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The studies on dehydration reaction mechanism of irradiated solid acid - nanostructured sodium - bentonite clay

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Research findings can offer data and a theoretical framework for a quantitative examination of the bentonite dehydration mechanism. The reasons for changes in pore water under the influence of gamma rays in vacuum and in the presence of oxygen was discussed using TGA and DTA, FT-IR spectroscopy. It was revealed that dehydration and pore characteristics are mutually dependent. A question about the associated evolution of dehydration pore water in nanostructured sodium – bentonite clay under the influence of ionizing rays with and without oxygen has been comparatively studied. The article is devoted to a discussion of how ionizing radiation, passing through nanoclays, produces, or rather begins to produce, chemical effects. It was used Infrared spectroscopy as the method for determining structural responses of natural clay from the Alpoid deposit in the Republic of Azerbaijan, to gamma rays exposure. It was found that under influence of ionizing rays in vacuum obtained hydrogen peroxide. It is of great interest for the study of the dehydration reaction mechanism and its role in formation of H₂ under gamma irradiation.

Keywords: dehydration reaction, solid acid, irradiation, nanostructured clay, chemical effect.

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Introduction

Recently, interest in bentonite clays has increased significantly and their deposits have been discovered in many countries around the world [1]. Chemical and physico-chemical properties of clays make them useful for industry [2-4].

Calcium - bentonite is difficult to use directly. Natural Na-bentonite the most popular material used today [8-11]. Sodium-rich clay content is more permeable to inorganic solutions. It has been established, that pore characteristics and hydration of clays are interdependent [6-10]. H. Wang et al. studied hydration and dehydration of solid state of bentonite by spectroscopy method [7]. Dehydration experiments demonstrated that there occurred two different interactions in bentonite's interlayer space: the H₂O - H₂O and cation - H₂O. The interaction of H₂O - H₂O

exceed at high water content, but cation- H₂O at lower water content. As a result of water-water interaction produced weakly bound water, and in case of water-cation interaction produced strongly bound water near the bentonite surfaces.

It has been established that sodium bentonite clay changed their surface characteristics under influence of ionizing rays in vacuum. Nanostructured sodium – bentonite clay from Alpoid deposit (Azerbaijan Republic), modified by gamma rays has been proposed as a catalyst for aromatization and isomerization of hydrocarbons [4, 11, 12]. Why these nanostructured sodium – bentonite clays are chemically active under gamma rays are studied in this presented paper and the key role of dehydration reaction mechanism of pore waters of nanostructured sodium-bentonite clay is researched.

Bentonite minerals' hydration and dehydration,

controls chemical and physico-chemical characteristics of sodium-bentonite. The interaction of H₂O - 2:1 layer structure of montmorillonite causes it to hydration or dehydration. Numerous scientific research have been carried out on the interaction of montmorillonite and water, but these chemical reactions are not yet fully understood at the molecular level [4, 6, 7]. Investigations of nanostructured sodium-bentonite clay pore and interlayer water under influence of ionizing irradiation and study the dehydration reaction mechanism of pore's water, using TGA and DTA, FT-IR spectroscopy is the main aim of this work.

I. Experimental part

Nanostructured Na-bentonite clay irradiated by gamma-rays of isotope ⁶⁰Co at 20°C. The dose rate was 10.5 Rad/sec. VARIAN 640-IR spectrophotometer was used to take measurements in the 4000-400 cm⁻¹ range.

Thermogravimetric analysis TGA and DTA conducted on a Perkin Elmer STA 6000 instrument (USA), with heating and cooling to 900°C, inert gas argon 20 ml/min.

Reaction conditions:

Nanostructured sodium-bentonite samples (1.0 - 2.0 g) were placed in glass ampules, sealed in liquid N₂ environment, and then exposed to radiation at levels between 0.7 and 300 kGy;

Nanostructured sodium-bentonite samples (1.0 - 2.0 g) were placed in glass ampules in presence of oxygen and closed, then exposed to radiation at levels between 0.7 and 300 kGy.

