RADIOLYSIS OF WATER IN NANOBENTONITE

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Abstract: In the present work, the effect of the chemical action of ionizing radiation on nanoclays is discussed. The dominant role in the radiolysis of pore water under the influence of gamma quantum should be attributed mainly to hydronium ions (protonated water molecules, H_3O^+). The effect of ionizing radiation on nanobentonite was studied in the presence of oxygen. The article is devoted to a discussion of how ionizing radiation, passing through nanoclays, produces, or rather begins to produce chemical effects. Infrared spectroscopy was used as the method for determining the structural responses of natural clay from the Alpoid deposit in the Republic of Azerbaijan to gamma-ray exposure. It is of great interest to examine the role of active centers of clay minerals in the adsorption interaction in the presence of gamma irradiation.

Keywords: nanoclay, ionizing radiation, protonated water molecules H_3O^+, infrared spectroscopy, active centers.

1. Introduction

In 2018, China became the top producer of bentonite, taking almost a quarter of the world's production, followed by the USA and India. Total worldwide production was 24,400,000 metric tons of bentonite and 3,400,000 metric tons of Fuller's earth [1].

Most high-grade natural sodium bentonite is produced in the western United States, in an area between the Black Hills of South Dakota and the Bighorn Basin of Wyoming, and the Tokat Resadiye region of Turkey. Mixed sodium/calcium bentonite is mined in Greece, Australia, India, Russia, and Ukraine. In the United States, calcium bentonite is mined primarily in Mississippi and Alabama. Other major locations producing calcium bentonite include New Zealand, Germany, Greece, Turkey, India, and China [1].

Bentonite is rich in montmorillonite, which is a nanostructured and nanoporous member of the smectite group. The mineralogical and physicochemical properties of bentonites play a key role in choosing appropriate bentonites for different applications. Based on their chemical composition and particle morphology, clays are organized into several classes, such as smectite, chlorite, kaolinite, illite, and halloysite [2-5]. The most common plate-like montmorillonite (MMT) nanoclay (smectite) consists of approximately 1 nm-thick aluminosilicate layers surface-substituted with metal cations and stacked in approximately 10 µm-sized multilayer stacks [2,6,7]. Clays and modified clays are particularly useful for the adsorption of heavy metals. Clays have received attention for being excellent adsorbents of As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, and Zn in their ionic forms in an aqueous medium. The adsorption capacities differ from metal to metal and also depend on the type of clay used. For this research, raw bentonite was used from the Alpoid deposit in Azerbaijan. The Alpoid bentonite deposit is far superior in quality to bentonite deposits in Greece, Turkey, India, and China and is equal to the benchmark Wyoming bentonite. The Alpoid deposit is located in the northwest part of the Gazakh region. It is one of the highest-quality natural

sodium bentonite deposits in the world and is represented by one flat-lying seam with no poor rocks inside. It relates to the sedimentary type formed as a result of continental–lacustrine conditions. The deposit is represented by montmorillonite and hydromica-montmorillonite clay. It is one of the highest-quality natural sodium bentonite deposits in the world. The deposit consists of montmorillonite and hydromica-montmorillonite clay [10].

It is necessary to pay special attention to the radioactive stability of clay minerals, whose interlayer bonds usually result from unlikely charged surfaces, or cations, which are between the same charged layers. Similar bonds are easily broken down when exposed to radioactive irradiation simultaneously with the structural bonds existing between mineral particles. When exposed to radiation over the long term, there is a change in the valent bond vibrations of Si-O and Al-O inside the layer up until its fracture. Besides, there is dehydration of crystallization water and structural water in the form of OH- groups from the crystal lattice. The removal of crystallization impacts the chemical, physical-chemical, and physical-mechanical properties of clays; the removal of structural water leads to a complete fracture of clay minerals. Na-bentonite clay from Alpoid (pH=10) may be compared with Cambrian blue clays. Because Lower Cambrian blue clays are represented by high-alkaline minerals, interlayer link destruction will take place at low enough radiation doses [2, 7, 9]. This paper aims to reveal the useful industrial aspects of the montmorillonite group of clays used as a catalyst after gamma-ray activation. A comparative study of the modified characteristics of clay samples has been explored based on industrial requirements.

2. Experimental part

The clay samples were taken from the Alpoid deposit [10].

