Вісник Дніпропетровського університету. Серія: Геологія, географія
Vìsnik Dnìpropetrovs'kogo unìversitetu. Serìâ Geologìâ, geographìâ
Dnipropetrovsk University bulletin. Series: Geology, geography

Dnipropetr. Univ. Bull. Ser.: Geol., geogr. 2015. 23(1), 24–32.
doi: 10.15421/111503

ISSN 2313-2159 print
ISSN 2409-9864 online

.

http://geology-dnu.dp.ua

УДК 553.3+54.01+542.9+549.5

Phase transformation of goethite into magnetite by reducing with carbohydrates

N. O. Dudchenko*, V. P. Ponomar**

**M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of NASU, Kyiv*
***Taras Shevchenko National University of Kyiv*

Phase transformations of synthetic goethite and goethite ore from Kryvyi Rih region by reducing with different carbohydrates (starch, glucose, fructose, sucrose and ascorbic acid) were investigated by thermomagnetic analysis. Thermomagnetic analysis was carried-out using laboratory device that allows automatic registration of sample magnetization with the temperature (the rate of sample heating/cooling was 65-80°/min). The reduction reaction of synthetic goethite for all carbohydrates starts at the temperature of ~250°C while reduction of goethite ore for all carbohydrates starts at the temperature of ~450°C. We could relate this increasing of reduction start temperature with shielding effect of admixtures in the ore. Reduction of synthetic goethite at this temperature range leads to formation of magnetic phase with saturation magnetisation ~70 A*m^2/kg. At the same time, reduction of goethite ore leads to formation of magnetic phase with saturation magnetisation ~25 A*m^2/kg. One could attribute this decreased value of saturation magnetisation to the presence of other minerals (quartz, etc.) in the ore. It was shown by X-Ray Diffraction method that goethite completely transforms into magnetite under heating with different carbohydrates up to 650°C. All carbohydrates reduce goethite to magnetite.

Key words: goethite, magnetite, phase transformations, thermomagnetic analysis.

*Інститут геохімії, мінералогії та рудоутворення імені М. П. Семененка НАН України, просп. Академіка Палладіна, 34, Київ, 03680, Україна.
M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of NASU, pr. Akademika Palladina, 34, Kyiv, 03680, Ukraine.
Tel.: +38-067-408-47-97. E-mail: ndudchenko@igmof.gov.ua
**Київський національний університет імені Тараса Шевченка, вул. Володимирська, 64/13, Київ, 01601, Україна
Taras Shevchenko National University of Kyiv, Volodymyrska Street, 64/13, Kyiv, 01601, Ukraine.
Tel.: +38-063-597-29-33. E-mail: vitaliyponomar.vp@gmail.com

Фазові перетворення гетиту в магнетит за його відновлення вуглеводами

Н. О. Дудченко*, В. П. Пономар**

**Інститут геохімії, мінералогії та рудоутворення імені М. П. Семененка, Київ*
***Київський національний університет імені Тараса Шевченка*

Досліджено фазові перетворення синтетичного гетиту і гетитової руди з Криворізького залізорудного басейну за допомогою термомагнітного аналізу при відновленні різними вуглеводами (крохмаль, глюкоза, фруктоза, цукроза та аскорбінова кислота). Термомагнітні дослідження проведено за допомогою лабораторної установки автоматичної реєстрації намагніченості залежно від температури (швидкість нагріву/охолодження 65 – 80°/хв). З'ясовано, що реакція відновлення синтетичного гетиту для всіх вуглеводів починається за температури ~250°C, а відновлення гетитової руди для всіх вуглеводів починається за температури ~450°C. Наведено припущення, що підвищення температури початку реакції відновлення пов'язано з ефектом екранування домішками в руді. Відновлення синтетичного гетиту в цьому температурному діапазоні зумовлює формування магнітної фази з намагніченістю насичення ~70 А·м^2/кг, у той час як відновлення гетитової руди призводить до формування магнітної фази з намагніченістю насичення ~25 А·м^2/кг. Зменшення намагніченості насичення можна пояснити наявністю інших мінералів (кварц та ін.) у руді. За допомогою рентгенофазового аналізу показано, що гетит повністю перетворюється на магнетит у разі нагрівання з різними вуглеводами до температури 650°C. Всі вуглеводи відновлюють гетит до магнетиту.

Ключові слова: гетит, магнетит, фазові перетворення, термомагнітний аналіз.