The nanostructured sodium-bentonite clay samples used in these experiments is nanostructured, with particle size 55 -175 nm. The Alpoide deposit from Republic of Azerbaijan contains 85% sodium-montmorillonite. The chemical formula for nanostructured bentonite is (Na,0.5Ca)_{0.7}(Al,Mg,Fe)₄(Si,Al)₈O₂₀(OH)₄•XH₂O [11]. Cations - Na⁺, Ca²⁺, Mg²⁺ ions, bonded with water molecules due to ion-dipole forces. These ions are the main reason of bentonite's hydration reaction in the clay's crystal lattice [12,13].

Montmorillonite is the aggregate containing interposition water [16]. Water molecules were found to be able to interact with different parts of clay, such as certain particles and the outer layer. This interaction causes a difference in how water molecules stick to the clay. The particles in the clay have a stronger pull on water molecules compared to the outer layer. This means that the particles are the main reason why water sticks to the clay. When water is removed from the clay, it starts with the outer layer first, which has less pull on the water molecules. Then, the particles lose their pull on the water molecules [13].

Reversible processes: hydration and dehydration reactions are observed in bentonite clay at temperatures above 100°C. Mineralogical analysis of the clay has shown that natural clay consists of discrete illite-smectite components with the ability to hydrate and dehydrate. The results of these studies showed that these components hydrate at different rates [14].

II. Results and discussion

In order to study the mechanism of the dehydration reaction of irradiated nanostructured sodium bentonite, the results of FT-IR spectroscopy, DTA and TGA were analyzed.

A change in the vibrations of Si-O and Al-O valence bonds inside the layer is observed up to the destruction of bentonite clay. In addition there are crystallization water's dehydration, and structural water in the form of OH-groups from the crystal lattice. The removal of crystallization impact of chemical, physical-chemical and physical and mechanical properties of clays and the elimination of structural water leads to a complete fracture of clay minerals. Dehydration reaction of nanostructured bentonite clay in vacuum takes place completely at dose of 57 kGy.

Experiments have confirmed this, as the Si-O bond belonging to silicates is broken in nanostructured bentonite clay at a dose of 57 kGy in vacuum (under the influence of gamma rays) at room temperature (in Fig. 1c, there is no band corresponding to 1056 cm⁻¹ presence) [15].

Band position near 3430 cm⁻¹ is caused by stretching vibrations of OH in H-bonded H₂O molecules. Band at 3451 cm⁻¹ is derived from vibrations of OH group corresponded to octahedral cations of nanostructured bentonite clay (Al-OH-Al, Fe-OH-Al, and Mg-OH-Al in the clay's octahedral layer). Approximately 1042 cm⁻¹ is the band created by the Si-O-Si bond. The decrease of the bands at 1642 cm⁻¹ related to Al-Al-OH, indicates a damage of clay's octahedral layer [16]. Formation of H₂O₂ during radiolysis of pore's water confirms by FT-IR spectroscopy. Band position near 3550 cm⁻¹ corresponded to H₂O₂ (Fig. 1.a).

Irradiation of nanostructured bentonite clay in presence of oxygen another picture is observed. Notable changes after irradiation were a decrease in the Si-O intensity spectral band from 1054 to 1038 cm⁻¹ [16]. In this case more than dose of 57 kGy radioactive exposure destruction of crystal lattice is not discovered (Fig. 2. a-c).

It was found that this chemical phenomenon - destruction reaction did not occur in the samples irradiated up to 400 kGy dose in the oxygen environment by the Fourier-transform IR spectroscopy method (Fig. 2. a-c).

TGA/DTA confirms the results of FT-IR spectroscopy. As shown in Fig. 3, (a-d) comparative study of the dehydration reaction of nanostructured Na-bentonite clay at various doses of gamma radiation in the presence of oxygen, showing that the main structure - the basic one doesn't change.

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In the studies conducted based on Fourier transform-IR spectral analysis, it was found that during gamma irradiation in the dose range of 1-400 kGy in the presence of oxygen, a slight destruction occurred in the radiolysis of the solid phase of nanostructured clay and pores.

