HECTORITE AS A CRITICAL ELEMENT IN THE MANUFACTURING OF FLOOR/WALL TILE

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Hectorite is a rare magnesium lithium clay mineral belonging to the Smectite clay mineral group. Smectites are a group of clays that are tri-layered hydrous alumino-silicates in the mica family of phylosilicates. The main difference between a smectite clay and mica is the intermellar surfaces of smectite clay contain readily exchangeable cations that hydrate easily. This accounts for the unique swelling properties of the smectite clays. The most common members of the smectite clay group are montmorillonite and hectorite. This paper discusses the mineralogical characteristics of both, the advantages of hectorite vs. montmorillonite, and the functions of hectorite in floor and wall tile applications.

The crystal structure is basically the same for all members of the smectite clay minerals, but differs in metallic cation content in the octahedral layer. Smectite clays are all composed of three layers, two outer layers of silica tetrahedra and a central octahedral oxide/ hydroxyl layer. The octahedral layer of montmorillonite consists of Al, Mg and Fe (figure 1) while the octahedral layer of hectorite contains Mg and Li (figure 2). This layer of the three sheets is repeated in the c-axis direction and ussually has a net negative charge. This net negative charge is due to some degree of charge deficiency in the octahedral layer. The charge deficiency in hectorite is naturally balanced by associated cations, mainly Na and small amounts of Ca and Mg, outside the structure loosely bonded to the interlayer surfaces. These exchangeable ions enable hectorite to hydrate and give them their unique sweeling properties.

Hectorite is a trioctahedral magnesium silicate with lithium substitution in the octahedral layer. It is considered trioctahedral because all three of the octahedral cation sites per half unit cell are occupied by divalent cations. The substitution of lithium for part of the magnesium in the crystal structure gives hectorite its high cation exchange capacity. Montmorillonite is a dioctahedral aluminum silicate with a magnesium substitution in the octahedral layer. Montmorillonite is dioctahedral because only two of the three octahedral cation sites are occupied by trivalent cations.

Because hectorites are naturally occurring minerals, they are found in different purity levels. Depending on the purity level, hectorites can be purified by water-washing or air classification. The most effective and functional purification process in water-washing. This process removes the non-clay particles producing a high purity hectorite that hydrates quickly making it very efficient. A water-washed hectorite common purification method is air classification. An air classified hectorite would be used where high purity is important, but due to cost restraints, slight contaminant levels are acceptable. An example of where such a product can be used is in a floor/wall tile body.

It is recommended that hectorite be fully hydrated in water prior to adding to the batch in order to optimize hectorite's valuable properties. Methods of hydration will be discussed later. Complete hydration yields optimum particle size of hectorite between 1/2 micron and 40 angstroms giving a surface area around 750 m^2/gram. During hydration, water molecules penetrate the interlayer spacing between platelets causing the exchangeable sodium cations to dissociate. As the sodium cations dissociate, the negatively charged platelets repel each resulting in anionic platelets and hydrated sodium cations in solution.

In the water phase, the hectorite platelets carries a surface negative charge due to lattice substitution, and a small positive charge on the edges due to the disruption of the lattice. In a dilute solution, the surface negative charges are stronger than the smaller edge positive charges; therefore, the platelets remain separated and the viscosity is low. Additions of more clay increase the ionic content of the solution which results in a greater attraction between platelets and cations. This resulting attraction is stronger than the negative surface charges repelling each other; therefore, the negative surface charge and positive edge charge of de platelets attract each other forming a gel. This often referred to as the «house of cards» structure and forms when energy is removed from the system. Because of the thixotropic behavior of hectorite, the «house of cards» structure can be broken apart when minimal energy is applied back to the system such as mixing.

The actual method of hydrating hectorite and the concentration of the dispersion will vary depending on the type of equipment available. One method of hydrating hectorite would be to add water to ball mill, add hectorite, and rotate the mill for about thirty minutes followed by adding the other batch ingredients to the mill. Adding the hectorite to the ball mill first enables complete hydration quicker. Another method would be to re-circulate hectorite/water slurry through a pump, either positive displacement or centrifuge, into a small tank. After about fifteen minutes, this dispersion could be added to the mill or mixer on any available tank and introduce water and hectorite simultaneously through the mixer. This mixer would fully hydrate the hectorite in about five minutes.

