# Influence Of Anionic Polymers On Water Absorption Of Bentonites

## Halyna Zadvernyuk

(The Institute of Environmental Geochemistry of National Academy of Sciences of Ukraine, Kyiv, Ukraine)

#### Abstract:

Bentonite is a potential material for its use in barriers. However, due to exposure to toxic substances and natural processes, such as compression, cracking, etc., the insulating properties of clay may deteriorate. The modification of clays with anionic polymers is proposed to prevent these consequences. The ability to absorb and hold water and solutions is one of the essential characteristics of clays for some applications. The influence of anionic polymers, such as polyacrylamide (PAA) and carboxymethyl cellulose (CMC), on the hydrosorption properties of the bentonite of the Cherkasy deposit of bentonite and palygorskite clays (Ukraine), was investigated in the research. Water absorption of clays was determined using the Enslin method. It was established that the nature of the polymer, its content, and the modification method affect the absorption of water by bentonites modified with polymers. It is shown that the modification of bentonite with polymers improves the water absorption of the clay. With an increase in the amount of polymer, water absorption of polymer-treated clays is growing. Bentonites modified with carboxymethyl cellulose absorbed more water than bentonites treated with polyacrylamide. It can be explained by the penetration of carboxymethyl cellulose molecules into the interlayer space of montmorillonite. The effect of the dehydration temperature during the clay modification on its water absorption was also investigated. It was found that polymer-treated clays dehydrated at 105°C absorbed more water than clays dehydrated at room temperature. It is probably because, at a temperature of 105 °C, an irreversible fixation of the polymer on the clay surface occurs, corresponding to chemisorption, while at room temperature, the reverse physical adsorption happens.

**Keys Words:** Modified bentonites, Polymer-treated bentonite, Polyacrylamide-treated bentonite, Sodium carboxymethyl cellulose-treated bentonite, Water absorption.

Date of Submission: 21-08-2023

Date of Acceptance: 31-08-2023

### I. Introduction

Clays are one of the most common non-metalic mineral resources and valuable raw materials for the metallurgical, mining, chemical, oil refining, agricultural industries, pharmacology and medicine. Clays are also used for environmental protection as sorbents and sealants. For example, bentonites are often considered as possible barriers to isolating contaminants from the surrounding environment and preventing pollutant migration. It is also suggested to use clays to minimize the effects of oil spills on water surfaces [1].

However, the insulating properties of clays may decrease due to shrinkage, cracking, etc. Therefore, the modification of clays to improve their properties is proposed [2–6]. One of the perspective materials for isolating pollutants is polymer-treated bentonites. Bentonite modified with carboxymethyl cellulose had lower hydraulic conductivity than untreated clay [7]. Another important characteristic of clays for some applications of the clays in ecology and industry is their ability to absorb aqueous solutions and retain them.

The research aims to study the hydrosorption properties of bentonites modified with anionic polyacrylamide and carboxymethyl cellulose.

### II. Materials and Methods

The bentonite from the Cherkasy deposit of bentonite and palygorskite clays (Ukraine) was used for the research. The mineral composition of the clay is represented mainly by montmorillonite (70–95%) and admixtures of calcite and quartz.

Anionic polyacrylamide A63023 (Hengflok, China) and carboxylmethyl cellulose were used for the modification.

The modification of clays was carried out in the following way: the bentonite was activated with sodium carbonate and mixed with a polymer solution of the appropriate concentration. The mixture was dehydrated in an oven at 105°C or dried at room temperature (20°C) and crushed. The fraction  $\leq$  100 µm was used for the research.

Water absorption was determined by the Enslin method using the device consisted of a Schott filter connected to a pipette by an elastic tube. The pipette was placed at the same level as the ceramic surface of the Schott filter. The device was filled with distilled water and the paper filter was placed on the ceramic surface of the filter. The initial water volume  $V_1$  in the pipette was determined. The sorbent (0.5 g) was placed on the surface of the paper filter. The upper part of the Schott filter was covered with a Petri dish. After a certain period, the volume of absorbed water  $V_2$  was determined.

Water absorption *W* was calculated by the formula:

$$W = \frac{V_1 - V_2}{m} \times 100\%,$$

Where W is water absorption, %;  $V_1$  is the initial water volume in the pipette, ml;  $V_2$  is the water volume after a certain period, ml; m is the sorbent weight, g.

#### **III. Results and Discussion**

The results of the experiments show that the addition of polymers to clays leads to an increase in water absorption (Fig. 1). The bentonite modified with carboxymethyl cellulose had a higher water absorption than bentonite treated with polyacrylamide. It can be explained by the probability of the penetration of carboxylmethyl cellulose into the interlayer space of montmorillonite. X-ray structural analysis and Fourier transform infrared spectroscopy showed that carboxymethylcellulose chains penetrated the interlayer space of montmorillonite [8]. The driving force of intercalation was the chemical interaction between the ether bonds of the polymer and the Si–O bonds of the clay. Ruehrwein and Ward [9] believe that the adsorption of anionic polymers on clays occurs by ion exchange. Michaels and Morelos [10] suggested that polymer adsorption is mainly due to hydrogen bonding. According to the version [11], adsorption can be caused by the interaction between polyvalent cations acting as crosslinking agents between the negatively charged clay surface and the anionic polymer [11]. Stutzmann and Siffert [11] compared the adsorption of anionic polymers on the montmorillonite surface during the dehydration at 60  $^{\circ}$ C can be considered an intense, irreversible fixation corresponding to chemisorption. The adsorption observed during vacuum drying at lower temperatures most likely corresponds to reversible physical adsorption.



