

<https://doi.org/10.15407/mineraljournal.43.02.074>
UDC 550.41 : 549.521 : 544.774.4 : 537.8

Yu.L. Zabulonov, DrSc (Tech.), Corresp. Member of the NAS of Ukraine, Prof., Director
E-mail: Zabulonov@igns.gov.ua; <https://orcid.org/0000-0001-8239-8654>

V.M. Kadoshnikov, Research Scientist

E-mail: IGNS_Kadoshnikov@igns.gov.ua; <https://orcid.org/0000-0001-8707-873X>

T.I. Melnychenko, PhD (Biology), Senior Research Scientist

E-mail: tim--@ukr.net; <https://orcid.org/0000-0003-2349-5395>

H.P. Zadvernyuk, PhD (Geology), Senior Research Scientist

E-mail: zadvernyuk@ukr.net; <https://orcid.org/0000-0001-6425-9845>

S.V. Kuzenko, Research Scientist

E-mail: IGNS_Kuzenko@nas.gov.ua; <https://orcid.org/0000-0003-2641-6699>

Yu.V. Lytvynenko, PhD (Tech.), Scientific Secretary

E-mail: Lytvynenko@igns.gov.ua; <https://orcid.org/0000-0003-1659-9831>

State Institution "The Institute of Environmental

Geochemistry of National Academy of Sciences of Ukraine"

34-a, Acad. Palladin Ave., Kyiv, Ukraine, 03142

GEOCHEMICAL BEHAVIOR OF FERRIC HYDROXIDE NANODISPERSION UNDER THE INFLUENCE OF WEAK MAGNETIC FIELDS

The change of geochemical properties of ferric hydroxide nanoparticles under the influence of a weak magnetic field was investigated. Ferric hydroxide nanoparticles formed as a result of the interaction of iron-containing minerals with natural aqueous solutions are of importance for geochemical processes, especially hypergenesis, sedimentation, and soil formation. The hydrolysis of ferric chloride in hot water ($t = 70-75\text{ }^{\circ}\text{C}$) was used to obtain ferric hydroxide nanoparticles under laboratory conditions. The nanodispersion (colloidal solution) was exposed to a weak pulsed magnetic field. The spectrophotometric properties of the colloidal solution of ferric hydroxide were determined using an SF-46 spectrophotometer in the wavelength range of 320–610 nm. The size of colloidal particles was calculated by a method based on the theory of Rayleigh light scattering. The size of colloidal particles depended on the exposure duration of a pulsed magnetic field on the colloidal solution. The size of colloidal particles was due to a change in the magnitude of the diffuse ionic atmosphere under the influence of a pulsed magnetic field. The kinetic stability of the colloidal solution was evaluated by the coagulation threshold, which was determined visually by the appearance of the turbidity of ferric hydroxide colloid when adding NaCl solution. The kinetic stability of a colloidal system was determined by the size of colloidal particles. These results can be used to better understand certain hypergenesis, sedimentation, and soil formation processes.

Keywords: ferric hydroxide nanoparticles, magnetic field, kinetic stability, colloidal particle size.

Introduction. In geochemical processes, the mass transfer of substances in the form of colloids plays a leading role, especially in the processes of soil formation and hypergenesis. Among the colloidal solutions circulating in the zone of hypergenesis and, especially, lateritization, colloids of ferric hydroxide

are of particular importance. These colloids have an increased sorption capacity, promote the migration of substances that are immobile under normal conditions, and are also catalysts for the transformation of aluminosilicates in lateritization processes [9, 12].