Introduction. Goethite (α-FeOOH) is an iron-containing mineral named by Johann Wolfgang von Goethe. It is widely spread in ores, sediments and soils and is one of the most thermodynamically stable iron oxide at ambient temperature [4]. Goethite powder has yellow colour. Goethite is often formed as sedimentary rock, and its formation requires the presence of water. That's why it is often found within spring water wetlands, and at lake and creek bottoms. It is always present in ore deposit oxidation zones. At the beginning of the 21st century, Mars Exploration Rover «Spirit» discovered goethite on the Red Planet's surface.

Goethite is antiferromagnetic [4] with Neel temperature (T_N) of 120°C. At high temperatures goethite can easily loose water and transforms into hematite. Transformation temperature depends on crystallinity of goethite.

Goethite now is mainly used for production of pigments and magnetic iron oxides [8], as an adsorbent for different toxic anions [6] and cations [3].

Nowadays, the usage of weakly magnetic iron ores for iron production is of very importance, because the deposits of magnetite iron ores are becoming exhausted. The main problem, that interferes the usage of weakly magnetic goethite ores for iron production is complexity of their beneficiation, i.e. separation of goethite from other admixtures in the ore. Therefore, number of investigations concerning transformation of goethite into magnetic iron oxides (mainly, magnetite, that is suitable for magnetic separation) by reduction with different reducing agents (coal [9], hydrogen and carbon monoxide [7], biomass etc. [10; 11] at increased temperatures have been carried-out in order to develop new technologies of goethite ore beneficiation.

The aim of this work was to investigate the phase transformations of synthetic goethite and goethite ore from Kryvyi Rih region into magnetic phase by reducing with different carbohydrates, i.e. starch, glucose, fructose, sucrose and ascorbic acid.

Materials and methods. Samples of synthetic goethite were synthesised by procedure [2]. Samples of goethite ore from Kryvyi Rih region were grinded up to 0,07÷0 mm. Starch, glucose, fructose, sucrose and ascorbic acid («Chimlaborreactive», Ukraine) were used as reducing agents.

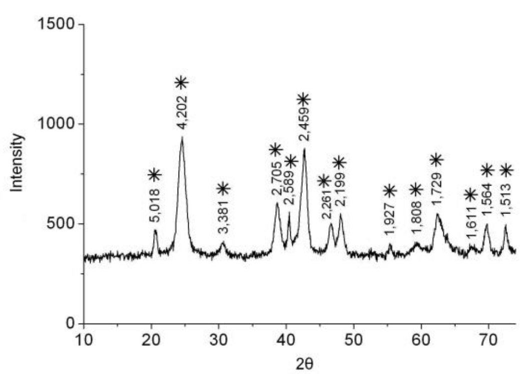
The changes of magnetization with the temperature were determined with laboratory build facility. This facility enables to measure the force that effects on the sample in non-uniform magnetic field. This force is proportional to magnetization and the gradient of magnetic field.

Initial samples were mixed with 4% (m/m) carbohydrates (starch, glucose, fructose, sucrose and ascorbic acid) and this mixture (0,2 – 0,5 g) was used further for thermomagnetic analysis. Reduction of goethite and goethite ore with different carbohydrates was performed in quartz mini-reactor, isolated from atmospheric oxygen ($V_{reactor}$=4 cm^3), under heating up to 650°C. The rate of sample heating/cooling was 65-80°/min.

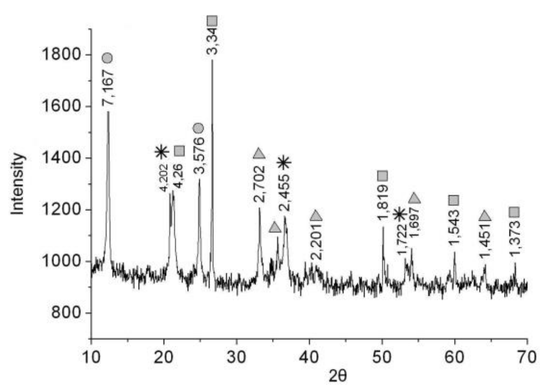
The initial and obtained samples were investigated by the methods of X-Ray Diffraction (XRD) and magnetometry. XRD measurements were performed with a diffractometer DRON-UM1 in filtered emission CuKα with recording geometry by Bragg-Brentano. Measurements of saturation magnetisation were performed using a magnetometer with Hall sensor (Ukraine).

The XRD phase diagnostics was performed using [1] by detected d-spacing.

