

SODIUM BENTONITE: ITS STRUCTURE AND PROPERTIES

The properties of sodium bentonite can be appreciably enhanced through a specialized treatment process patented by CETCO's parent company, AMCOL International. The treatment process involves the application of chemical additives to specially selected and processed sodium bentonite. These additives work both individually and synergistically to render the bentonite more resistant to attack by chemical contaminants. Various formulations of the additives in this treatment process have been incorporated into CETCO's sodium bentonite waterproofing products.

This paper presents a detailed description of AMCOL's chemical enhancement technique. In order to properly understand this discussion, however, it is first necessary to explore the basic molecular structure and physiochemical properties of sodium bentonite.

1.0 THE STRUCTURE OF SODIUM BENTONITE

Sodium bentonite is the name for the ore whose major constituent is the mineral, sodium montmorillonite. Montmorillonites are three-layer minerals consisting of two tetrahedral layers sandwiched around a central octahedral layer (Figure 1). Oxide anions at the apices of the tetrahedral subunits are directed inward where they surround interior aluminum, iron, and magnesium cations, thereby forming the octahedral subunits of the octahedral layer. Bonding, between the shared interior oxide anions and cations in both the tetrahedral and the octahedral layers, links the layers together and yields the unique sheet structure characteristic of clay mineral. For montmorillonite, the total negative charge contributed to the structure by the sum of all the oxide anions (O-) is somewhat in excess of the total positive charge contributed by the sum of all the structural cations (Si+4, Al+3, Fe+2, Fe+3, Mg+2) and imparts a slight overall negative charge to the surfaces of the clay sheets. This slight excess negative charge on the sheets is counterbalanced by free-moving (exchangeable) cations which exist between them. These three layers in each sheet comprise individual bentonite platelets which are typically 1 nm in thickness and 0.2-2 microns in diameter. Dry platelets of sodium bentonite are most commonly grouped together in a face-to-face arrangement, with exchangeable cations and small amounts of absorbed water in an interlayer region between each platelet. The thickness of the interlayer region is variable depending on the amount of water absorbed between the platelets.

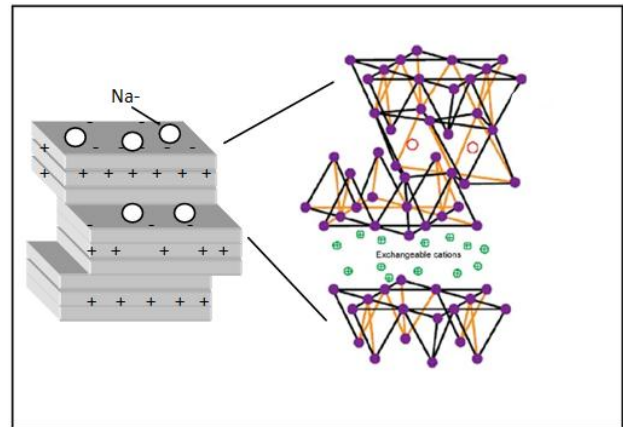


Figure 1. Crystalline structure of sodium montmorillonite with interlamellar water layer

Bentonites are generally classified according to their dominant exchangeable interlayer cation, either sodium or calcium, although magnesium may also be present. When sodium predominates, a large amount of water can be absorbed in the interlayer, resulting in the remarkable swelling properties observed with hydrating sodium bentonite. As will be discussed, the presence of sodium facilitates the almost unlimited absorption of oriented layers of water molecules, a phenomenon which does not occur when calcium is predominate. Consequently, calcium bentonites are generally low swelling.

2.0 PROPERTIES OF SODIUM BENTONITE

2.1 PHYSICAL PROPERTIES

Sodium bentonite is most widely known for its ability to swell. It can absorb nearly 5 times its weight in water and at full saturation may occupy a volume 12 to 15 times its dry bulk. The high water absorption capacity of bentonite also makes it very plastic and resistant to fracturing or cracking.

Interestingly, bentonite can be hydrated and dried an infinite number of times without losing its original swelling capacity. It can similarly be frozen and thawed repeatedly without losing its ability to swell.

Because the platelets are uniformly broad and flat, sodium bentonite has an exceptionally high surface area of 600 to 800 square meters per gram. Less than 10 grams of bentonite, if fully dispersed, could cover a football field. It is a combination of these physical properties that make sodium bentonite an ideal waterproofing material. A layer of hydrated bentonite provides a dense, low porosity barrier to fluid flow that exhibits a typical hydraulic conductivity of 1×10^{-9} cm/sec.