Cite: Zabulonov, Yu.L., Kadoshnikov, V.M., Melnychenko, T.I., Zadvernyuk, H.P., Kuzenko, S.V. and Lytvynenko, Yu.V. (2021), Geochemical Behavior of Ferric Hydroxide Nanodispersion Under the Influence of Weak Magnetic Fields. *Mineral. Journ. (Ukraine)*, Vol. 43, No. 2, pp. 74–79. <https://doi.org/10.15407/mineraljournal.43.02.074>

Colloidal solutions are heterogeneous systems, in which as a dispersion medium is a natural water, and, as the solid phase is nanoparticles of amorphous or crystalline minerals. In geochemical studies, it should be taken into account that external magnetic fields, including the Earth's field, can change the properties of both the dispersion medium and the dispersed phase. It is known that under the influence of magnetic fields, water can exhibit increased dissolving properties and change the hydration of nanominerals [16]. The influence of magnetic activation of water on the properties of mineral composites is associated with changes in the properties of solid and liquid phases [3]. Ultra-high frequency radiation enhances the speed and efficiency of mineral transformation. The transformation occurs as a result of the influence of ultrahigh-frequency radiation on water molecules and hydroxyl groups (there is a change in their chemical properties) and iron ions (there is a change in charge of iron ions) [13].

For both dispersions of ferromagnets and dispersions of diamagnets, external magnetic and electric fields influence, the size of particles and their aggregate stability [1, 11, 15]. The study of the influence of the magnetic field on the mechanical mixture of γ - Fe_2O_3 (maghemite) and flakes of beidellite clay showed that the magnetic field, changing the zeta potential, promoted flocculation and accelerated sedimentation of the mixture and could be used for water purification [6]. In diamagnetic hydrosols, an external magnetic field significantly affected the size and composition of the hydration shell of colloidal particles, changing their sizes and lowering aggregative stability [4]. It was noted that depending on the density of the magnetic flux and the duration of the magnetic treatment, the coagulation rate constant changed.

It is interesting that after the cessation of a magnetic field, the changes caused by the influence of the magnetic field persisted for some time (up to six days) [5]. These effects can be explained mainly by changes in the diffuse ionic atmosphere and the structure of water molecules adsorbed on the surface of the colloidal particle core.

The common mechanism of the coagulation of diamagnetic and submagnetic particles under the influence of a weak magnetic field was presented in the papers [17]. It was shown that the coagulation of dispersions of weakly magnetic ultrafine minerals (such as hematite and chromite) in an external magnetic field could be theoretically described by using the intermolecular London forces. The coagulation occurred when the short-time interactions of London-van der Waals and the long-term magnetic forces outweighed the stabilizing repulsion of the double electric layer. The potential energy components for particles of different sizes were calculated.

More complex processes occur during the interaction of diamagnetic colloids with an alternating magnetic or electromagnetic field. It was found that the negative zeta potential of CaCO_3 in water, measured immediately (within 2-3 min) after exposure to an electromagnetic field, fluctuated depending on the irradiation time [2]. For the sample exposed to an electromagnetic field for 15 min, the zeta potential decreased by 5-7 mV comparing to the untreated sample. Residual changes also happened oscillating, within 40 min after the ending of the field effect. Similar behaviour was found for calcium carbonate colloid in 10^{-2} M NaCl, as well as for bentonite and palygorskite particles [7]. The changes in the zeta potential were accompanied by the changes in the electron donor component of the free energy of the surface and the appearance of a small electron acceptor component that was due to the presence of a hydrogen bond of the adsorbed water molecule to the surface of the solid phase of the colloidal particle [2].

Analyzing the data on the influence of magnetic fields on the properties of colloids, it should be noted that the number of studies on the effect of an alternating magnetic field on the properties of the dispersions of diamagnets is limited that necessitates further investigations in this area. The effect of a weak pulsed magnetic field on the geochemical properties of ferric hydroxide nanoparticles in an aqueous medium is considered in the paper.

Materials and methods. Chemicals: Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was used for the synthesis of ferric hydroxide colloid (the solution with FeCl_3 mass concentration of 10%). Sodium chloride (NaCl) was applied to determine the coagulation threshold (the solution with NaCl mass concentration of 10%). Chemicals ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and NaCl) were of analytical grade and used without additional purifications.

