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KINETIC MODEL OF THE INITIAL STAGE OF THE PROCESS OF COLLOID RETENTION BY THE PORE SPACE OF SOKYRNITE

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Abstract. *The physicochemical phenomena occurring on the surface of sokyrnite grains in complex system "medium grain surface – dispersion medium – surface of suspended particles" have been studied. The framework structure of the sokyrnite structure (rough surface, presence of pores and channels, entrance windows) enables it to work as a "molecular sieve" and to be a highly efficient sorbent-ion exchanger. The porosity of the filter media was determined. Namely: the porosity of the media grains (also called the internal porosity) and the porosity of the intergranular space (media layer). The internal surface area, which is an important quality parameter for sokyrnite as a physical adsorbent, was determined. Several other properties associated with sokyrnite and retained colloidal particles, which affect the strength of the physical adsorption, were investigated. The relationships characterizing the parameters of the zeolite filter media layer were formulated and given. In these studies, the requirements for determining the filter charging time and the optimal technological and design parameters of the filter, according to the operating conditions at a specific water treatment facility, were considered. They determined the need for more detailed research and development of a kinetic model for the initial stage of filtering an aqueous suspension through a filter containing zeolite media. A differential material balance expression for the zeolite filter was formulated. Based on the developed kinetic model, comparative experiments on iron removal from underground natural waters using the above-mentioned filter material were planned and carried out. The mechanism of the distribution of iron ions in the filter space due to the phenomenon of diffusion, in accordance with Fick's first law, is given. The mechanism of iron flake retention by the zeolite media pore space, the consolidation of which occurs during the transition of iron from a divalent to trivalent form, is described. The factors that interfere with autocatalytic processes in iron sediments were described. The dynamics of changes in the concentration of iron in the filtrate after the end of the ion-exchange resource of sokyrnite were studied.*

Key words**:** *kinetic model, filtration, pore space, sokyrnit, iron removal*

Relevance of research. Despite the wide range of physical properties of the existing granular filter medium, most stages of filtering through them are similar for different medium materials. An exception is the initial stage of filtering, which is usually called the "charging" of the filter. This is due to the fact that it is during it that all the diversity of the physical properties of the filtering medium is manifested. This entails a significant difference in the nature of the mechanisms and kinetics of the processes of interaction of the filter medium with colloidal particles contained in the purified water suspension. In the case of zeolite media, pore space plays a major role in filtering the colloidal suspension. The ion-exchange properties of zeolite are a determining factor in the process of iron removal from underground natural water. The study of the specified factors will allow the development of a kinetic model of the initial stage of the filtering process under given conditions.

Analysis of recent research and publications. Sokirnites are natural zeolites of volcanic origin with the general formula $K_2Na_2Ca \times Al_2Si_7O_{18} \times 6H_2O$. The sorption capacity of sokyrnite is due to its high content of clinoptilolite – more than 75 %; impurities – montmorillonite, quartz, feldspar, opal, and volcanic glass. The share of free intracrystalline volume for clinoptilolite is 34 % of the total volume [1; 2]. The sokyrnite had a rough surface and the size of the crushed stone ranged from 1 to 10 mm. The density of sokyrnites is 2,2–2,3 g/cm^3 and a hardness on the Mohs scale of 3,5–4 points. The specific surface area is 50–65 m^2/h. The colors are pink, white, gray, and light yellow.

The features of the sokyrnite structure (rough surface, presence of pores and channels, and entrance windows) are explained by the frame structure. The framework consists of tetrahedra that form eight-membered rings at their vertices, thereby creating channels in the zeolite structure. Water molecules ("zeolite water") as well as cations of alkaline and alkaline earth metals (Ca^{2+}, Na^{+}, and K^{+}) located inside the channels. With a large number of entrance windows on the surface, a structure permeated with channels, and a complex of cations inside itself, it is possible to use sokyrnite as a "molecular sieve" and replace cations that can pass through the molecular window with structural cations of the mineral.

The outer surface of sokyrnite with a grain size of 0,8–1,2 mm has a surface area of 18 m^2/g. Considering that the micropore space of zeolite is inaccessible to suspended and colloidal particles, the surface available for the adhesion of suspended and colloidal particles is 1–2 $m^2 \cdot g^{-1}$. For comparison, the effective rough surface area of quartz sand grains is only 0,12 $m^2 \cdot g^{-1}$. It is important to note that the NH^{+}_{4} ion exchange potential of sokyrnite is 1,23 mg-eq/g, and the size of the input windows is 3,5–4,8 Å. Indicators regarding the number of replaceable cations, mg-eq·g^{-1}: Ca^{2+} – 1,08; Na^{+} – 0,13; K^{+} – 0,02. Thus, sokyrnite is a highly effective ion-exchange sorbent [3–8].