Results and discussion. It was shown by the XRD-data that the initial sample of synthetic goethite was pure goethite (fig. 1, *a*) and the initial sample of goethite ore was composed by quartz, kaolinite, goethite and hematite (fig. 1, *b*). Saturation magnetisation of synthetic goethite was 0,14 $A \cdot m^2/kg$ and of initial goethite ore was 0,7 $A \cdot m^2/kg$.



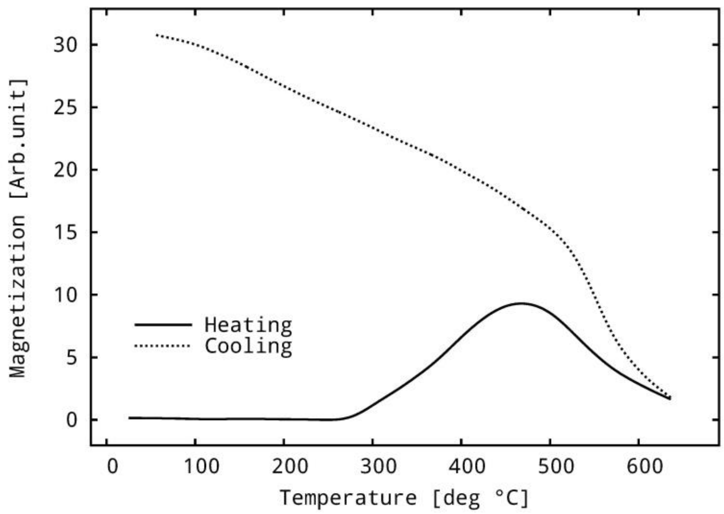
a



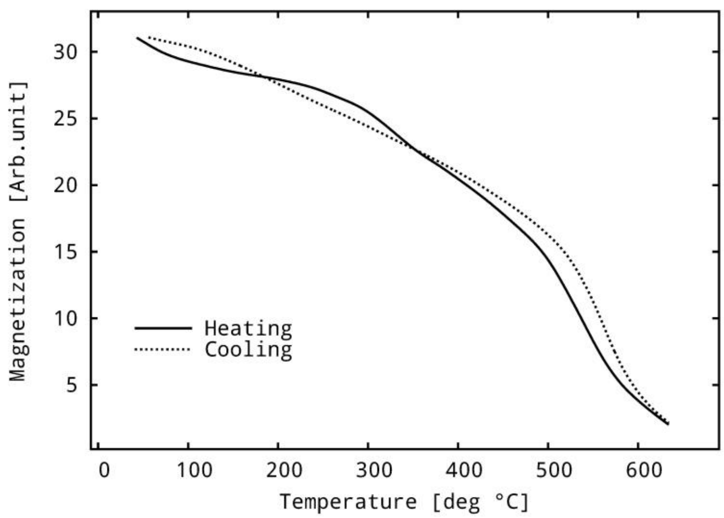
b

Fig. 1. XRD patterns of the initial samples of synthetic goethite (*a*) and goethite ore (*b*). The numbers correspond to the phases:
1 – goethite γ-FeOOH; *2* – quartz; *3* – hematite Fe_2O_3; *4* – caolinite

The thermomagnetic curves for synthetic goethite with starch are shown in the fig. 2. Fig. 2, *a* presents first cycle of heating/cooling and fig. 2, *b* presents second cycle of heating/cooling.



a



b

Fig. 2. Thermomagnetic curves for synthetic goethite with starch:
a – first cycle; *b* – second cycle

Thermomagnetic analysis of synthetic goethite shows that the reaction of iron reducing with starch starts at the temperature of 260°C with the maximum at 465°C. Magnetisation of the sample after cooling increases considerably.

The disappearance of magnetisation of the sample above Curie temperature and the cycle of heating and cooling provide us additional information about the present phases. Curie temperature, determined by cooling curve is ~560°C that is close to Curie temperature of magnetite (580°C). Therefore one could conclude that the phase of magnetite is formed in the reaction.

Saturation magnetisation, determined for obtained sample was ~70 A·m^2/kg (magnetisation curve is shown at fig. 3), that is close to saturation magnetisation of pure magnetite (92 A·m^2/kg). The result of XRD-measurements (fig. 4) shows that obtained sample consists of magnetite.