2.2 ELECTROCHEMICAL PROPERTIES

The structure of sodium bentonite gives it some important electrochemical properties. As previously discussed, bentonite platelets naturally possess an overall negative charge as a consequence of having more charge contributed by the negatively charged oxide anions than is contributed by the positively charged cations. This unbalanced negative charge resides mainly in the oxide atoms found in the flat edges of the platelets where positively charged aluminum cations in the octahedral layer may be exposed without a full complement of oxide anions, some localized positive charge (edge charge) is possible. It will later be seen that selective neutralization of these positive edge charges is a critical aspect of CETCO's chemical enhancement process.

2.3 HYDRATION PROPERTIES

Research indicates that the hydration process of sodium bentonite is a combination of four primary mechanisms contributing to the swelling properties of sodium bentonite. The following provides a general description of the principal mechanisms involved in water absorption:

1. Physical Orientation of Water Molecules.

The water molecule is a V-shaped arrangement of atomic nuclei, with the two hydrogen protons forming an angle of 105 degrees with the oxygen nucleolus (Figure 2). Because oxygen atoms tend to attract electrons (e^-), and hydrogen atoms tend to donate them, regions of water molecules around the oxygen atom are somewhat negative in character while the regions around the hydrogen atom are somewhat positive in character. While the amount of charge separation is small, it is nevertheless crucial in determining many of the remarkable properties of water.

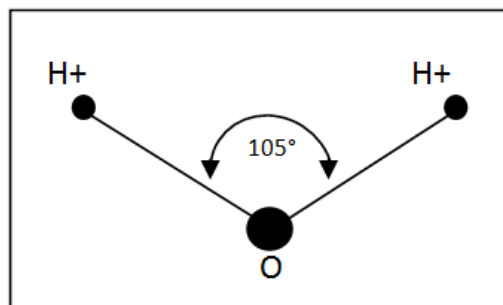


Figure 2. Dipolar geometry of water molecule

Thus when two liquid water molecules approach each other, there is an electrostatic attraction between the negatively charged oxygen atom at the base of the 'v' in one water molecule and a positively charged hydrogen atom at one corner or the other. Although the force of this attraction, called hydrogen bonding, is only about 5-10% as strong as the normal covalent bonding between atoms in a molecule, it is, nevertheless considerably stronger than the even weaker van der Waals forces which hold uncharged molecules together in the liquid and solid states. The most important consequence of

this type of bonding is that it can impose an ordering effect (structure) on the molecules (Figure 3). This physical orientation of the water molecules facilitates their ordered absorption onto the surface of the bentonite platelet.

2. Position of Oxygen in the Tetrahedral Sheets.

Viewed from above the bentonite platelet surface, oxygen atoms within the tetrahedral sheets are arranged in a hexagonal pattern (figure 4). Like matching pieces in a jigsaw puzzle, this pattern physically coincides with the pattern of the available hydrogen atoms in water molecules, and hydrogen bonding between the bentonite's oxygen and the water's hydrogen atoms are possible.

3. Excess Electrons on Bentonite Surface.

We have already seen that the isomorphous substitution of cations within the octahedral lattice results in the presence of excess electrons on the bentonite surface. These electrons enable the formation of hydrogen bonds of partially covalent character between the water molecules and the bentonite surface. The effect of the excess electrons is therefore to not only strengthen the bentonite-water bond but also to facilitate the bonding of additional layers of water. It is believed that these strong bentonite-water bonds alter the electron distribution of the first layer of water molecules and facilitate the formation of another water layer. Those bonds in the next layer allow the formation of a subsequent layer to the extent that 3 or 4 similarly oriented water layers are formed. However, the kinetic nature of water causes the strength of the orienting forces to decrease with distance, and (if enough free water is present), the additional layers of water molecules become increasingly less rigid as the distance from the bentonite surface increases (Grim, 1968).

4. The Presence of Sodium.

When enough clean water is available, sodium ions in the interlayer are the “engines” that drive the above reactions beyond the first 3-4 monolayers of water. The negative charge and hexagonal arrangement of oxygen atoms on the bentonite surface facilitate the formation of the first few oriented water layers. Thereafter, it is generally accepted that the presence of sodium ions produces osmotic pressure which draws water molecules into the interlayer, in an attempt to equalize the high concentrations of ions between platelets with the low concentrations of ions outside the platelets (Grim, 1968; van Olphen; Newman). Upon being drawn into the interlayer, these water molecules are subsequently organized and layered as already described. A high quality sodium bentonite will absorb 25-50 water layers (Grim, 1968).