Figure 1. The dependence of water absorption of untreated bentonite, the bentonite with 5% PAA and the bentonite with 5% CMC on time.

The study of bentonites treated with carboxylmethylcellulose showed that with an increase in the polymer amount in bentonite, their water absorption increased (Fig. 2).



Fig. 2. The dependence of water absorption of untreated bentonite and modified bentonites with different CMC concentration on time.

Water absorption of clays also depends on the method of their modification. The research on the influence of the dehydration temperature of the samples during their treatment on the water absorption of modified bentonites was carried out. One part of the samples was dried at room temperature, and the other – at a temperature of 105 °C. Polymer-modified bentonites dried at 105°C had higher water absorption than the corresponding air-dried bentonites (dehydrated at room temperature ( $20^{\circ}C$ )) (Fig.3).



**Fig. 3.** The dependence of water absorption of the bentonite with 5% PAA and the bentonite with 5% CMC dehydrated at 105 °C and room temperature (air drying) on time.

According to [11], irreversible adsorption of the polymer to the clay surface occurred as a result of the dehydration of modified clays at a temperature of above 60 °C.

### IV. Conclusions

The modification of bentonites with polymers leads to an increase in the water absorption of clays. As the amount of polymer increases, the water absorption of clays increases. The water absorption of clays was

higher for bentonites modified with carboxymethyl cellulose compared to bentonites treated with polyacrylamides. It is probably related to the penetration of carboxylmethyl cellulose molecules into the interlayer space of montmorillonite.

The dehydration temperature of polymer-modified clays also affects their water absorption. Thus, polymer-modified bentonites dehydrated at 105 °C had higher water absorption than the corresponding clays dehydrated at room temperature. This can be explained by the fact that at a temperature of 105 °C irreversible polymer adsorption on the clay surface occurred.

Therefore, the literature analysis and the preliminary experimental data indicate the prospects of using clays modified by anionic polymers for engineering barriers. However, further research is needed to develop the optimal composition of modified clays to improve their insulating characteristics for reliable isolation of toxic substances.

#### References

- Zadvernyuk H. Sorption Capacity Of Clay Minerals For Oil And Oil Products From Water Areas. In: Broekmans, M. (Eds) Proceedings Of The 10th International Congress For Applied Mineralogy (ICAM). Springer, Berlin, Heidelberg, 2012, 789–794. https://Doi.Org/10.1007/978-3-642-27682-8\_95
- Di Emidio G., Verastegui-Flores R.D., Mazzieri F., Dominijanni A. Modified Clays For Barriers: A Review. Innov. Infrastruct. Solut., 2017. 2, 47. Https://Doi.Org/10.1007/S41062-017-0073-8
- [3]. Kondo M. Method Of Activation Of Clay And Activated Clay. USA Patent Nr: US 5573583A. 1996.
- [4]. Qiu H., Yu J. Polyacrylate/(Carboxymethylcellulose Modified Montmorillonite) Superabsorbent Nanocomposite: Preparation And Water Absorbency. J Appl Polym Sci., 2007. 107. P. 118–123.
- [5]. Theng B.K.G. Formation And Properties Of Clay-Polymer Complexes. Elsevier, Amsterdam, 2012, 526 P.
- [6]. Bohnhoff G., Shackelford C., Malusis M., Scalia J., Benson C., Edil T., Di Emidio G., Katsumi T., Mazzieri F. Novel Bentonites For Containment Barrier Applications. Proceedings Of The XVIII International Conference For Soil Mechanics And Geotechnical Engineering, Paris, France, 2013. P. 2997–3000.
- [7]. Zadvernyuk H. The Hydraulic Conductivity Of Bentonites Treated With Sodium Carboxymethyl Cellulose. IOSR Journal Of Environmental Science, Toxicology And Food Technology, 2022. 16, 9. P. 40–42. https://Doi.Org/10.9790/2402-1609014042
- [8]. Di Emidio G. Hydraulic And Chemico-Osmotic Performance Of Polymer Treated Clays. Phd Dissertation. Ghent University, Belgium, 2010. 298 P.
- [9]. Ruehrwein R.A., Ward D.W. Mechanism Of Clay Aggregation By Electrolytes. Soil Sci., 1952. 73. P. 485–492.
- [10]. Michaels A.S., Morelos S. Polyelectrolyte Adsorption By Kaolinite. Ind Eng Chem., 1955. 47, 9. P. 1801–1809.
- [11]. Stutzmann T., Siffert B. Contribution To The Adsorption Mechanism Of Acetamide And Polyacrylamide On To Clays. Clays Clay Miner., 1977.