

STUDY OF MODIFICATION OF SODIUM MONTMORILLONITE FROM THE DARBAZINSK DEPOSIT

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ABSTRACT

This article provides information about the possibility of studying modified sodium montmorillonite obtained on the basis of bentonite clays from the Darbazinsky deposit in order to use it as a modifier for the production of polymer composite materials. In the course of experimental studies, it was revealed that a feature of the structure of montmorillonite is that weakly bound water molecules are located between the layers and due to this the crystal lattice is mobile. The results of experimental studies of the modification of montmorillonite in the presence of sodium at a temperature of 353 K, characterized by high values of cation exchange, are presented and it is determined that the modified montmorillonite is 95 mg-eq/100 g with an average diameter of silicate plates ~ 77 nm, which are suitable as a modifier for the production of composite polymer materials

Keywords: Bentonite, Refractory Clay, Activation, Modification, Montmorillonite.

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INTRODUCTION

Bentonite clays occupy a special place among clay natural materials. The composition and structure of bentonite determine its specificity—high absorption capacity. Bentonites have significant activity in the absorption of water, organic molecules, and salt ions, this property of bentonite determines the extensive possibilities of its use in various fields of industrial production.¹⁻³ The most preferred technological properties are those bentonites, the main mineral of which (montmorillonite) mainly contains exchangeable sodium cations. There are huge reserves of clay minerals on the territory of the Republic of Kazakhstan, one of which is bentonite from the Darbazinsky deposit, which is located in the Turkestan region. Darwaza bentonite (Fig.-1) enters the second horizon of the Suzak formation and is alkaline-earthly.⁴⁻⁵



Fig.-1: Location and appearance of the Darbaza deposit, Republic of Kazakhstan

The use of modified montmorillonite as a modifier in order to expand the range and improve the physical and mechanical properties of composite polymer materials, reduce the cost and simplify the process, as well as reduce the cost of production.

EXPERIMENTAL

IR spectroscopic, differential thermal, and analytical methods of investigation were carried out to clarify the nature and obtained data on Darbaza bentonite studies.⁶⁻⁷ The results of the chemical composition studies are shown in Table-1.

Table-1: Chemical composition of Darbaza bentonite, mass. %:

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	N ₂ O	K ₂ O	SO ₃
57-61	14-15	5,5-5,90	0,6-0,8	2,2-2,3	0,92-1,1	2,0-2,4	0,5-2,5

It follows from Table-1 that these minerals belong to the smectite group, that is, layered silicates with a three-layer crystal lattice package. The most common among the smectite group are bentonite clays, where the main rock-forming mineral is montmorillonite. The bulk of the rock consists of a fine-scaled aggregate of clay material and belongs to montmorillonite clays.⁸⁻⁹ Montmorillonite is a two-dimensional silicate with an aqueous layer belonging to the phyllosilicate family. The main backbone of montmorillonite is silicate layers formed as a result of condensation of extremely stable SiO₄-tetrahedral units. SiO₄ tetrahedra are separated by three oxygen atoms, dividing the angle of the silicate layer. In this case, oxygen atoms are located at the base of an equilateral triangle, forming repeating structures of regular hexagons.¹⁰⁻¹²

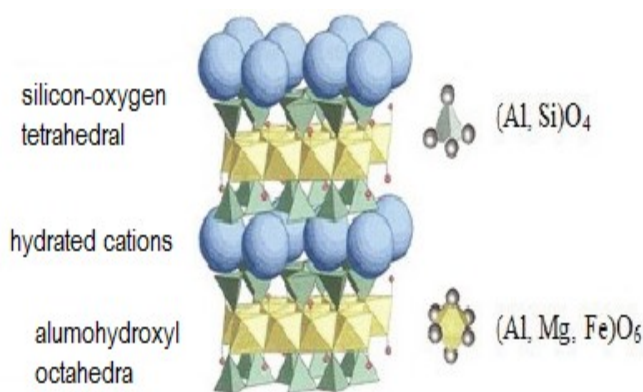


Fig.-2: Silicate Sheet of Montmorillonite SiO₄⁻

From Fig.-2, it follows that each tetrahedron in the silicate layer has a spare oxygen atom, which is not common and is usually located away from the tetrahedral silicate sheet. These silicate planes are then condensed into various octahedral plane units through oxygen atoms and various metals MeO₆⁺ (M = Al, etc.). Each octahedron contains two oxygen atoms, usually directed above or below the polymerization plane. Trivalent aluminum occupies only two-thirds of the octahedron and forms dioctahedral montmorillonite, whereas magnesium forms trioctahedral montmorillonite. The structure of the alumina layer is shown in Fig.-3.