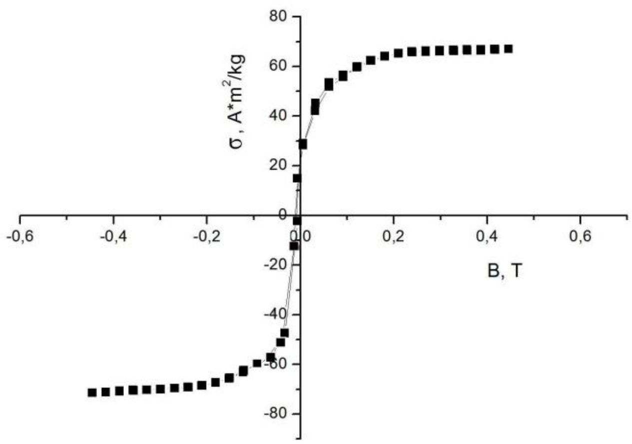


Fig. 3. Magnetisation curve of obtained sample

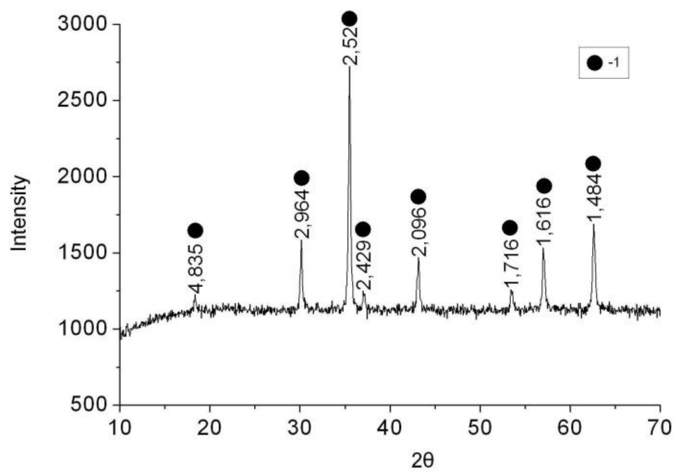


Fig. 4. XRD pattern of obtained sample. The number corresponds to the phase: *1* – magnetite.

Thermomagnetic curves for synthetic goethite with other carbohydrates (data not shown) are similar to the thermomagnetic curve for synthetic goethite with starch. Characteristics of these samples (temperature of reaction start, temperature of reaction maximum at heating curve, Curie temperature, phase composition of obtained sample, saturation magnetisation of obtained sample) are shown in the tab. 1.

Table 1

Temperature of reaction start, temperature of reaction maximum at heating curve, Curie temperature (T_c), phase composition of obtained sample, saturation magnetisation (M_s) of goethite, reduced with different carbohydrates

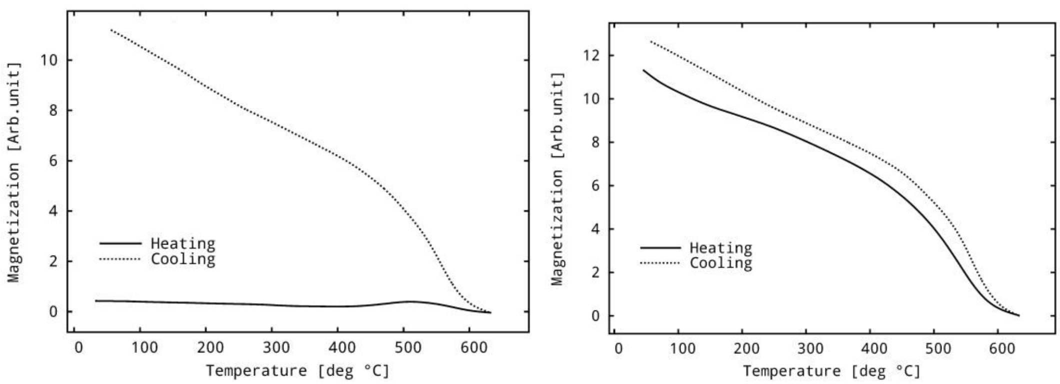
Sample name	Reductant	M_s, $A \cdot m^2/kg$	T_c, °C	Temperature of reaction start, °C	Temperature of reaction maximum, °C	Phase composition
Goethite	4 % starch	71	564	260	465	Magnetite
Goethite	4 % glucose	69	548	250	480	Magnetite
Goethite	4 % sucrose	69	548	250	470	Magnetite
Goethite	4 % fructose	67	547	260	475	Magnetite
Goethite	4 % ascorbic acid	69	560	280	493	Magnetite

So, we could conclude that reduction of synthetic goethite by different carbohydrates leads to formation of magnetite with rather high saturation magnetisation. For all types of carbohydrates, the reduction reaction starts at ~260°C with the maximum at ~470°C.

