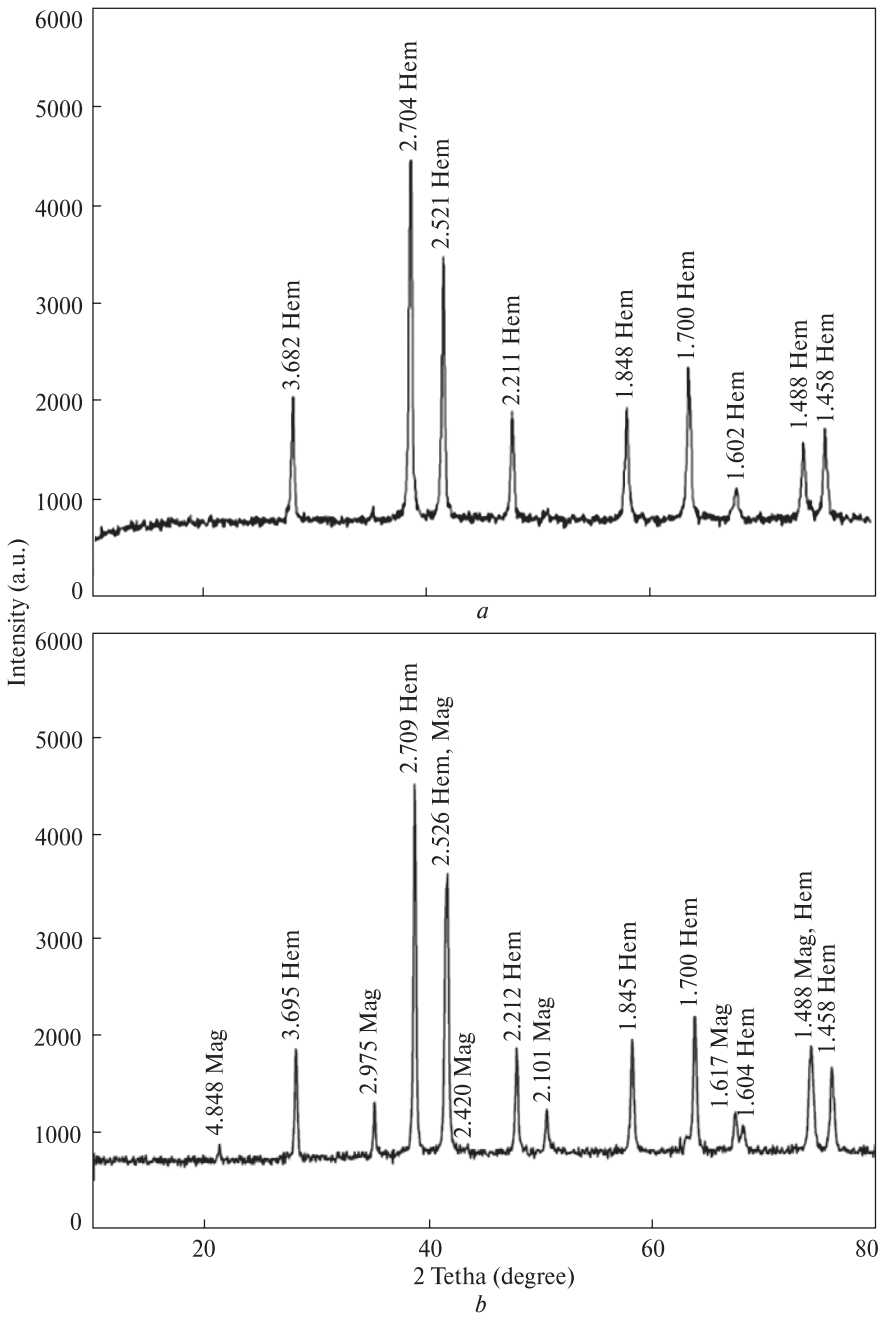


*Fig. 1.* XRD patterns of initial sample of synthetic hematite (*a*) and sample, obtained at $T$ = = 260 °C (*b*), (Hem — hematite, Mag — magnetite)

tite and magnetite phases (Fig. 1, *b*): the characteristic peaks (d-spacing) of magnetite occur at 4.848, 2.975, 2.526, 2.420, 2.101, 1.617, 1.488.

The phase composition of initial natural sample was mainly hematite with quartz traces (Fig. 2, *a*). Characteristic peaks of hematite in XRD pattern are (Å): 3.687; 2.701; 2.521; 2.296; 2.209; 1.843; 1.696; 1.601 and peaks of quartz in XRD pattern are (Å): 3.344. It was shown by XRD, that after phase transformation of natural hematite the new phase of magnetite appeared (Fig. 2, *b*).