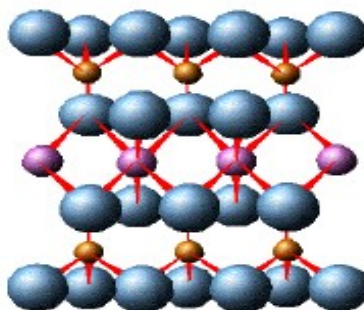


Fig.-3: Alumina Octahedral Sheets in a Clay Mineral

The structure of montmorillonite is constructed of negatively charged silicate layers; exchange cations with a positive charge located on the surface of silicate layers; and molecularly bound water, which neutralizes positive and negative charges.

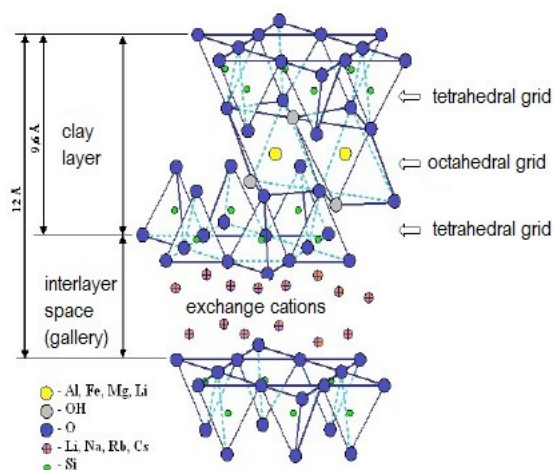


Fig.-4: Structure of 2:1 Clay Mineral Montmorillonite

It follows from the Fig.-4 a layer of alumohydroxyl octahedra is located between the lower and upper layers of silicon-oxygen tetrahedra. Silicon located in tetrahedra is partially replaced by aluminum, and in the middle layer, aluminum is replaced by magnesium, iron, nickel, zinc, and other elements.

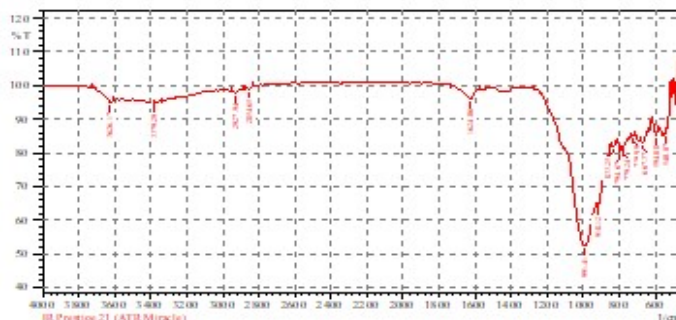


Fig.-5: IR Absorption Spectra of a Sample of Darbazinsk Montmorillonite before Modification