The thermomagnetic behaviour of iron oxides in the presence of glucose was analysed in [5]. It was shown, that in the presence of 5-10% of glucose, synthetic goethite starts transform into highly magnetic mineral at 420°C with Curie temperature of 580°C. Authors proposed the formation of highly magnetic maghemite, which then turns into haematite, which is slightly magnetic. In our case, we have obtained highly magnetic magnetite after thermal treatment of synthetic goethite with different carbohydrates, including glucose, which does not loose its magnetisation during further thermal treatment (fig. 2, *b*).

The thermomagnetic curves for goethite ore with starch are shown in the fig. 5. Fig 5, *a* presents first cycle of heating/cooling and fig. 5, *b* presents second cycle of heating/cooling.

Thermomagnetic analysis of goethite ore shows that the reaction of iron reducing with starch starts at the temperature of 420°C with the maximum at 510°C and Curie temperature ~560°C. Magnetisation of the sample after cooling increases considerably.



a *b*

Fig. 5. Thermomagnetic curves for goethite ore with starch:
a – first cycle; *b* – second cycle

Saturation magnetisation determined for obtained sample was ~30 $A \cdot m^2/kg$ (magnetisation curve is shown at the fig. 6).

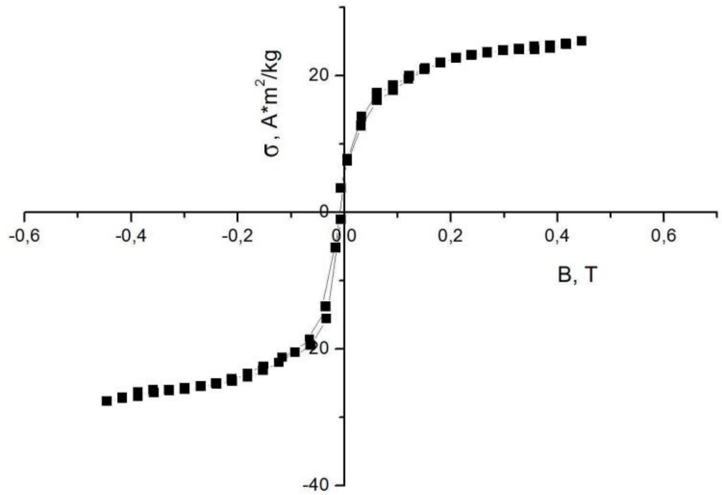


Fig. 6. Magnetisation curve of obtained sample

The result of XRD-measurements (fig. 7) shows that obtained sample consists of magnetite, quartz and hematite.

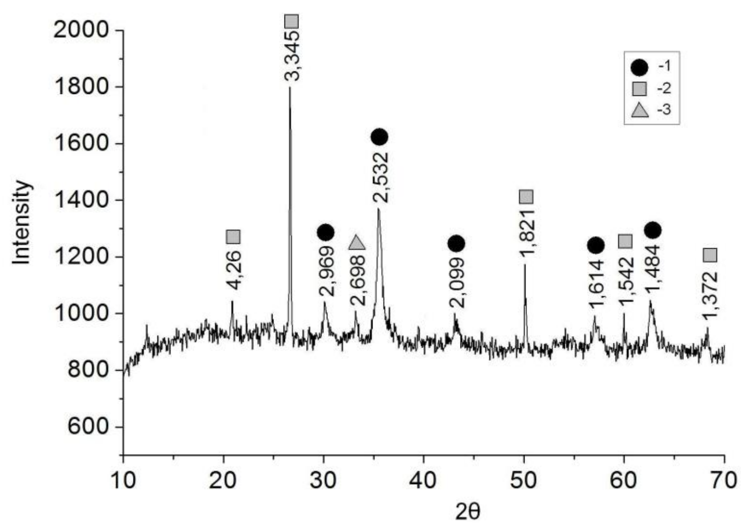


Fig. 7. XRD pattern of the obtained sample. The numbers correspond to the phases:
1 – magnetite Fe_3O_4; *2* – quartz; *3* – hematite Fe_2O_3

Thermomagnetic curves for goethite ore with other carbohydrates (data not shown) the same dependencies as for goethite ore with starch. Their characteristics (temperature of reaction start, temperature of reaction maximum at heating curve, Curie temperature, phase composition of obtained sample, saturation magnetisation of obtained sample) are shown in the tab. 2.