The morphology of the nanostructure was studied with scanning electron microscopy (SEM from ZEISS, Leo 1530 VP). The raw bentonite clay sample used in these experiments has a nanostructured composition with particle sizes in the range of $55 \leq d$ [nm] ≤ 175 nm [2,7,8].

Clay samples were packed in a closed Pyrex glass container. The bentonite clay samples were irradiated with gamma radiation using the ^{60}Co isotope under static conditions within glass tubes at room temperature. The dose rate was 10.5 rad/s. The irradiated and unirradiated samples were characterized by FT-IR spectroscopy. Spectrophotometric measurements were performed in a VARIAN 640-IR spectrophotometer in the 4000…400 cm^{-1} region. Reaction conditions: A given amount of nanobentonite (2 g) was added to glass containers and closed, then subjected to various doses of radiation energy (from 1 to 260 kGy). Irradiation was performed at room temperature in an environmental atmosphere.

3. Results and discussion

The detailed molecular structure of pure montmorillonite, the best-known end-member of the smectite group, was taken from the literature [10-12]. The interlayer space between two successive TOT (Tetrahedra- Octahedra- Tetrahedra) layers is filled with hydrated cations (mainly Na^+ and Ca^{2+} ions) compensating for the negative electrical charges of the TOT layers and with water molecules causing the interlayer expansion (Fig. 1.).

The TOT is a structure (Figure 2) of clay minerals, where T stands for the tetrahedral layer (mainly Si) and O stands for the octahedral layer (mainly Al). The density is relative to pure water, with a specific volume of 3.00×10^{-29} m^3/mol H_2O. Meanwhile, the spacing and number of water molecules per water layer vary gradually, suggesting mixed-layer formation and a complicated distribution of the water over hydration water associated with the exchangeable cation and free water [13]. Figure 1 shows that the density of water in the interlayer space is smaller than that of

bulk water, except for the value extracted from Pitteloud et al. [14]. When spacing increases, it approaches 1, but not in the MD (modular dynamics) calculations of Karaborni et al.[15].
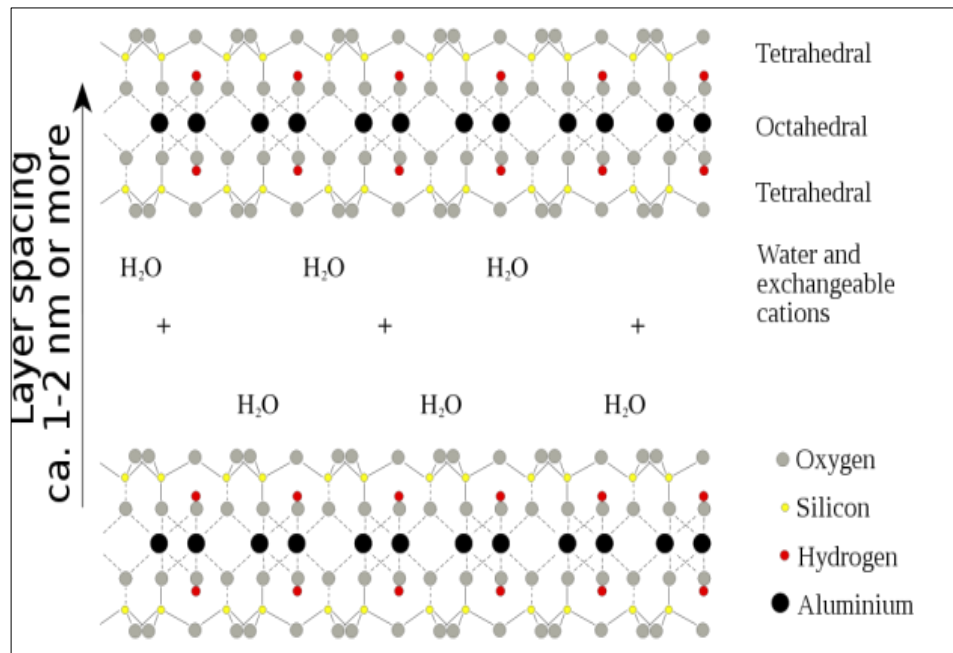