Synthesis of ferric hydroxide colloid. The lyophobic colloid of ferric hydroxide was synthesized by the method of hydrolysis with subsequent condensation. The solution of ferric chloride was added gradually to hot distilled water ($t = 70-75$ °C). Hydrolysis resulted in the formation of ferric hydroxide.

$$\text{FeCl}_3 + 3\text{HOH} \rightarrow \text{Fe}(\text{OH})_3 + 3\text{HCl}.$$

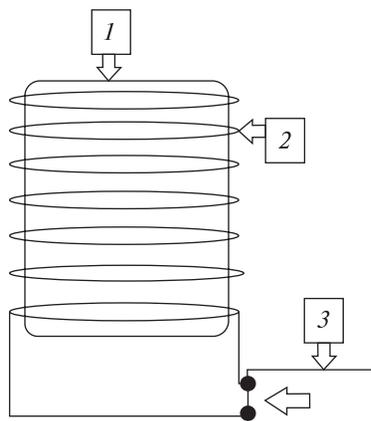


Fig. 1. Scheme of the laboratory setup for creating a pulsed magnetic field: 1 – working cell; 2 – inductive coil; 3 – microprocessor, driver unit

Molecules of the ferric hydroxide obtained as a result of hydrolysis, interacting with each other (due to the London – van der Waals forces), form an amorphous core of a colloidal particle.

On the surface of ferric hydroxide nanoparticles, ferric ions were adsorbed that determined the core charge of a colloidal particle (potential-forming ions). A part of compensator ions (chloride ions) was immediately adjoined to ferric ions, which partially compensated for the core charge, and the other part was located at some distance from the core and formed a diffuse ionic atmosphere, which determined the value of the zeta potential.

Dialysis against distilled water was used to remove the excess of chloride ions. The obtained colloidal solution had a bright crimson colour, was transparent in transmitted light, and the opalescence (the Tyndall cone) was observed in a lateral light. The resulting solution was kinetically stable at room temperature.

Interaction of ferric hydroxide colloid with a weak pulsed magnetic field. The special setup, the schematic diagram of which is shown in Fig. 1, was developed to study the effect of a pulsed magnetic field on the colloidal solution obtained in laboratory conditions. The setup generated a rectangular pulse with a duration of $500 \pm 10 \mu\text{s}$ consisting of a high-frequency magnetic field with a frequency of 5.2 kHz. Pulse repetition frequency was $1 \pm 0.1 \text{ Hz}$, field strength was 0.6–1.0 A/m, pulse voltage was 1200 V and magnetic induction was 15 mTl. The magnetic induction inside the working cell was measured using an external sensor of an HT-208 milliteslameter (made in China) with an error of 2.0%.

Conducting experiments to study the effect of a pulsed magnetic field on the colloid of ferric

hydroxide, the investigated colloidal solution was placed in a cuvette, which was brought into the working area of the unit cell. After turning on the microprocessor unit, a pulsed magnetic field was generated in the working area of the unit cell as a result of a pulse current applied to the coils.

The initial colloidal solution of ferric hydroxide was exposed to a pulsed magnetic field for 1–5 min to find out the field effect on the colloidal solution.

Spectrophotometry method. The spectrophotometric properties of the colloidal solution of ferric hydroxide were determined using an SF-46 spectrophotometer (manufactured by LOMO, JSC St. Petersburg). The measurements were carried out in a quartz cuvette $l = 1 \text{ cm}$ in the wavelength range of 320–610 nm with an error of 1.0%. Distilled water was used as a comparison solution. The particle size was calculated using the well-known technique [14] based on the theory of Rayleigh light scattering.

Determination of the coagulation threshold. The coagulation threshold was determined visually by the onset of turbidity of a colloidal solution of ferric hydroxide when sodium chloride solution was added to it. The coagulation threshold was expressed in mol/L of sodium chloride content in the colloidal solution of ferric hydroxide at the moment of turbidity.

Results and discussion. *The study of the influence of a pulsed magnetic field on the spectrophotometric properties of ferric hydroxide colloid.* The absorption spectra presented in Fig. 2 were obtained for the colloidal solution without the interaction with a pulsed magnetic field and with exposure to a pulsed magnetic field for the time of 1–5 min.