The purpose of the study is to develop a kinetic model for the retention of colloids from an aqueous suspension in the pore space of zeolite media, as well as verifying its adequacy by conducting experimental studies on iron removal from underground natural waters.

Materials and methods of research. Field and laboratory experimental studies of physicochemical parameters of the investigated water suspensions; physico-mathematical modeling of the processes of filtration and purification of water suspensions using filter media from zeolite grains; use of experimental data obtained during experimental studies of the process of iron removal from underground natural waters.

Results of the study and their discussion. First, porosity of the researched filter media was determined. As a rule, the porosity determines the proportion of the cavity space from the total volume. Depending on the total volume under consideration, the porosity of the media grains ε_G and the porosity of the intergranular space (media layer) ε_I can be distinguished. Both porosities can be determined from the densities [9].

The grain porosity (also known as internal porosity) determines the cavity part of the zeolite grain volume. Therefore, it is defined as the ratio of the pore volume V_{por} and the zeolite grain volume V_G:

$$\varepsilon_G = \frac{V_{por}}{V_G} = \frac{V_{por}}{V_{zeol} + V_{por}} . \tag{1}$$

The grain porosity is related to the density of the media grain and the density of the zeolite skeleton of the grain:

$$\varepsilon_G = \frac{V_{por}}{V_G} = \frac{V_G - V_{zeol}}{V_G} = 1 - \frac{V_{zeol}}{V_G} = 1 - \frac{\rho_G}{\rho_Z} . \tag{2}$$

The porosity of the intergranular space (the outer part of the cavity space) ε_I is defined as the ratio of the water-filled volume of the cavities between the zeolite grains V_W and the filter volume V_F.

$$\varepsilon_G = \frac{V_W}{V_F} = \frac{V_W}{V_Z + V_W} . \tag{3}$$

The porosity of the intergranular space is related to media grain density and intergranular density as follows:

$$\varepsilon_G = \frac{V_W}{V_F} = \frac{V_F - V_Z}{V_F} = 1 - \frac{V_Z}{V_F} = 1 - \frac{\rho_I}{\rho_G} . \tag{4}$$

In the case of adsorption by a layer of filter media, instead of the porosity of the intergranular space, the term porosity of the filter media layer

1. Correlations characterizing the parameters of the zeolite filter media layer

Correlation	Expression
$\dfrac{\text{volume of water}}{\text{the total volume of the filter}}$	$\dfrac{V_W}{V_F} = \varepsilon_I$
$\dfrac{\text{volume of zeolite}}{\text{the total volume of the filter}}$	$\dfrac{V_Z}{V_F} = 1 - \varepsilon_I$
$\dfrac{\text{volume of zeolite}}{\text{volume of water}}$	$\dfrac{V_Z}{V_W} = \dfrac{1 - \varepsilon_I}{\varepsilon_I}$
$\dfrac{\text{mass of zeolite}}{\text{volume of water}}$	$\dfrac{m_Z}{V_W} = \rho_G \dfrac{1 - \varepsilon_I}{\varepsilon_I}$

is often used [10–15]. Table 1 presents the most important correlations.

The porosity of the intergranular space can be used to express various volume/volume or solid/volume correlations, which are characteristic of the conditions specified for a particular filter media. Therefore, they are often found in the equations that describe the parameters of the studied filter media.

Next, we determined the area of the outer surface of the researched filter media. The area of the outer surface of the zeolite grains has a strong influence on the mass transfer rate during physical adsorption. Thus, the area available for mass transfer in the mass transfer equation can be approximated by using the outer surface of the zeolite grains. The outer surface area can also be determined using a weighting method. In this method, the number of zeolite grains (Z_{gr}) in a representative sample is counted after weighing the sample ($m_{,Zgr}$).

As a rule, porous adsorbents have internal surfaces that are significantly larger in area than external ones. In particular, zeolite sand has an extremely large internal surface area. Therefore, almost all its physical adsorption capacity is provided by its internal surface area. Therefore, the internal surface area is a very important quality parameter for zeolites as physical adsorbents. However, it should be noted that the internal surface area alone is not a sufficient parameter for characterizing or predicting the physical adsorption capacity of a zeolite because the physical adsorption power is additionally affected by a number of other properties related to the zeolite and retained colloidal particles.

The standard method for determining the internal surface area is based on low-temperature gas adsorption (usually nitrogen adsorption at 77 K) and subsequent application of the Brunauer-Emmett-Teller (BET) isotherm. This method is called the BET method, and the area of the inner surface determined by this method is often called the BET surface area, A_{BET} [9].

The internal surface area is related to the pore system size. The highly microporous adsorbents used for water purification have large internal surfaces.