Table 2

Temperature of reaction start, temperature of reaction maximum at heating curve, Curie temperature (T_c), phase composition of obtained sample, saturation magnetisation (M_s) of goethite ore, reduced with different carbohydrates

Sample name	Reductant	M_s, $A \cdot m^2/kg$	T_c, ºC	Temperature of reaction start, ºC	Temperature of reaction maximum, ºC	Phase composition
Goethite ore	4 % starch	30	559	420	510	Quartz, magnetite, hematite (traces)
Goethite ore	4 % glucose	22	567	445	535	Quartz, magnetite, hematite (traces)
Goethite ore	4 % sucrose	31	564	425	515	Quartz, magnetite, hematite (traces)
Goethite ore	4 % fructose	22	569	450	550	Quartz, magnetite, hematite (traces)
Goethite ore	4 % ascorbic acid	23	571	450	520	Quartz, magnetite, hematite (traces)

So, we could conclude that reduction of goethite ore by different carbohydrates leads to formation of magnetite. For all types of carbohydrates the reduction reaction starts at ~450°C with the maximum at ~520°C.

Conclusion. It was slight difference of different carbohydrates (starch, glucose, fructose, sucrose and ascorbic acid) influence on the reduction rate of goethite or goethite ore. Synthetic goethite reduction with carbohydrates (starch, glucose, fructose, sucrose and ascorbic acid) under heating up to 650°C leads to formation of magnetite with saturation magnetisation ~70 $A \cdot m^2/kg$. Goethite ore reduction with carbohydrates (starch, glucose, fructose, sucrose and ascorbic acid) under heating up to 650°C leads to formation of magnetite. Saturation magnetisation ob obtained magnetic samples is ~25 $A \cdot m^2/kg$. The reduction of synthetic goethite with carbohydrates starts at rather low temperatures, i.e. ~260°C, while the reduction of goethite ore with carbohydrates starts at ~450°C. We could attribute this increase of reduction start temperature with shielding effect of admixtures (quartz, etc.) in the ore. Obtained results are promising for development of new low-energy technologies of goethite ore beneficiation.

References

1. ASTM. Diffraction data cards and alphabetical and grouped numerical index of X-ray diffraction data [Text]: – Philadelphia, 1977. – 880 p.
2. **Brauer, G.** Handbuch der Praparativen Anorganischen Chemie (in drei Banden) [Text]: Ferdinand Enke Verlag / G. Brauer, W. P. Fehlhammer, O. Glemser. − Stuttgart: Ferdinand Erike Verlag, 1981. – 1776 p.
3. **Christophi, C.** Competition of Cd, Cu, and Pb adsorption on goethite. [Text]/ C. Christophi, L. Axe // J. Environ. Eng. – 2000. − № 126 (1). − P. 66 – 74.
4. **Cornell, R. M.** The iron oxides: structure, properties, reactions, occurrences and uses (second ed.) [Text]/ R. M. Cornell, U. Schwertmann/Weinheim: Wiley – VCH GmbH& Co., KgaA, 2003. – 694 p.
5. **Hanesch, M.** Thermomagnetic measurements of soil iron minerals: the role of organic carbon [Text]/ M. Hanesch, H. Stanjek, N. Petersen// Geophys. J. Int., − 2006. – № 165 (1). − P. 53 − 61.
6. **Hongshao, Z.** Competitive adsorption of phosphate and arsenate on goethite [Text]/ Z. Hongshao, R. Stanforth // Environ. Sci. Technol, 2001. − № 35 (24). − P. 4753–4757.
7. **Jozwiak, W. K.** Reduction behavior of iron oxides in hydrogen and carbon monoxide atmospheres [Text]/ W. K. Jozwiak, E. Kaczmarek, T. P. Maniecki // Applied Catalysis A., 2007. № 326 (1). P. 17 − 27.
8. **Legodi, M. A.** The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste [Text]/ M. A. Legodi, D. de Waal // Dyes Pigments, 2007. – № 4 (1) – P. 161 − 168.
9. Rapid and direct magnetization of goethite ore roasted by biomass fuel, Separation and Purification Technology [Text]/Y. Wua [et al.]. – Thermochimica Acta, 2012. – P. 34-38.
10. The reduction mechanism of biomass roasting of goethite ores [Text]/ Y. Wua [et al.]. / Adv. Mat. Res., 2012. - P. 560 − 561, 441-446.
11. Thermal investigations of direct iron ore reduction with coal [Text]/ G. S. Liu [et al.]. - Thermochimica Acta, 2004. – № 410 (1). – P. 133 − 140.

Надійшла до редколегії 27.02.2015