The analysis of the absorption spectrum of the initial colloidal solution revealed that there was a diffuse absorption band with peaks in the range of 360–420 nm that was due to the polydispersity of the colloidal solution. The average size of the colloid particles before exposure to a pulsed magnetic field, according to our calculations, was about 11–12 nm.

Colloidal solution treatment with a pulsed magnetic field for 1 min led to the change in the shape of the spectrum, the intensity of the absorption bands, and the location of the absorption peaks.

The peak in the region of 360 nm was characterized by a narrower intense absorption band compared to the same band for the initial colloidal solution. This band was displaced to the short-wavelength part of the spectrum to 380 nm, and the peak in the region of 420 nm was shifted to 440 nm. The change in the intensity of the absorption bands and their locations was due to the change in the

shape and the size of the particles of the dispersed phase.

The effect of a pulsed magnetic field on the nanodispersion for 2 min was accompanied by changes in the spectrum pattern. The absorption band in the range of 360–380 nm was split into a doublet with the formation of two absorption bands with the peak in the field of 360 nm and 390 nm, and the absorption peak in the region of 440 nm did not have visible changes. We believe that the splitting of the absorption band (360–380 nm) is because of the size and, probably, the shape of colloidal particles change under the influence of the pulsed magnetic field.

The treatment of a colloidal solution of ferric hydroxide with a pulsed magnetic field for 3 min practically did not lead to a significant change in the spectrum pattern.

The treatment for 5 min or more resulted in the formation of singlet in the region of 360 nm with high intensity, and the absorption peak in the field of 440 nm practically did not change the location, but its intensity was slightly weaker.

Assessment of the influence of a pulsed magnetic field on the size of colloidal particles of ferric hydroxide. The average sizes of colloidal particles of ferric hydroxide were calculated based on the results of spectrophotometric measurements. Since the shape of colloidal particles can be approximated as spherical, Rayleigh scattering theory was used to calculate their size [10], relating the particle size to the intensity of the scattering band. The calculation procedure is given in the paper [14]. The equivalent particle radii were calculated, and they are shown in Fig. 3.

It is seen from Fig. 3 that when a colloidal solution exposed to a pulsed magnetic field for 1 min, the size of the colloidal particles slightly increased.

At present, there is no clear understanding of the effect of weak magnetic fields on nanodispersions. Since ferric hydroxide micelles are hydrophobic, changes under the influence of a pulsed magnetic field are possible mainly in a diffuse ionic atmosphere consisting of hydrated chloride ions. We believe that the increase in the size of the colloidal particle was due to the loosening of the diffuse ionic atmosphere as a result of the partial absorption of the energy of the external magnetic field by the ionic atmosphere. It is because the field mainly affects the water molecules [16] associated with the chloride ion and, accordingly, influences the magnitude and properties of the diffuse ionic atmosphere.

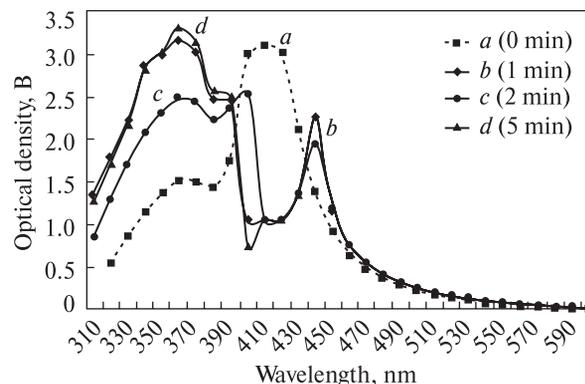


Fig. 2. Changes in the spectrophotometric properties of ferric hydroxide colloid after exposure to a pulsed magnetic field

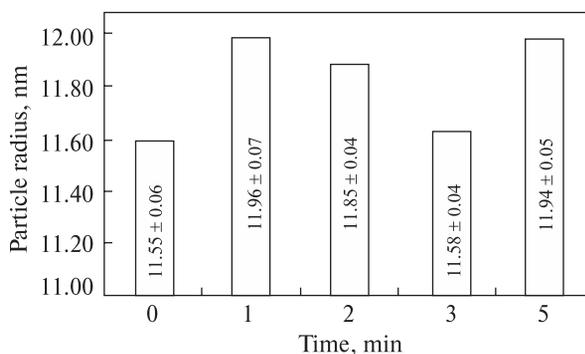


Fig. 3. The size of colloidal particles after exposure to a pulsed magnetic field