Factors that affect the rate of hydration of hectorite include: 1. water temperature, 2. shear, and 3. solids content. Hectorite will hydrate in cold or hot water, but it will hydrate faster with hot water. Low or high shear will hydrate hectorite, but the higher the shear, the faster the hydration time and the higher solids content allowed. Hectorite cannot be damaged by hot water or high shear. The typical dispersions are between 3% to 6% solids and can be easily diluted to desired concentration.

Hectorites exhibit unique properties which allow them to perform several functions in the production of floor/wall tile at low addition levels. These properties include small particle size, swelling ability up to thirty five times its weight, thixotropic behavior, and fired white color. Minimal addition levels, 0.5 - 1.5%, of an air classified hectorite to a tile body can greatly increase the green strength. This occurs because of the high surface area of hectorite which enables greater ionic bonding to other raw materials as well as hydroxyl bonding to water molecules in the batch. Hectorite additions allow for production of larger tiles without breakage, and more screen printing glaze applications without warping on the edges. This reduction in breakage minimizes losses which in turn saves money. Hectorite also acts as a lubricant to ease extrusion which reduces wear on the die and lowers energy consumption during extrusion. Hectorite is a non-migratory binder; therefore, it will not migrate to the surface of the tile causing scumming.

Another application for hectorites in floor/wall tile production is in the glaze. A water-washed hectorite can be used to keep a glaze in suspension. The interaction of the hectorite platelets with each other, which forms the «house of cards» structure, disrupts the flow of the glaze. This gel structure produces excellent suspension properties and prevents sedimentation rather than just slowing it down. These bonds between platelets which form the gel structure are easily broken and reformed. This results in a thixotropic system with low viscosity under shear and high yield value.

Because hectorite is a mineral, it is not affected by microbe attack like organic gums. This would lower overall costs because biocides are not required in the glaze. When fully hydrated, hectorites stable over a wide pH range between 3.5 to 11. Hectorites are compatible with low levels of electrolytes which usually increase performance. However, excessive amounts of electrolytes may cause flocculation of the clay. The addition of small percentages of organic gums or other colloids greatly enhance the effectiveness of hectorites, and vie versa. Because of the synergism between hectorites and cellulose, the addition levels of hectorite in a glaze vary from 0.2% if there are cellulose present to 1.5% if no cellulose or electrolytes are present.

The unique properties of hectorite mentioned earlier in this paper give hectorites distinct advantages over monmorillonite in floor/wall tile production. These advantages are listed in Table I.

Table 1 Advantages of Using Hectorite in Ceramics

1. Hectorites hydrate easily
2. Smaller particle size
    - allows for greater ionic and hydroxyl which increases green strength
    - excellent suspending properties to minimize settling and prevent hard packing of glaze
    - very efficient: therefore, only minimal amounts are required
3. Low iron content: therefore, it fires out white
4. It is inorganic so no biocides are required
5. Thixotropic behavior enhances suspension properties

In summarizing, hectorite is a magnesium silicate with lithium substitution. This mineral exhibits unique properties which enable it to act as a binder in a tile body to increase green strength and also act as a suspending agent to eliminate sedimentation in a glaze. Due to the samll particle size of hectorites, they are very efficient and require only minimal additions, 0.5% to 1.5% by dry weight. It is recommended that hectorite be fully hydrated prior to adding to a bach in order to optimize its valuable properties in ceramic applications.