Fig.1. Montmorillonite structure

The XRD results are more consistent and show that water starts by hydrating the cation and that the structure expands slightly. As humidity increases and more water enters the interlayer space (displacing the gas molecules from the laboratory atmosphere if not pumped vacuum), the relative density increases until a threshold value is identified at which the structure converts from the 1- to the 2-layer hydrate. With Na^+ as an exchangeable cation, the structure expands further into the 3-layer hydrate when the RH increases above 85 % [16]. With increasing spacing, the interlayer water can be expected to gain the density of free water, as observed in the XRD studies. Thus, the decreasing density calculated by Karaborni et al. and others [17] may be an artifact that is associated with approximations in the MD simulations [18]. In the model for calculating the distribution of the porosities, it was assumed that the density is 1 kg/L ($f_{dens} = 1$), and that may look erroneous given the results in Figure. However, the XRD measurements are done at less than 90 % relative humidity, corresponding to an activity of water less than 0.9. On the other hand, in free-pore water, where the ionic strength is below 1, the activity of water is close to 1, and hence, the assumed density may be realistic.

The tetrahedral-octahedral-tetrahedral coordination of oxygen around cations in the bentonite structure is taken from the literature [19]. A sketch of water in montmorillonite shows the heterogeneous distribution of anions and cations in three water types. Interlayer water has cations only; diffuse double-layer water has an excess of cations; and free porewater is charge-neutral. TOT indicates the tetrahedral-octahedral-tetrahedral coordination of oxygen around cations in the structure of sodium-bentonite.

Experiments based on FTIR spectrum analysis, in which radiolysis of nanobentonite in the presence of oxygen occurs, show insignificant destruction of the solid phase of clay and radiolysis of pore water between doses of 1 and 260 kGy.
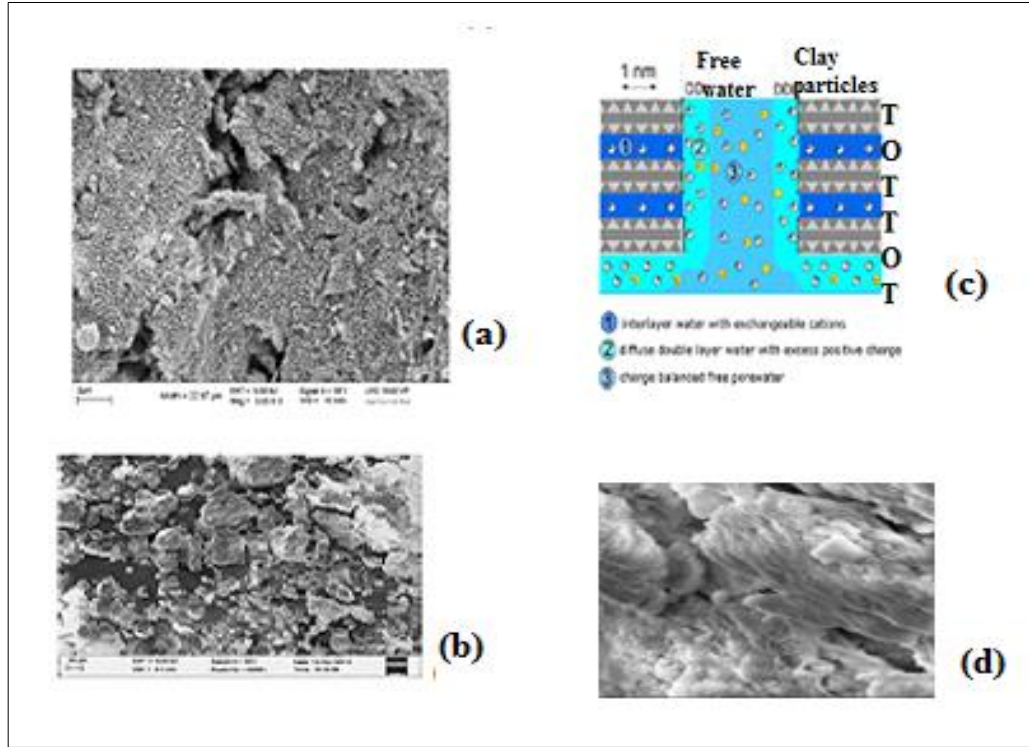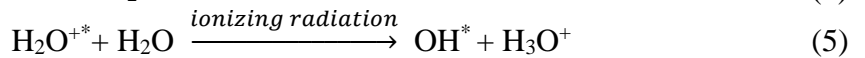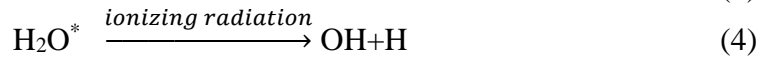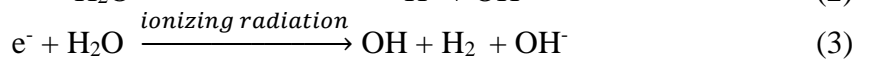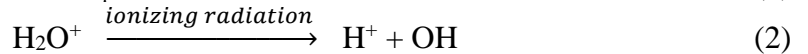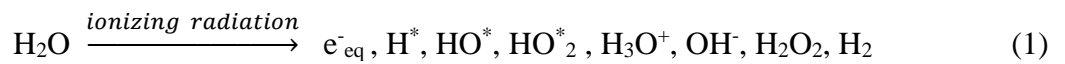
Fig. 2. Illustrations of the bentonite structure and porosity types. (a) -SEM overviews of magnification: 5000 X and (b) - 500 X of samples bentonite clay; (c) - tetrahedral-octahedral-tetrahedral coordination of oxygen around cations in the structure; d)- layer structured agglomerates of sodium bentonite from Alpoid deposit.