The following characteristic peaks at XRD pattern of obtained samples (Å): (4.821, 2.963, 2.532, 2.097, 1.716, 1.617, 1.486) were attributed to magnetite. Weak peaks in the area less than 20 degree were referred to impurities, which content is less than 1%. Comparing figures 2, *a*, *b* one could conclude, that both natural and synthetic hematite are partly transformed into magnetite under abovementioned thermal conditions.

Magnetization measurement. The saturation magnetization ($M_s$) of initial samples was less than 1 $A \cdot m^2/kg$. The saturation magnetization of all samples, obtained after transformation, increased up to 27 $A \cdot m^2/kg$. Saturation magnetization, determined for magnetic samples, obtained from syn-

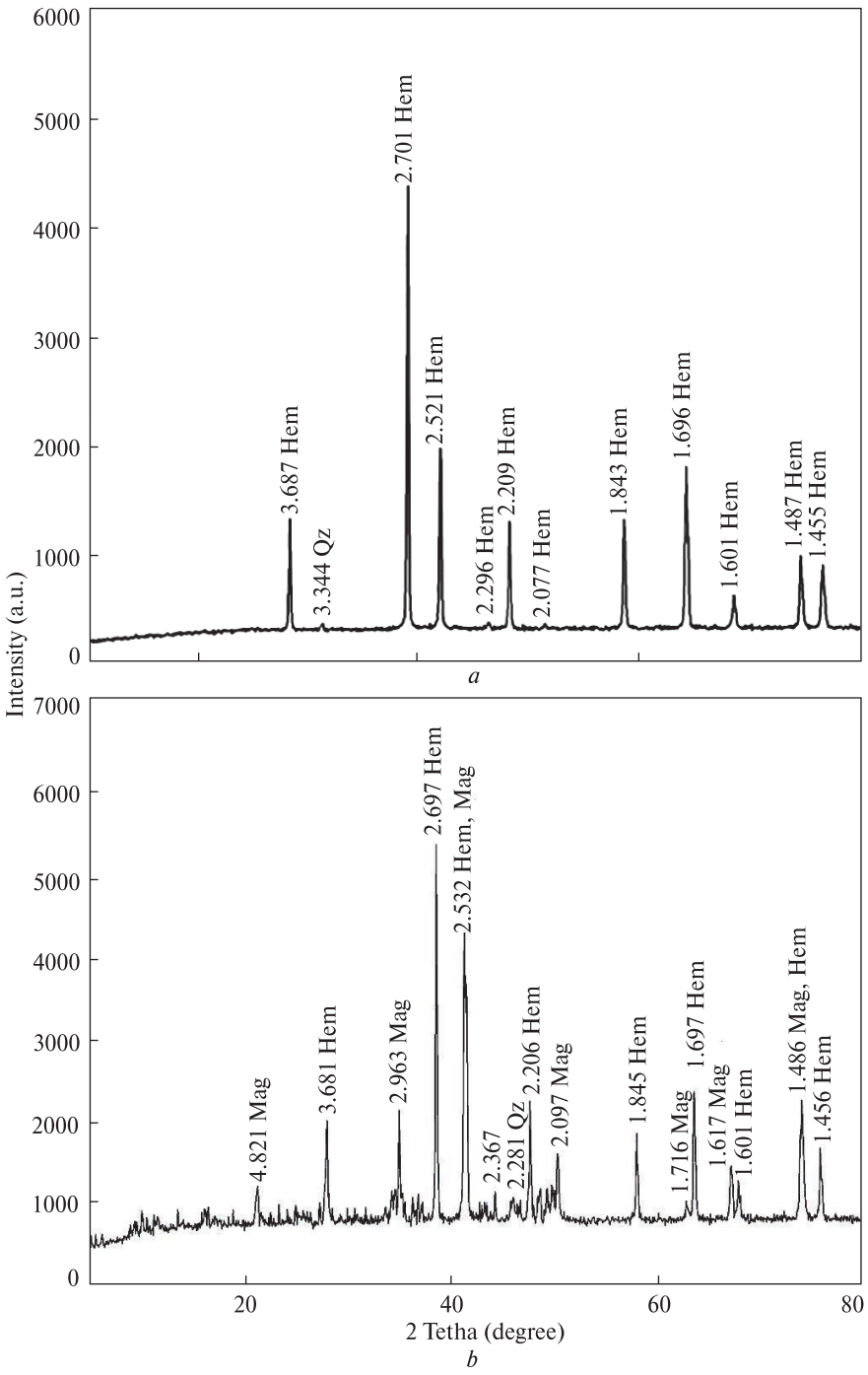


*Fig. 2.* XRD patterns of initial sample of natural hematite (*a*) and sample, obtained at $T$ = = 260 °C (*b*) (Hem — hematite, Mag — magnetite, Qz — quartz)

thetic hematite, was in the range of 17-23 $A \cdot m^2/kg$. Saturation magnetization, determined for magnetic samples, obtained from natural hematite was in the range of 21-27 $A \cdot m^2/kg$ (magnetization curve for the sample, obtained from natural hematite is shown at Fig. 3).