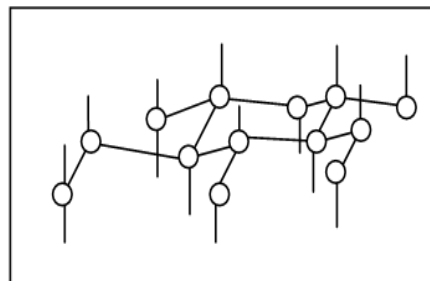


Figure 3. Tetrahedral hydrogen bonding in water (From Grim, 1968)

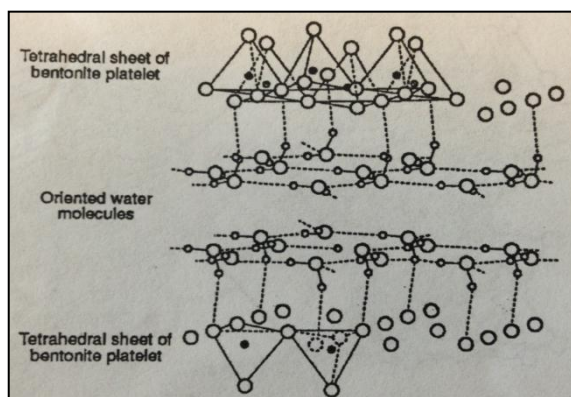


Figure 4. Configuration of the interlayer water system showing hydrogen bonding to the adjacent bentonite surfaces (From Grim, 1968)

3.0 CHEMICAL TREATMENT OF SODIUM BENTONITE

Although the oriented water layers in sodium bentonite may be affected by the presence of contaminants, it is possible to protect the clay/water system by treating it with certain chemicals. This section describes the patented process developed by CETCO LLC which renders sodium bentonite resistant to degradation by contaminants.

3.1 BASE BENTONITE SELECTION

Of primary importance in the chemical enhancement of bentonite is the selection of the untreated bentonites themselves. AMCOL's extensive experience has shown that certain bentonites are much more receptive to chemical enhancement than others. It is important that the mining and processing of the selected bentonites is as carefully controlled as the actual chemical enhancement procedures.

CETCO's contaminant resistant products are made with bentonite whose tetrahedral inversions and inter-lattice ionic substitutions are minimal, as these phenomena have been identified as exerting a strong influence over the bentonite's treatability. This "start-to-finish" control over the base mineral ensures that the effectiveness of AMCOL's patented chemical treatment process is maximized.

3.2 POLYMER TREATMENT

Free swell is a measure of the ability of sodium bentonite to absorb water. In general, the higher the swell of sodium bentonite, the better its performance. High swelling sodium bentonites make superior waterproofing products. Bentonite free swell is therefore a significant indicator of its performance in these applications.

Polymers used in bentonite treatment are specially selected, water-soluble polyelectrolytes consisting of long-chain molecules with anionic groups located along the entire length of the chain. When the polymers are dissolved in water, they uncoil and assume a straightened configuration due to the mutual repulsion of like-charged groups along the chain.

Polymers enhance the performance of sodium bentonite primarily by promoting the disaggregation of bentonite platelets. An aggregate may contain tens of thousands of platelets. Unhydrated platelets are aggregated by face to face and edge to face electrostatic bonding, with perhaps only one or two oriented water monolayers between adjacent sheets (Figure 5). When water is added to the bentonite/polymer system, the anionic functional groups of the polymer absorb onto and neutralize the positively charged bentonite platelet edges. This reaction assists platelet separation as the polymer overcomes the bond forces of the macrostructure (Figure 6).

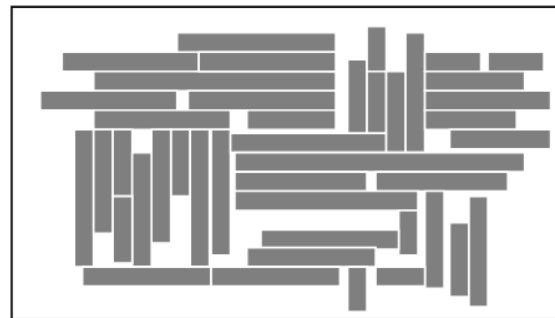


Figure 5. Orientation of bentonite platelets in an aggregate before hydration

When the polymer chains absorb onto many different platelets within an aggregate, the polymer physically separates the aggregate, and an extremely large bentonite surface becomes available for further hydration. Because a greater fraction of the bentonite is "activated" (e.g., hydrated), it is believed to become more effective than untreated bentonite in buffering the potentially damaging effects of chemical contaminants (Alther).

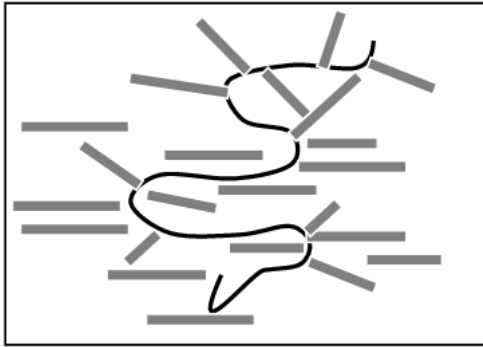


Figure 6. One effect of anionic polymers is to reduce edge-to-face bonding between bentonite platelets to enhance disaggregation during hydration

The extent of disaggregation has been found to be dependent upon the stability of the macrostructure of the aggregate, the degree of ionic substitution in the tetrahedral and octahedral sheets, and the distribution of interlayer cations. These properties of the base clays are monitored by AMCOL during bentonite processing and treatment.