The water radiolysis process leads to the formation of the following primary products [20]:

$$H_2O \xrightarrow{\text{ionizing radiation}} e^-_{eq}, H^*, HO^*, HO^*_2, H_3O^+, OH^-, H_2O_2, H_2 \qquad (1)$$

$$H_2O^+ \xrightarrow{\text{ionizing radiation}} H^+ + OH \qquad (2)$$

$$e^- + H_2O \xrightarrow{\text{ionizing radiation}} OH + H_2 + OH^- \qquad (3)$$

$$H_2O^* \xrightarrow{\text{ionizing radiation}} OH+H \qquad (4)$$

$$H_2O^{+*} + H_2O \xrightarrow{\text{ionizing radiation}} OH^* + H_3O^+ \qquad (5)$$

As a result of water radiolysis with gamma-radiation, excitation, and ionization of water molecules occur, a phenomenon that leads to the formation of various ion species, radicals, and new molecules - the radical theory of water radiolysis [21-23]. The released water molecules, in turn, react with another bentonite clay fracture. Also, the attack of water molecules on excited bentonite clay is not excluded. In this excited configuration of the catalyst, water molecules are subjected to Coulomb forces of attraction-repulsion of the ionic species in the clay structure.

Under the influence of gamma radiation, the H-OH bonds in water molecules adsorbed on the catalyst surface will be easier to split into non-adsorbed water molecules. Ionic species in the composition of clay as Coulomb attraction–repulsion forces on the dipole water molecules, facilitating H-OH bond break under the nuclear radiation.

In the case of sodium-bentonite clay, through the interaction of nuclear radiation on the surface, there might appear "charge carriers" e- and fraction of clay+, namely:

$$\overset{h\gamma}{\rightarrow} \text{ bentonite clay} \rightarrow (\text{fraction of clay}^+, e^-) \tag{6}$$

Water molecules can be broken down as follows:

$$g+ + \text{ H-O-H} \rightarrow H_2O+ \rightarrow H^+ + HO* \tag{7}$$
$$e- +H+ \rightarrow 1/2 \ H_2 \tag{8}$$
$$H^*+H^* \rightarrow H_2 \tag{9}$$

Sodium bentonite has a single water layer containing Na^+ as exchangeable ions (with swelling properties). The surface defects formed in radiocatalytic reactions under the influence of ionizing beams play a key role in obtaining molecular hydrogen.

Under the effect of ionizing radiation, valence electrons (F) and hole centers (V) form in bentonite clay crystals. As for relatively larger particles (taking into account that bentonite clay's particle size changes in the range of $55 \leq d \ [nm] \leq 175 \ nm$), the electrons formed in bulk migrate to the surface, are captured by the existing holes (V) on the surface, and are recombined.

$$F^+ + V^- = \text{product} \tag{10}$$
$$2 \ H^+ + 2 \ e^- = H_2 \tag{11}$$
$$2 \ OH^- + 2F^+ = H_2O_2 \tag{12}$$