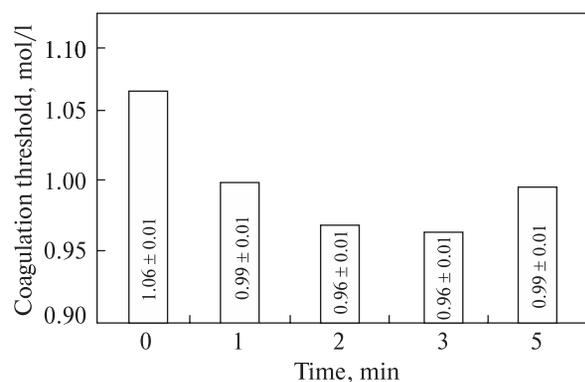


Fig. 4. The coagulation threshold for a colloid of ferric hydroxide after exposure to a pulsed magnetic field

An increase in the time of exposure to a pulsed magnetic field for 2–3 min led to an insignificant reduction in the size of the colloidal particle, which was associated with the processes of self-organization of chloride ions in a diffuse ionic atmosphere. Similar processes have been observed for magnetically sensitive nanoparticles [8].

After a colloid treatment for 5 min or more, an increase in the colloidal particle size was observed to almost 12 nm that was associated with additional

energy absorption of a pulsed magnetic field by the diffuse ionic atmosphere and, as a consequence, it was loosed.

Assessment of the influence of a pulsed magnetic field on the kinetic stability of the colloidal system. The effect of a pulsed magnetic field on the aggregative stability of ferric hydroxide colloid, which was evaluated by the coagulation threshold, was studied.

The coagulation threshold was determined visually at the beginning of the turbidity of the colloidal solution by adding the solution of sodium chloride. The obtained results are shown in Fig. 4.

Initially, under the influence of a pulsed magnetic field during the first 5 min, a gradual decrease in the coagulation threshold occurs. Exposure to a pulsed magnetic field for more than 5 min leads to stabilization and a slight increase in the coagulation threshold.

We believe that the decrease in the colloid coagulation threshold during the first five minutes of the treatment with a pulsed magnetic field is due to the compression of the diffuse ionic atmosphere. It is associated with a change in the zeta potential and particle size that leads to a decrease in kinetic stability. The interaction of a pulsed magnetic field with a colloidal solution for five minutes or more, leading to a slight increase in the coagulation threshold, is due to the loosening and stabilization of the diffuse ionic atmosphere.

Thus, the principal mechanism of the coagulation of ferric hydroxide colloid under these conditions was the change in particle size, and accordingly, the zeta potential under the influence of electrolytes of a dispersion medium.

The authors [15] believe that the colloid aggregate stability and the zeta potential are affected by a weak alternating magnetic field that is associated with the specific adsorption of ions on the surface of colloids under the influence of the induction component of the electric field instead of the magnetic field itself.

The expressed point of view is interesting for practical purposes, but it contains some uncertainties and requires further investigations.

Conclusions. It is established that under the influence of a pulsed magnetic field, the geochemical properties of ferric hydroxide nanoparticles change, in particular, their size and, accordingly, the kinetic stability of the aqueous dispersion.

Initially, when a pulsed magnetic field was exposed to the colloidal solution for 1 min, the size of the colloidal particles slightly grew. An increase in the influence time of a pulsed magnetic field on the colloidal solution for 2–3 min led to a reduction in colloidal particle size that was associated with self-organization processes in the diffuse ionic atmosphere. The colloid treatment with a pulsed magnetic field for 5 minutes or more increased the size of nanoparticles that were related to absorbed energy gain and, correspondingly, the loosening of the diffuse ionic atmosphere. The kinetic stability of the dispersion depends on the time of interaction of the magnetic field with ferric hydroxide nanoparticles.