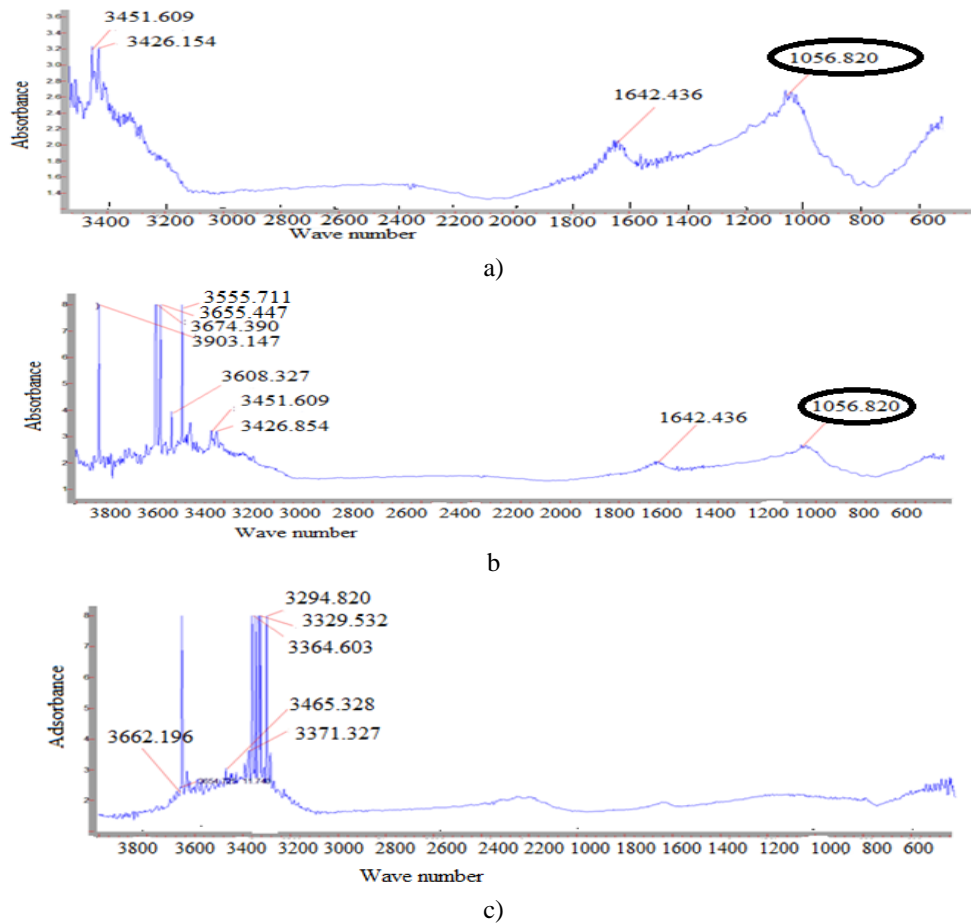


Fig. 1. FT-IR spectra of irradiated nanostructured Na- bentonite clay at different gamma radiation doses in vacuum: a – at 6; b – 28; c – 57 kGy (at 20⁰C).