The relationship between pore water particles' yield and radiolysis time shown in Figure 3 is based on literature data [24]. An analysis of the literature shows that the dominant role should be attributed mainly to hydronium ions (protonated water molecules H_3O^+) in the radiolysis of pore water under the influence of ionizing radiation.
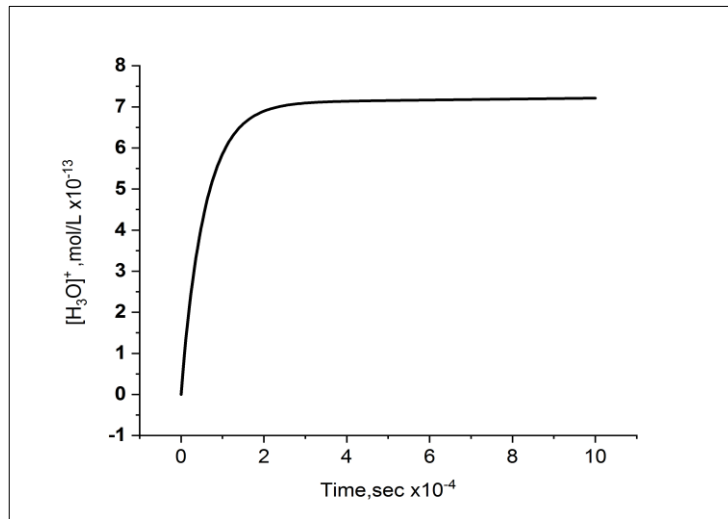

Fig. 3. Radiolysis of bentonite porewater: Time dependence for concentration or yield of H_3O^+

4. Conclusions

- This study reveals the radiochemical characterization and catalytic behavior of nano-sodium bentonite clay.

- The dominant role should be attributed mainly to hydronium (hydroxonium in traditional British English) ions (protonated water molecules H_3O^+) in the radiolysis of pore water under the influence of ionizing radiation.
- The novelty of this study is about sodium bentonite characterization, and the results show prominent behavior with structural, elemental, morphological, and radio analysis.

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РАДИОЛИЗ ВОДЫ В НАНОБЕНТОНИТЕ

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Резюме: В настоящей работе обсуждается эффект химического действия ионизирующих излучений на наноглины. В радиолизе поровой воды под воздействием ионизирующего излучения доминирующую роль следует приписать преимущественно ионам гидроксония (протонированным молекулам воды H_3O^+). Воздействие ионизирующего излучения на нанобентонита исследовано в присутствии кислорода. Статья посвящена обсуждению того, каким образом ионизирующие излучения, проходя через наноглины, производят, точнее, начинают производить химические действие. Для исследования нанобентонитовой глины из месторождения Алпоид в республике Азербайджан, применили метод инфракрасной спектроскопии. Большой интерес представляет исследование влияния роли активных центров глинистых минералов в адсорбционном взаимодействии в присутствии гамма облучения.

Ключевые слова: наноглина, ионизирующее излучение, протонированные молекулы воды H_3O^+, инфракрасная спектроскопия, активные центры.

NANOBENTONİTDƏ SUYUN RADİOLİZİ

M.K. İsmayılova, İ.İ. Mustafayev

Xülasə: Təqdim edilən məqalədə ionlaşdırıcı şüalanmanın nanogilin tərkibinə kimyəvi təsiri müzakirə olunur. İonlaşdırıcı şüalanmanın təsiri altında məsamə suyunun radiolizində dominant rol əsasən hidroksonium ionlarına (protonlaşdırılmış H_3O^+ su molekullarına) aid edilməlidir. İonlaşdırıcı şüalanmanın nanobentonitə təsiri oksigenin iştirakı ilə tədqiq edilmişdir. Məqalə nanokillərdən keçən ionlaşdırıcı şüaların hansı kimyəvi təsirlər yaratdığına, daha doğrusu, radiokimyəvi proseslərin baş verməsinin müzakirəsinə həsr edilmişdir. Azərbaycan Respublikasında Alpoid yatağına məxsus olan nanobentonit gilinin tədqiqi üçün infraqırmızı spektroskopiya üsulundan istifadə edilmişdir. Qamma şüalanmanın təsiri

altında gedən radioliz prosesində gil minerallarının aktiv mərkəzlərinin rolunun təsirinin öyrənilməsi böyük maraq doğurur.

Açar sözlər: nanogil, ionlaşdırıcı şüalanma, protonlaşdırılmış H_3O^+ su molekulları, infraqırmızı spektroskopiya, aktiv mərkəzlər.