It is suggested that another mechanism by which polymers increase a bentonite’s contaminant resistance is in providing a protective encapsulation around hydrated bentonite platelets. The long-chain polymer bonds at the edges of the platelets and “wraps” over the absorbed water layers held by the platelet to another bond site on the same or on a different platelet (See Section 3.3). The distance from the platelet surface at which the polymer wrap occurs is that distance where the stability of the absorbed water layers is weak enough to be overcome by the

presence of the polymer chain. The polymer chain and its large functional groups then act as physical barriers to protect the oriented water layers inside the polymer and prevent ion exchange reactions or other effects which cause water layer shrinkage.

3.4 SYNERGISTIC EFFECTS

All of CETCO’s treated bentonites contain additive polymers, and contaminant resistance is provided through a synergistic effect between these additives. It is theorized that the additives occupy a significant fraction of the available edge bond sites and force the polymer to bridge across the platelets rather than simply to bond along the edge of a platelet. This polymer bridging effect creates a protective encapsulation and physically prevents damaging organic and inorganic substances from reaching the interlayer water system (Figure 6).

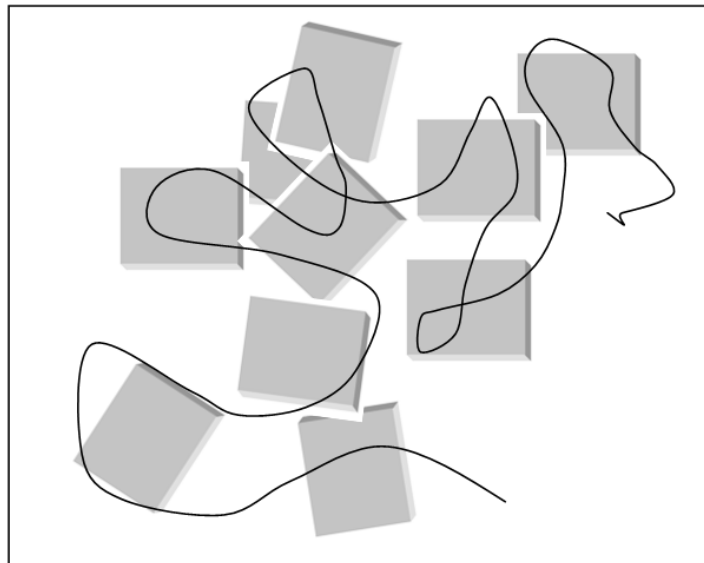


Figure 2. Synergistic effects protect the bentonite/water system from potentially harmful contaminants

4.0 CONCLUSION

Treated bentonites are superior to untreated bentonite in retaining their physical and chemical properties when permeated with contaminated solutions. With many years of performance success on thousands of projects around the world, combined with research data, CETCO's treated bentonites have demonstrated that this additive enhancement is effective in providing long-term waterproofing performance. When CETCO's sodium bentonite waterproofing products are specified, for quality assurance CETCO utilizes a laboratory water sample testing process to assess the suitability of the product for the site specific groundwater conditions.

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REFERENCES

- Alther, G.R.. "The Function and Effect of Polymers in Polymer-Treated Bentonites." Bulletin of Association of Engineering Geologists, Vol. XXI, No. 1, February 1984.
- Bennet, Richard H. and Matthew Hulbert. "Clay Microstructure." International Human Resources Development Corp., Boston, 1986.
- Grim, Ralph E. "Clay Mineralogy" (2nd Ed.) McGraw Hill Book Company, New York, 1968.
- Grim, Ralph E. "Applied Clay Mineralogy" (2nd Ed.) McGraw Hill Bok Company, New York, 1962.
- Newman, A.C.D. (ed.). Mineralogical Society Monograph No. 6 "Chemistry of Clays and Clay Minerals." John Wiley and Sons, New York, 1987.
- Odom, I.E. "Na/Ca Montmorillonite: Properties and Uses." Society of Mining Engineers Transactions, Vol. 282, 1986.
- Stanley, C.S. "Acrylic Polymers as Drilling Mud Additives." American Cyanimid Company, Stamford, Connecticut.
- van Olphen, H. "An Introduction to Clay Colloid Chemistry" (2nd Ed.) John Wiley and Sons, New York 1977.

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