The obtained results can be used in the study of lithogenesis, hypergenesis and soil formation processes.

REFERENCES

1. Arteaga-Cardona, F., Martha-Aguilar, N.G., Estevez, J.O., Pal, U., Méndez-Rojas, M.A. and Salazar-Kuri, U. (2019), *SN Appl. Sci.*, 1, Art. 412. <https://doi.org/10.1007/s42452-019-0447-y>
2. Chibowski, E., Hołysz, L. and Wójcik, W. (1994), *Colloid Surf. A*, Vol. 92, Iss. 1-2, pp. 79-85. [https://doi.org/10.1016/0927-7757\(94\)02949-0](https://doi.org/10.1016/0927-7757(94)02949-0)
3. Gorlenko, N.P., Safronov, V.N., Abzaev, Yu.A., Sarkisov, Yu.S., Kugaevskaya, S.N. and Ermilova, T.A. (2015), *Vestnik TSUAB*, Vol. 50 (3), Tomsk, RU, pp. 134-150 [in Russian].
4. Gu, Y., Li, S., Xu, Y., Han, J., Gu, M., Cai, Z., Iv, Y., Xie, G., Ma, T. and Luo, J. (2019), *Colloid Surf. A*, Vol. 582, Art. 123822. <https://doi.org/10.1016/j.colsurfa.2019.123822>
5. Higashitani, K., Okuhara, K. and Hatade, S. (1992), *J. Colloid Interface Sci.*, Vol. 152, pp. 125-131. [https://doi.org/10.1016/0021-9797\(92\)90013-C](https://doi.org/10.1016/0021-9797(92)90013-C)
6. Housni, S., Abramson, S., Guigner, J., Levitz, P. and Michot, L. (2020), *Nano Res.*, Vol. 13, pp. 3001-3011. <https://doi.org/10.1007/s12274-020-2964-9>
7. Kadoshnikov, V.M., Zabulonov, Yu.L., Litvinenko, Yu.V., Makarov, A.S. and Savitsky, D.P. (2010), *Mineral. Journ. (Ukraine)*, Vol. 32, No. 4, Kyiv, pp. 41-50 [in Russian]. <https://doi.org/10.15407/mineraljournal>
8. Kashevskii, B.E. (2003), *Colloid Journ.*, Vol. 65, pp. 319-322. <https://doi.org/10.1023/A:1024254722602>
9. Kukovskiy, Ye.G., Movchan, N.P., Ostrovskaya, A.B. et al. (1984), *Strukturnye prevrashcheniya mineralov*, Nauk. dumka, Kyiv, UA, 118 p. [in Russian].
10. Landau, L., Lifshitz, E. and Pitaevski, L. (1984), *Electrodynamics of Continuous Media*, Pergamon, Oxford, 460 p.
11. Medvedeva, I., Bakhteeva, Y., Zhakov, S., Revvo, A., Byzov, I., Uimin, M., Yermakov, A. and Mysik, A. (2013), *J. Nanopart. Res.*, Vol. 15, Art. 2054. <https://doi.org/10.1007/s11051-013-2054-y>

12. Samchuk, A.I., Kuraieva, I.V., Voitiuk, Yu.Yu., Matvienko, A.V. and Vovk, K.V. (2016), *Mineral. Journ. (Ukraine)*, Vol. 38, No. 4, Kyiv, pp. 66-74 [in Ukrainian]. <https://doi.org/10.15407/mineraljournal.38.04.066>
13. Savchenko, T.S. (2017), *Bull. Univ. Dnepropetrovsk, Ser. geology, geography*, Vol. 25 (1), Dnipro, UA, pp. 93-100 [in Ukrainian]. <https://doi.org/10.15421/111711>
14. Sliapniova, L.M., Gorbunova, V.A. and Sliapniou, G.E. (2014), *Science and Technique (Belarus)*, Vol. 6, pp. 55-59 [in Russian].
15. Umeki, S., Kato, T., Yoshikawa, N. and Taniguchi, S. (2006), *AIP Conf. Proc.*, Vol. 833, p. 85. <https://doi.org/10.1063/1.2207081>
16. Usanov, A.D., Rebrov, V.G. and Verhov, D.G. (2013), *Biomedical Radioelectronics*, Vol. 2, Publ. house "Radiotekhnika", Moscow, pp. 55-58 [in Russian].
17. Wang, Y.Y., Pugh, R.J. and Forssberg, E. (1994), *Colloid Surf. A*, Vol. 90, pp. 117-133. [https://doi.org/10.1016/0927-7757\(94\)02908-3](https://doi.org/10.1016/0927-7757(94)02908-3)