A commercial BET surface analyzer is required to determine the BET surface area. As an alternative option, to save money, the iodine number was used to determine the BET surface area. The iodine number can be determined easily without expensive equipment. The determination is based on an adsorption experiment with iodine as adsorbate and with defined initial and residual concentrations (0,1 M and 0,02 M, respectively). The adsorbent dose should be varied to achieve a specified residual concentration. With the adsorbent dosage determined from the variation and initial and residual concentrations, the amount of adsorbed substance can be calculated using the material balance equation for isothermal studies. The amount of adsorbed substance, expressed in mg/g, was the iodine number. Because the numerical value of the iodine number is approximately equal to that of the BET surface area, the iodine number can be used as a compensating parameter to characterize the internal surface area, for example, to compare different types of adsorbents.

Next, a kinetic model for the initial stage of the colloid retention process in sokyrnite pore space was developed. In general, the kinetic model includes mass transfer equations, equilibrium relations, and material balance for the investigated filter. This is schematically illustrated in Fig. 1.

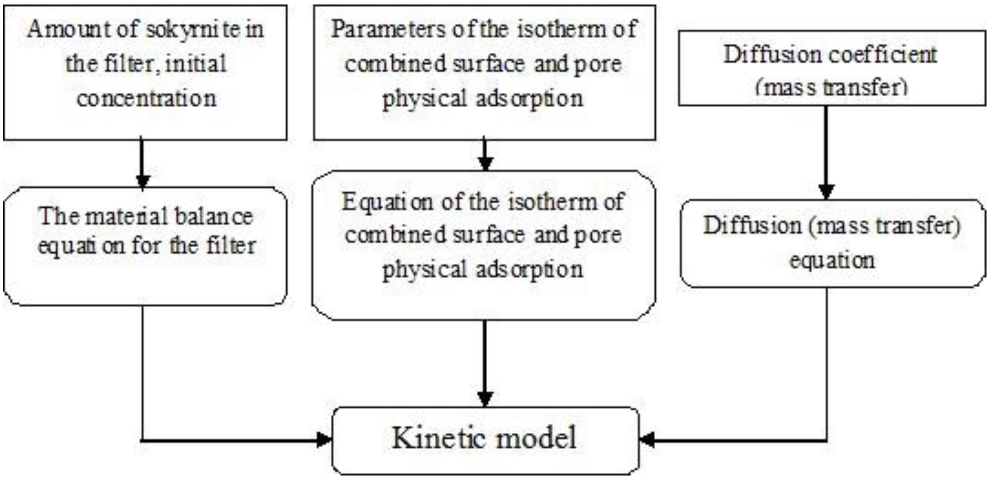

Fig. 1. General block diagram for modeling the kinetics of colloid retention in the pore space of sokyrnite. Model components and input data

The general assumptions in the kinetic model are as follows: (a) the colloidal suspension is assumed to be completely mixed, (b) the temperature is assumed to be constant, (c) the mass exchange with the zeolite surface and within it can be described as a diffusion process, (d) the attachment of colloids to the surface of the zeolite grains occurs much faster than the diffusion processes, and (e) zeolite grains are assumed to be spherical and isotropic.

The differential material balance for a zeolite filter can be expressed as:

$$m_Z \frac{d\bar{q}}{dt} = -V_W \frac{dc}{dt}, \qquad (5)$$

where m_Z is the mass of zeolite, and V_W is the volume of water in the filter. This equation relates the change in the average load on zeolite filter media with time to the change in the aqueous phase concentration over time. Integration of Equation (5) with the initial conditions $c(t = 0) = c_0$ and $\bar{q}\ (t = 0) = 0$ leads to the following form of the material balance equation:

$$\bar{q}(t) = \frac{V_W}{m_Z}\left[c_0 - c(t)\right]. \qquad (6)$$

During the process of iron removal from underground natural waters with the use of simplified aeration with atmospheric air and subsequent filtering, zeolite begins to retain iron ions almost immediately because of its ion-exchange properties. Figure 2 shows the curve of the averaged experimental data for iron removal using zeolite.

In the space of the filter, iron ions spread owing to the diffusion phenomenon in accordance with Fick's first law owing to the difference in their concentrations in the aqueous suspension. Adsorption of iron in the inner space of zeolite grains occurs owing to immobilization of its divalent soluble form. With the further transition of iron from divalent to less soluble trivalent form, iron flakes consolidate and are retained by the pore space of the zeolite media. Further filtering was accompanied by the process of contact coagulation of the iron flakes on the surface of the filter media. The process of fixing on it occurs because of the phenomenon of physical adsorption caused by London or Van der Waals forces. However, after the end of the ion exchange resource of the zeolite, the concentration of iron content in the filtrate increased sharply. This is due to the fact that the intensive extraction of iron ions from the purified aqueous suspension serves as an inhibitor of the autocatalytic process in the iron deposit, where the main part of the transformation of the iron form takes place. Therefore, a further decrease in the iron content of the filtrate can be explained by the disappearance of the factor that interferes with the autocatalytic process. Experimental studies have confirmed that the retention of colloids by the pore space of the zeolite media from an aqueous suspension occurs in accordance with the parameters of the developed kinetic model, which confirms its adequacy.