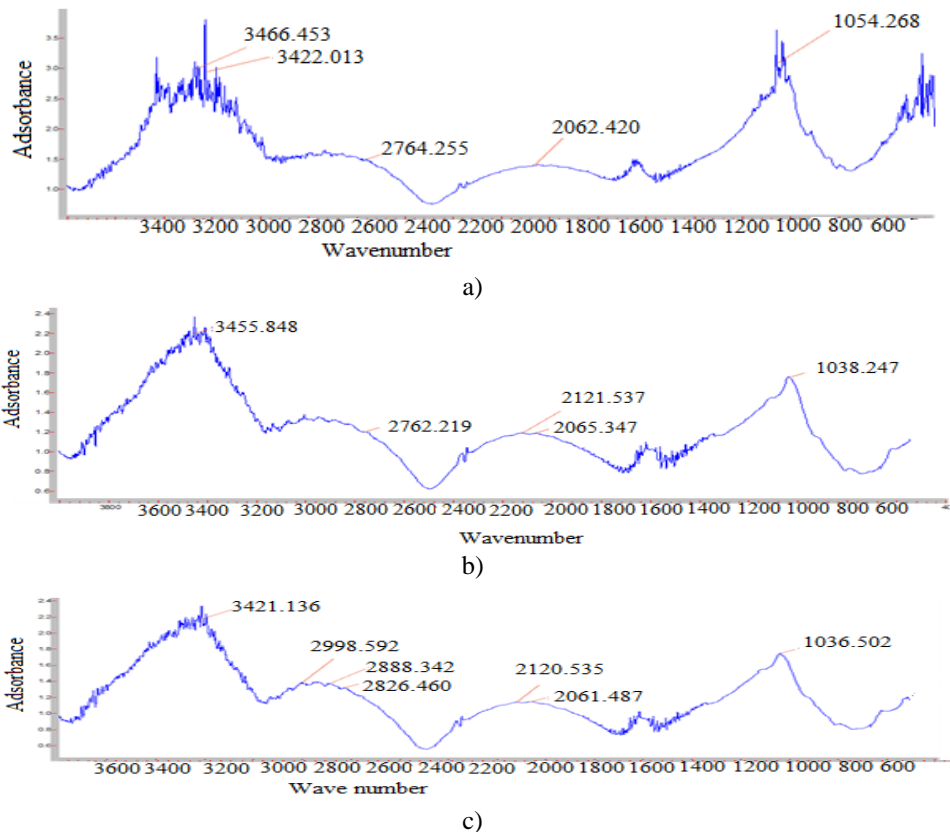


Fig. 2. FT-IR spectra of irradiated nanostructured Na- bentonite clay at different gamma radiation doses in presence of oxygen: a – 6; b – 57; c- 400 kGy (at 20⁰C).