The values of saturation magnetization of obtained samples are lower than that of pure magnetite (92 $A \cdot m^2/kg$). We relate this to the remnant of non-transformed hematite in the sample.

The dependence of the saturation magnetization values on the temperature was investigated (Fig. 4).

We could conclude that saturation magnetization increases with the temperature of reaction. For samples obtained from natural hematite, the values of saturation magnetization increases rapidly in the temperature range of 100-120 °C. No further increasing was detected in the higher temperature range up to 260 °C. The values of satura-

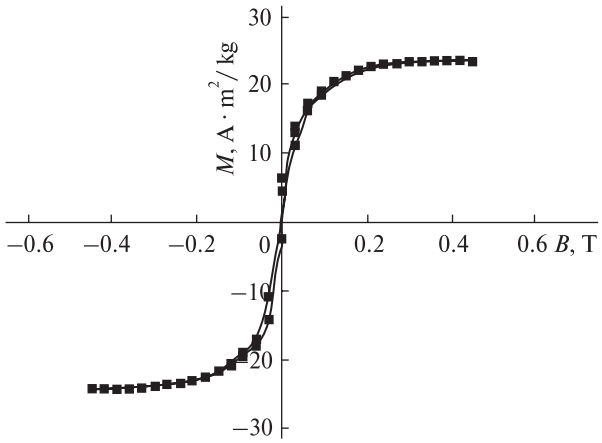


*Fig. 3.* Magnetization curve of magnetic sample, obtained from natural hematite. The curve was obtained with step-by-step changing the external magnetic field, first up from 0 to +0.45 T, then backward from +0.45 to –0.45 T, and finally again up from –0.45 to +0.45 T. Due to hysteresis phenomenon, corresponding parts of the curve don't coincide, forming three slightly different lines

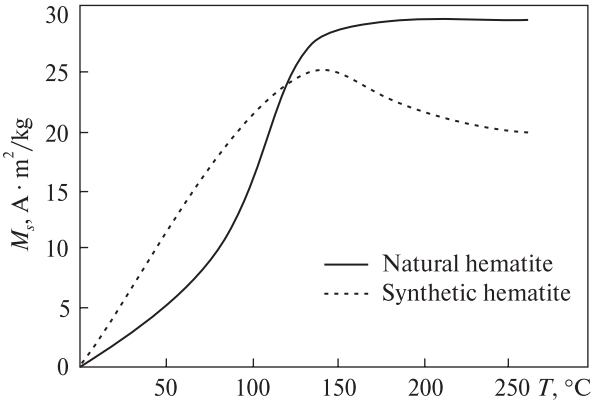


*Fig. 4.* Dependence of the saturation magnetization values on the temperature for the samples obtained on natural and synthetic hematite

tion magnetization of the samples, obtained from synthetic hematite, showed a similar tendency in the temperature range of 100-120 °C with its further decrease in the range of 120-260 °C.

Also, the magnetic properties of samples were studied by thermomagnetic analysis. The thermomagnetic curves of the samples, obtained from synthetic and natural hematite are shown at Fig. 5. Curie temperature was ~560 °C for both samples which is close to the Curie temperature of pure magnetite (580 °C). From that, we can assume that the obtained samples contain pure or isomorphically substituted magnetite.

Also, we observed a decrease of magnetization after the heating of the samples, obtained from synthetic hematite, up to 650 °C (Fig. 5, *a*). This