Conclusions. The parameters of the pore space of the filter media layer are described by

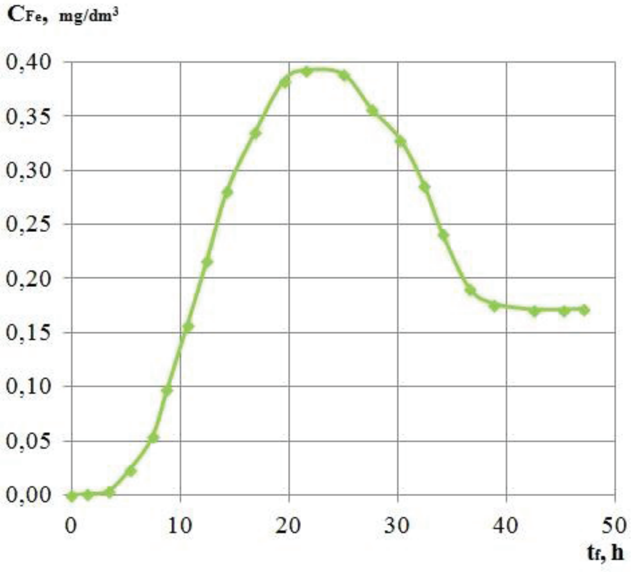

Fig. 2. Change in iron concentration C_{Fe} in the filtrate depending on the filtration time t_f (initial iron concentration – 1,2 mg·dm^{-3}, filtration speed – 7 m·h^{-1}) through zeolite-clinoptilolite grains (media fraction – 1,5–3 mm)

the developed physico-mathematical model, which includes the determination of the porosity (grains of zeolite media and intergranular space) and the areas of the outer and inner surfaces of the zeolite grains.

Experimental studies have shown the high efficiency of zeolites during the initial stage of iron removal from water. This is because of its ion-exchange properties, significant internal porosity, and well-developed outer-grain surface.

The developed kinetic model for the retention of colloids in the pore space of sokyrnite from an aqueous suspension was verified through experimental studies that confirmed its adequacy.

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КІНЕТИЧНА МОДЕЛЬ ПОЧАТКОВОЇ СТАДІЇ ПРОЦЕСУ ЗАТРИМАННЯ КОЛОЇДІВ ПОРОВИМ ПРОСТОРОМ СОКИРНИТУ

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Анотація. *Досліджено фізико-хімічні явища, що відбуваються на поверхні зерен сокирниту в складній системі «поверхня зерна завантаження – дисперсійне середовище – поверхня зважених часток». Каркасна структура будови сокирниту (шорстка поверхня, наявність пор і каналів, вхідних вікон) дає йому можливість працювати як «молекулярне сито» і бути високоефективним сорбентом-іонообмінником. Було визначено пористість досліджуваного фільтрувального завантаження. А саме: пористість зерен завантаження (яку також називають внутрішньою пористістю) і пористість міжзернового простору (шару завантаження). Визначено площу внутрішньої поверхні, що є дуже важливим параметром якості сокирниту як фізичного адсорбенту. Досліджено низку інших властивостей, пов'язаних із сокирнитом та затримуваними колоїдними частинками, які додатково впливають на силу фізичної адсорбції. Сформульовано та наведено співвідношення, що характеризують параметри шару цеолітового фільтрувального завантаження. Під час даних досліджень враховано вимоги до визначення часу зарядки фільтра та його оптимальних технологічних і конструктивних параметрів відповідно до умов експлуатації на конкретному об'єкті водопідготовки. Вони обумовили необхідність більш детального дослідження та розробки кінетичної моделі початкової стадії фільтрування водної суспензії через фільтр із цеолітовим завантаженням. Сформульовано вираз диференціального матеріального балансу для цеолітового фільтра. На основі розробленої кінетичної моделі було заплановано та проведено порівняльні досліди із знезалізнення підземних природних вод за допомогою вищезазначеного фільтрувального матеріалу. Наведено механізм розповсюдження іонів заліза у просторі фільтра завдяки явищу дифузії, відповідно до першого закону Фіка. Описано механізм затримання поровим простором цеолітового завантаження пластівців заліза, консолідація яких відбувається при переході заліза із двовалентної у тривалентну форму. Описано чинники, що заважають автокаталітичному процесу в осаді заліза. Досліджено динаміку зміни концентрації вмісту заліза у фільтраті після закінчення іонообмінного ресурсу сокирниту.*

Ключові слова: *кінетична модель, фільтрування, поровий простір, сокирнит, знезалізнення*