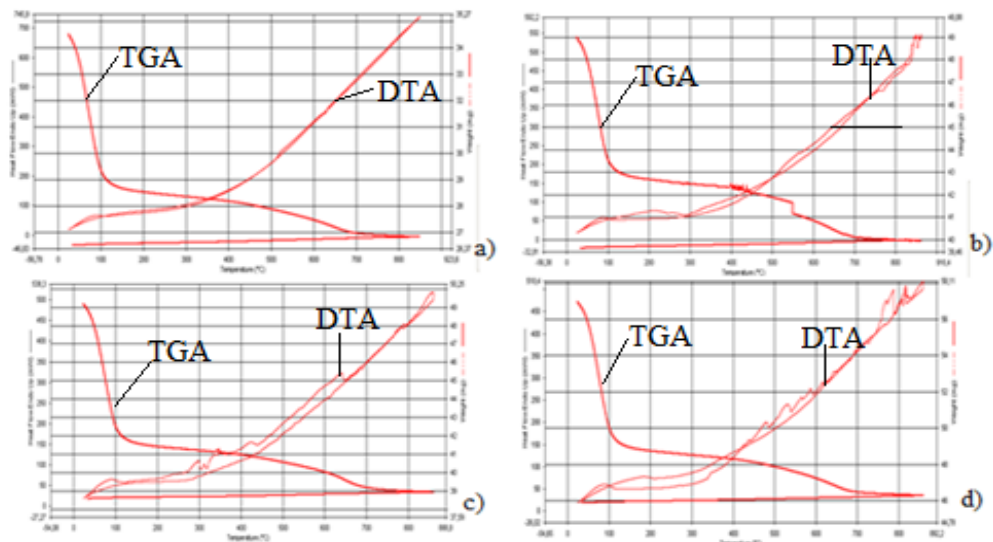


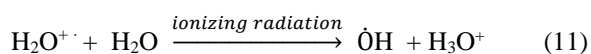
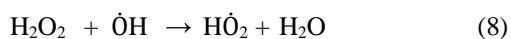
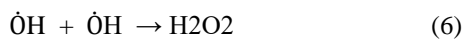
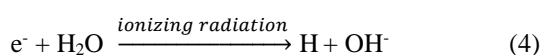
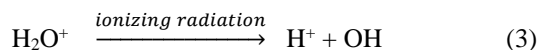
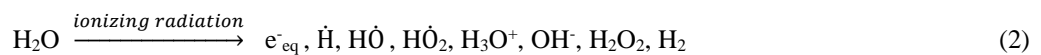
Fig. 3. TGA / DTA curves nanostructured Na-bentonite clay irradiated at different gamma radiation doses in presence of oxygen: a – 6; b – 57; c- 170; d- 400 kGy (at room temperature).

According to the radical hypothesis of water radiolysis, when water is exposed to a gamma-radiation beam, the water molecules are excited and ionized, which results in the production of numerous ion species, radicals, and new molecules [17]. Water molecules that have been released again react with other bentonite clay's fracture.

Additionally, it is not ruled out that water molecules will attack excited bentonite clay. Water molecules are subjected to Coulomb forces of attraction-repulsion of the ionic species in the clay structure in this excited form of the nanostructured bentonite [18].



During the radiolysis of pore water, the next primary reaction products are formed [17]:



Hydrogen peroxide can also decompose when reacting with H and OH (7, 8). The structure water of nanostructured sodium-bentonite under influence of gamma-rays has the capacity to furnish exogenous

hydrogen for the production of molecular hydrogen (H₂) at room temperature (5).

Conclusions

Nanostructured sodium bentonite clay in a vacuum and in the presence of oxygen under the influence of gamma rays exhibits various chemical effects. They highlight differences in their behavior. Destruction of bentonite begins at a dose of 57 kGy in a vacuum, but when irradiated in the presence of oxygen it is stable above 400 kGy at room temperature.

It is discovered that chemical effects of dehydration reaction are connected with the breakdown of the crystal structure of the dehydrated montmorillonite at room temperature. It has been established that bentonite clay nanostructures are more chemically active under vacuum conditions, since they are capable of agglomerating in the presence of oxygen. Therefore, dehydration in this case occurs very slowly.

Taking into account the differences among dehydration reactions in these cases we can say that modification of bentonite clay under influence gamma rays in vacuum is effective. The study of hydration reaction gives opportunities to carry modification of

nanostructured clays. Considering the differences in dehydration reactions in these cases, it can be said that modification of bentonite clay under the influence of gamma rays in a vacuum is effective. Studying the hydration reaction makes it possible to manipulate the modification of nanostructured clays.

Data Availability

Date is not shared because information based on date is already available in the paper.

Conflicts of Interest

The author fully declare that no conflicts of interest.

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Дослідження механізму реакції дегідратації опроміненої твердої кислотно-наноструктурної натрій-бентонітової глини

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Результати статті демонструють дані та теоретичну основу для кількісного дослідження механізму дегідратації бентоніту. Причини зміни «пористої» води під впливом гамма-випромінювання у вакуумі та в присутності кисню обговорювали за допомогою TGA, DTA та FT-IR спектроскопії. Виявлено взаємозалежність між характеристиками дегідратації та порами. Розглянуто питання про асоційовану еволюцію «пористої» води дегідратації в наноструктурованих натрій-бентонітових глинах під впливом іонізуючих променів з киснем і без нього. Стаття присвячена обговоренню процесів, як саме іонізуюче випромінювання, проходячи через наноглини, викликає, а точніше починає виробляти хімічні ефекти. Інфрачервону спектроскопію використовували як метод для визначення структурних реакцій природної глини родовища Альпоїд в Азербайджанській Республіці на вплив гамма-випромінювання. Було встановлено, що під впливом іонізуючих променів у вакуумі виходить перекис водню. Він являє великий інтерес для вивчення механізму реакції дегідратації та її ролі в утворенні H₂ при гамма-опроміненні.

Ключові слова: реакція дегідратації, тверді кислоти, опромінення, наноструктурована глина, хімічний вплив.