From Fig.-5, it follows that the IR spectra before the modification of Darbazinsk montmorillonite revealed absorption bands in the 1624cm^{-1} region of deformation vibrations of the hydroxyl group, that is, the presence of adsorption water and hydroxyl groups in the composition of clays. In absorption bands in the region of 3400 and 3628cm^{-1} , a valence oscillation of the OH group is observed in the form of weak intensity. There is a wide absorption band in the region of $1180\text{--}837\text{cm}^{-1}$ with a peak of 987cm^{-1} corresponding to the valence vibrations of the Si-O-Si group and the vibrations of SiO_4 tetrahedron rings. Modification of¹⁵⁻¹⁶ sodium montmorillonite is carried out as follows: A certain mass of sodium montmorillonite is suspended in an aqueous sprite solution (ratio 1:1 cm^3 , temperature 80°C) for 30 minutes and a modifier solution is prepared in parallel by dissolving octadecyl amine in an aqueous alcohol solution containing an equimolar amount of hydrochloric acid (up to $\text{pH}=7.0$) at the same temperature. A solution of octadecyl ammonium chloride salt is added in portions to a suspension of sodium montmorillonite with continuous stirring throughout the entire period of the modification process. After the dosing of the modifier solution is completed, the suspension is stirred for an additional 30 minutes and cooled to room temperature. To separate the unbound or excessive amount of surfactants, modified montmorillonite is repeatedly centrifuged by washing with a hot water-alcohol solution, and then with distilled water.¹³⁻¹⁵ The completeness of the washing is estimated by the residual content of chlorine ions by adding several drops of 5% silver nitrate solution to the mother liquor. The resulting product is dried at a temperature of 80°C in a vacuum to a constant mass. The cation exchange capacity of modified montmorillonite is $95\text{ mg-eq}/100\text{ g}$ with an average diameter of silicate plates $\sim 77\text{ nm}$.

According to the results of the IR spectra (Fig.-6), it was revealed that the modified derivatives of Darbaza montmorillonite appear in absorption bands in the region of 2924 and 2854cm^{-1} related to the valence vibrations of the methylene group, as well as in the region of 1458cm^{-1} corresponds to an

asymmetric deformation vibration of methyl groups. 1597-1706 cm^{-1} absorption bands are characteristic of the valence vibrations of acrylate groups. Pendulum oscillations of methylene groups in the region of 798 cm^{-1} are also observed.

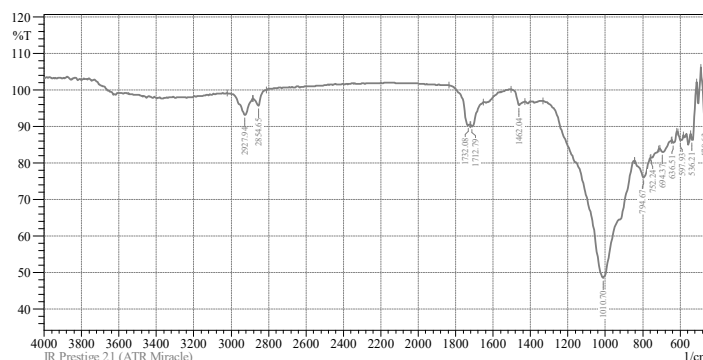


Fig.-6: IR Absorption Spectra of a Sample of Darbazinsk Montmorillonite after Modification

RESULTS AND DISCUSSION

It has been found that the same chemical elements (calcium, iron, magnesium, sodium, and aluminum) are extracted from all bentonite samples, regardless of the concentration and type of acid, at different rates, bringing the chemical composition of the modified samples closer. It is revealed that the speed of this process is significantly higher in the initial period of bentonite modification. Depending on the chemical composition of bentonite, it is possible to extract cations with weak organic acids during the modification process. It is determined that the valence vibrations of acrylate groups after modification of montmorillonite, fatty acids, that is, once again indicate high hydrophilicity and the ability to swell when interacting with water. It was found that a feature of the structure of montmorillonite is that weakly bound water molecules are located between the layers and due to this the crystal lattice is mobile. This ensures a sharp swelling of the mass of montmorillonite clays, which increase in volume by almost 15-20 times. Optimal conditions for activation of bentonite clays (montmorillonite) have been determined: temperature 80°C, activation duration 0.5 h, acid ratio: clay 1:1. Experimental work was carried out to determine the exchange capacity and it was determined that the cation exchange capacity of modified montmorillonite is 95 mg-eq/100 g with an average diameter of silicate plates ~77 nm.