Received 06.12.2020

Ю.Л. Забулонов, д-р техн. наук, чл.-кор. НАН України, проф., дир.

E-mail: Zabulonov@igns.gov.ua; <https://orcid.org/0000-0001-8239-8654>

В.М. Кадошніков, наук. співроб.

E-mail: IGNS_Kadoshnikov@igns.gov.ua; <https://orcid.org/0000-0001-8707-873X>

Т.І. Мельниченко, канд. біол. наук, старш. наук. співроб.

E-mail: tim--@ukr.net; <https://orcid.org/0000-0003-2349-5395>

Г.П. Задвернюк, канд. геол. наук., старш. наук. співроб.

E-mail: zadvernuyuk@ukr.net; <https://orcid.org/0000-0001-6425-9845>

С.В. Кузенко, наук. співроб.

E-mail: IGNS_Kuzenko@nas.gov.ua; <https://orcid.org/0000-0003-2641-6699>

Ю.В. Литвиненко, канд. техн. наук, учений секретар

E-mail: Lytvynenko@igns.gov.ua; <https://orcid.org/0000-0003-1659-9831>

Державна установа "Інститут геохімії навколишнього

середовища Національної академії наук України"

03142, м. Київ, Україна, пр-т Акад. Палладіна, 34-а

ГЕОХІМІЧНІ ОСОБЛИВОСТІ ПОВЕДІНКИ НАНОДИСПЕРСІЙ ГІДРОКСИДУ ЗАЛІЗА ПІД ВПЛИВОМ СЛАБКИХ МАГНІТНИХ ПОЛІВ

Досліджено зміни геохімічних властивостей наночастинок гідроксиду заліза під дією слабого магнітного поля. Особливе значення для геохімічних процесів, передусім процесів ґрунтоутворення, седиментації і гіпергенезу, мають наночастилки гідроксиду заліза, які утворюються в результаті взаємодії залізовмісних мінералів з природними водними розчинами. У лабораторних умовах для отримання наночастинок гідроксиду заліза, диспергованих у воді, використовували реакцію гідролізу хлориду заліза у гарячій воді ($t = 70-75$ °C). Отриману нанодисперсію (колоїдний розчин) піддавали впливу імпульсного магнітного поля. Спектрофотометричні властивості колоїдного розчину гідроксиду заліза визначали за допомогою спектрофотометра СФ-46 в діапазоні довжин хвиль 320—610 нм. Розмір колоїдних частинок розраховували за методикою, що ґрунтується на теорії релеевського розсіювання світла. Розмір колоїдних частинок залежав від тривалості впливу імпульсного магнітного поля на колоїдний розчин. Зміна розміру колоїдних частинок обумовлена зміною величини дифузної іонної атмосфери під впливом імпульсного магнітного поля. Кінетичну стійкість колоїдного розчину оцінювали за порогом коагуляції, який візуально визначали за появи помутніння колоїду гідроксиду заліза під час додавання до нього розчину хлориду натрію. Кінетичну стійкість розглянутої колоїдної системи визначено за розміром колоїдних частинок. Отримані дані можуть бути використані для кращого розуміння певних процесів гіпергенезу, осадконакопичення і ґрунтоутворення.

Ключові слова: наночастилки гідроксиду заліза, магнітне поле, кінетична стійкість, розмір колоїдної частинки.