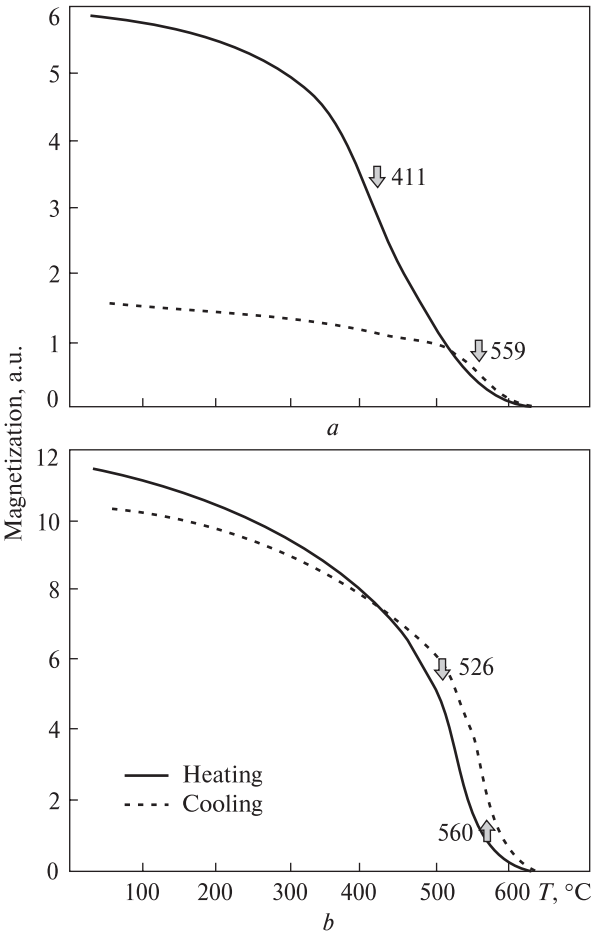


*Fig. 5.* Thermomagnetic curves of samples, obtained from synthetic (*a*) and natural (*b*) hematite

tendency maybe due to the phase transition of magnetite into hematite/maghemite. The temperature of phase transition was about 411 °C. Another pattern was observed for samples, obtained from natural hematite (Fig. 5, *b*). There is almost no drop in magnetization after the heating to 650 °C.

We associate the decrease of the saturation magnetization of the samples, obtained from synthetic hematite, with their phase transformation (oxidation) under the heating. The reaction of transformation occurs from the surface of the particle toward its centre. Due to the nano-dimensions, the synthetic particles are characterized by a large specific surface area. The higher is the specific surface of sample, the faster is its oxidation reaction. We haven't observed such rapid decrease of the saturation magnetization at heating in case of the samples, obtained from natural hematite. Probably, the thermomagnetic analysis time was not long enough for oxidation of bigger particles, obtained from natural hematite.

We could conclude that magnetite, obtained from synthetic hematite, is oxidized and converted into hematite at high temperatures (650 ºC). Since hematite is the final product of reaction, the conversion reaction for synthetic hematite could be described by the following scheme: hematite → magnetite → hematite.

Conclusion. Incubation of hematite in Fe (II)-containing solution under the influence of microwave radiation, pressure and increased temperatures lead to phase transformations of weakly magnetic samples and formation of strongly magnetic minerals. It was shown that synthetic and natural hematite partly transformed into magnetite in aqueous Fe (II)-containing medium under the influence of microwave radiation at temperature range up to 260 ºC. The samples, thermally obtained from synthetic and natural hematite, acquire high value of saturation magnetization, 23 $A \cdot m^2/kg$ and 27 $A \cdot m^2/kg$, respectively. The results could be used as for solving fundamental problems, associated with the transformation of iron oxides and hydroxides in aqueous medium, as for development of new technologies for producing iron ore concentrates from hematite-containing waste of mining and processing plants.

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## ФАЗОВІ ПЕРЕТВОРЕННЯ ГЕМАТИТУ НА МАГНЕТИТ ПІД ВПЛИВОМ ЗОВНІШНІХ ФАКТОРІВ

Досліджено фазові перетворення природного та синтетичного гематиту у водному середовищі, що містить Fe (II), під впливом мікрохвильового випромінювання за температури 260 °С та підвищеного тиску (6 МПа). Намагніченість насичення всіх вихідних зразків становила ~1 $А \cdot м^2/кг$, а після фазових перетворень зразків значно зростала (до 27 $А \cdot м^2/кг$). Значення намагніченості насичення перетворених зразків дещо нижчі за намагніченість насичення чистого магнетиту (92 $А \cdot м^2/кг$). Ми пов'язуємо це з наявністю в отриманих зразках вихідного неперетвореного гематиту. За допомогою методу рентгенофазового аналізу показано, що у всіх зразках гематит перетворюється на магнетит. Для перетворених зразків зареєстровано термомагнітні криві та визначена температура Кюрі. Показано, що температура Кюрі для зразка, отриманого з природного гематиту, становила 560 °С, а для зразка, отриманого з синтетичного гематиту — 559 °С, що близько до температури Кюрі чистого магнетиту (580 °С). За температурою Кюрі (560 °С) можна зробити висновок, що зразки містять магнетит або ізоморфно заміщений магнетит. Показано, що відбувається значне зменшення намагніченості насичення після нагріву зразків перетвореного синтетичного гематиту до 650 °С. Ми пов'язуємо це з окисненням отриманого магнетиту до гематиту. Температура такого фазового переходу становить 411 °С. Для зразків перетвореного природного гематиту така тенденція не спостерігається, тобто магнетит, отриманий з природного гематиту не окиснюється за підвищених температур. Отримані результати мають важливе значення для розроблення технологій отримання залізорудних концентратів із гематитовмісних відходів гірничо-збагачувальних комбінатів.

*Ключові слова*: гематит, магнетит, фазова трансформація, розчин, що містить Fe(II), рентгенофазовий аналіз, магнітометрія.