CONCLUSION

A method of modification of bentonites from the Darbazinsk deposit, of various chemical compositions, activated and organo-modified in aqueous solutions of a number of acids, depending on their concentration and duration of the process, is proposed. The resulting modified modifier based on bentonite clay improves the rheology of the melt of secondary polymer materials and the plasticization of compositions based on polyvinyl chloride. It also provides uniform melting during the production of composite polymer materials. Promotes the formation of high-quality bonds between polymer molecules and the introduced additives, Improves the dispersion of the introduced components while reducing the amount of scrap. Restores molecular bonds lost as a result of thermal degradation during processing, which allows you to use a larger amount of secondary polymer, as well as improve the physical and mechanical properties of the finished product. The structure and mechanism of the transition of montmorillonite (bentonite) into the form of modification have been studied and can be used as a modifier to obtain polymer composite materials. It has also been studied that bentonite, regardless of the concentration and type of rock, can be used to obtain not only a modifier but also a sorbent for wastewater treatment in chemical industries.¹⁶ Thus, the use of modified montmorillonites allows you to expand the range of functional products, reduce the cost and simplify the process, as well as reduce the cost of production.

REFERENCES

1. <http://ugpc.ru/stati/tehnologii/aktivaciya-i-modifikaciya-bentonita.html>(19.12.2021)
2. O.K. Beisenbayev, A.B. Issa and E. Kovaleva, *Oriental Journal of Chemistry*, **31**(4), 2369(2015), <https://doi.org/10.13005/ojc/310466>

3. [https://1nerudnyi.ru/bentonitovaya-glina-01\(24.12.2021\)](https://1nerudnyi.ru/bentonitovaya-glina-01(24.12.2021)).
4. State Commission for Reserves, Guidelines on the Application of the Classification of Reserves and Forecast Resources of Solid Minerals Deposits, M: *Clay Rocks*, pp.215-219(2007).
5. <https://7universum.com/ru/tech/archive/item/7515> (24.12.2021).
6. P.E. Belousov, Yu.I. Bocharnikova, N.M. Boeva. *RUDN Bulletin, Engineering Research Series*, **4**, 94(2015).
7. V. I. Osipov, V. N. Sokolov, *Clays and their Properties*, M.: GEOS, 2013, pp.125-128.
8. N.M. Boeva, V.V. Nasedkin, *Geology and Exploration*, **6**, 27(2017).
9. S.V. Bortnikov, G.A. Gorenkov. *Tambov: Diploma*, **8**,32-34(2013).
10. M.S. Dzhusueva, S.P. Ismatillaev, *International Journal of Applied and Basic Research*, **7**, 71(2021).
11. R.I. Narro-Céspedes , M.G.Neira-Velázquez , L. F. Mora-Cortes, E. Hernández-Hernández, A. O.Castañeda-Facio, M. C.a Ibarra-Alonso, Y. K. Reyes-Acosta, G. Soria-Arguello, and J.J.Borjas-Ramos, *Hindawi Journal of Nanomaterials*, **6(4)**, 2(2018), <https://doi.org/10.1155/2018/2480798>
12. V.V. Krupskaya, S.V. Zakusin, E.A. Tyupina, O.V. Dorzhieva, A.P. Zhukhlistov, P.E. Belousov, M.N. Timofeeva, *Minerals*, **7(49)**, 2(2017), <https://doi.org/10.3390/min7040049>
13. S.Yu. Khashirova, N.S. Sivov, Patent RF No. 2369584C2 23.07.2007, Method for Organomodification of Bentonites.
14. E. Dzhakipbekov, S. Sakibayeva, N. Dzhakipbekova, B.Tarlanova, G.Sagitova and Zh. Shingisbayeva, *Rasayan Journal of Chemistry*, **13(3)**,1417(2020), <http://dx.doi.org/10.31788/RJC.2020.1325709>
15. B.M. Smailov, O.K. Beisenbayev, A.S.Tleuov, A.A Kadirbaeva, B.S. Zakirov and B. Mirzoyev// *Rasayan Journal of Chemistry*, **13(3)**, 1372(2020), <http://dx.doi.org/10.31788/RJC.2020.1335726>
16. B.M. Smailov, M. A. Zharkinbekov, K. T. Tuleshova, N.N. Issabayev, A.S. Tleuov, O.K. Beisenbayev, M.M. Esirkepova and A.M. Azimov, *Rasayan Journal of Chemistry*, **14(3)**, 1899(2021), <http://doi.org/10.31788/RJC.2021.1436391>

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