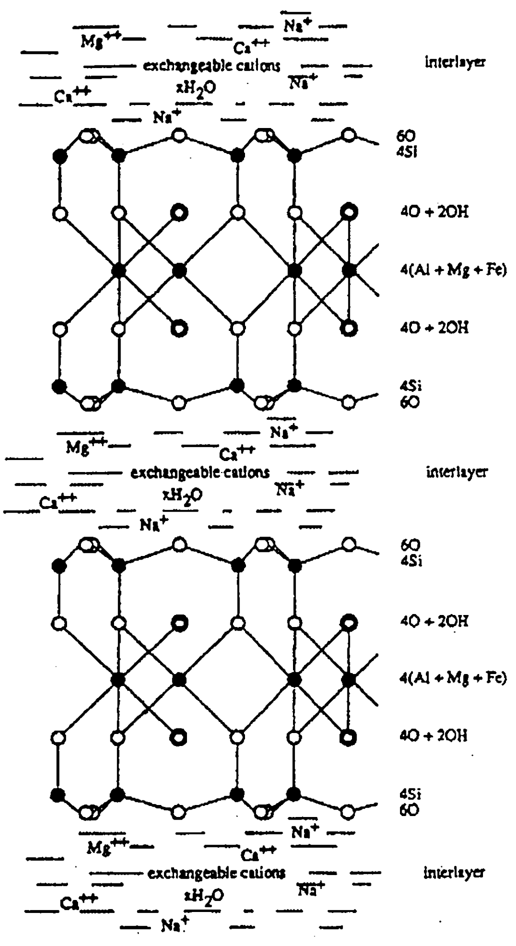


Figure 1. The structure and chemical composition of montmorillonite

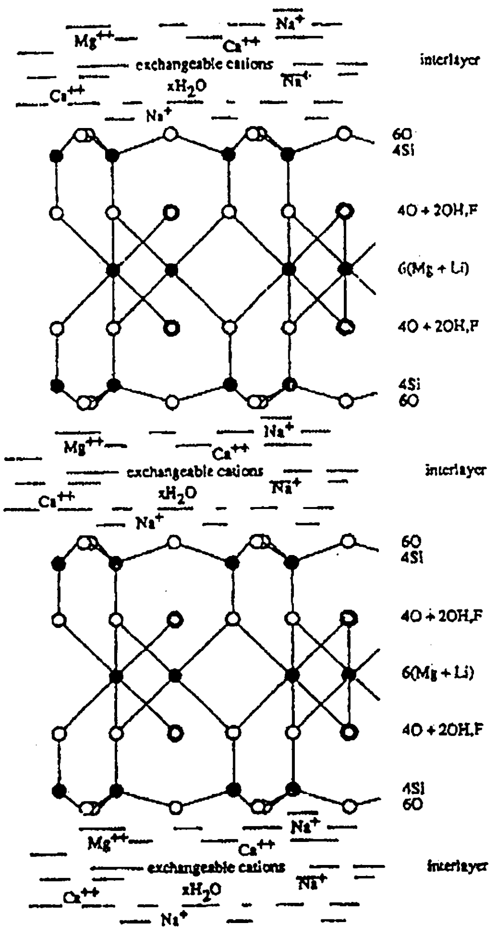


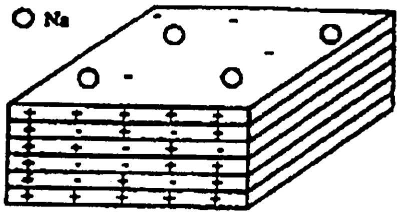
Figure 2. The structure and chemical composition of hectorite.

Figure 3. Explanation of hydration cycle

1. A hectorite flake consisting of several platelets which are dipolar with negatively charged surfaces and positively charged edges. The platelets are separated by a layer of water molecules and Na cations are on present on the platelets surfaces.

2. Water molecules penetrate the interlayer spacing. The Na cations dissociate as they hydrate allowing the negatively charged platelets to repel each other.

3. An internal structure forms in which the negatively charged surfaces of the platelets are attracted to the positively charged edges upon standing. This structure is known as the «house of cards» structure and can be easily disrupted by additional mixing. Due to the thixotropic nature of hectorite, this «house of cards» structure reforms after mixing stops.



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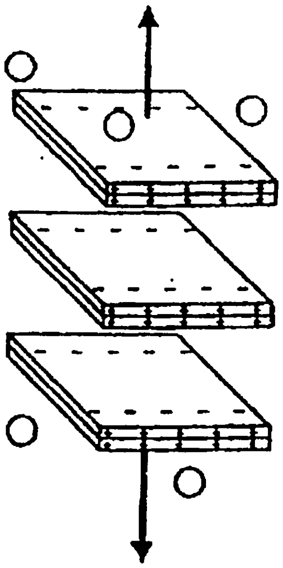

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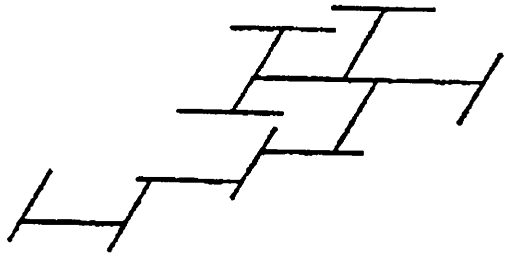

Top view, House-of-cards structure.

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