

Nanoclay development may benefit feeding

A new technology is being used in the animal industry to improve the natural qualities of clay. It is time to take a new look at what clays can do to improve your bottom line.

By SHEILA SCHILS*

**Dr. Sheila Schils is with Animal Nutritional Consulting. She currently consults with Olmix in the U.S.*

DOCUMENTATION of the use of clays as medicinal aids has been found in cultures as old as the Ancient Egyptians. It has been estimated that more than 200 cultures have used clays for therapeutic purposes.

Today, with advances in science due to nanotechnology, the benefits of clays have been drastically increased through the production of a nanoclay. It is time to take a fresh look at the clays and find out why they may be a useful addition to your feeding program.

Clays have been used in the animal industry for a variety of purposes, with the most common application being an adsorbent for moisture and mycotoxins. The efficacy of clays to bind certain mycotoxins is well documented through many research trials. The attraction of the mycotoxins to the clay is due to the electrical imbalance between the layers of the clay. This electrical imbalance attracts the mycotoxins and holds them firmly between the layers, resulting in deactivation of the negative effects of the mycotoxin.

Typically, the clays are most effective in binding the smaller-sized water molecules and the smaller mycotoxins such as aflatoxin and ochratoxins. The clays are the least effective in binding the larger mycotoxins such as fumonisin and deoxynivalenol (also called DON or vomitoxin) because the distance between the layers of clay is not wide enough to accommodate the larger molecules. Through the use of nanotechnology, the space between the layers of clay has been expanded 10 times. Therefore, the nanoclay can bind the entire family of mycotoxins.

When clays are discussed as a feed additive for animals to protect against mycotoxins, there is typically some confusion as to why they can be a useful addition. Many overzealous claims have been made by some companies producing clay products, resulting in producers being skeptical of the benefits of clays. Confusing terminology and explanations have also caused the end user to be uncertain of exactly what they are feeding and why.

What is clay?

Clay is a substance present in most kinds of soils. Clays have certain properties that have been developed by specific and long-term environmental conditions and cannot be made by

mechanically grinding up sand or silt. Clay has many uses, including in pottery, ceramics, linings for landfills, computer chips, cosmetics and pharmaceuticals.

In agriculture, the clay in soil provides a vital element for the farmer. Clay will slow the seepage of water through soil to help the soil retain its moisture. However, too much clay will make the soil heavy, stiff and prevent the movement of air and water through the soil. Clay will adsorb ammonia and other gases needed for plant growth as well as help retain minerals for growth. Fertility from year to year will be better maintained with some clay content to the soil.

Areas where clay is mined may contain many different variations of the same type of clay or even several different clays in a small sample. In addition, samples from certain areas may contain other elements such as micas, quartz, feldspars or carbonates.

Clay differences

Classes of clays are based on the minerals contained in the clay, logically referred to as clay minerals. The two main ingredients of all clays are alumina and silica, bound together in sheets to form layers. This may tend to imply that all clays have similar properties and can be viewed as inert fillers, but this is quite untrue.

There is a wide variety in the exact chemical makeup of clays, so the physical characteristics as well as the chemical and structural characteristics are important in defining the different clays. Four criteria must be met for a mineral to be considered a clay mineral.

First, clay minerals are very small in size (by definition less than 0.002 mm) and can only be seen with the aid of an electron microscope. Particle size is an important consideration when discussing the effectiveness of clays for specific purposes. A smaller particle size will have more surface area available for adsorption and, therefore, will probably be more effective for adsorption than a larger particle size of the same material.

Second, clay minerals are made up of particles that can slide across each other, which gives them plasticity and makes them malleable.

Third, the particles must be able to form colloidal suspensions when mixed with water. There are two general types of clay based on how the substance reacts when mixed with water. Expandable clay swells when water is added to it. Expandable clay can adsorb so much water that the clay itself becomes a liquid. The petroleum industry uses expandable clays to make drilling mud. Non-expandable clay becomes soft but not liquid when mixed with water. The ceramics industry uses non-expandable clay for the manufacture of bricks, pottery, tile and many other products.

Fourth, the sample must have the chemical makeup that will produce the first three characteristics. The chemical makeup of clays varies widely, so there is a large list of chemical names of which clay is composed. Sometimes, only one molecule will be different, but this difference can result in a large variation in the application of the clay.

The basic classifications of clays are somewhat complex because of the wide variety of clays. Therefore, there are many crossovers between categories for some general clay names. For example, the name "Semecite" can describe a clay mineral with eight silicon ions or fewer, making these two Semecites distinctly different. Therefore, more information than just the name Semecite would be necessary to truly understand the nature of that particular clay.

Phyllosilicate clays

Within the phyllosilicate clays are the clays that are expandable and have adsorption qualities. These adsorption qualities are important when the purpose of the material is to attract moisture and/or mycotoxins.

The term phyllosilicate designates one of the six subclasses of the rock-forming minerals called the silicate minerals. The phyllosilicates are also called the clay minerals and have a distinct layered and crystalline structure. The term aluminosilicates (or silica-alumina) is also used to describe some types of phyllosilicates. Aluminosilicates are an oxide-like combination of aluminum, silicon and oxygen, which are the major components of clays.

Hydrated clays are also sometimes used to designate a specific clay, but this is not an accurate description. Hydrated simply means the clay contains water molecules that are either bound to a metal center or crystallized with the metal complex.

A specific phyllosilicate clay is defined by its group, subgroup and species. The group is determined by the thickness of the layer, which is dependent upon the number and type of sheets joined together. The two main sheet types are tetrahedral and octahedral sheets.

The subgroup is determined by the density of the tetrahedral and octahedral sheets and on the charge of the layer (which is mainly a concern for the 2:1 [referring to the type and number of sheets that form layers in a clay] phyllosilicates). The higher the chemical reactivity, the better the clay can attract and adsorb molecules such as mycotoxins.

The species depends on the substitution cations within the octahedral sheet that gives the clay its specific characteristics. In addition, the species is dependent upon how many layers are piled together, which can influence the clay's stability. Again, there are several clays that have overlaps between the designations of group, subgroup and species.

Adsorptive qualities

Certain types of clays are more effective for use as adsorbents than other types are. The chemical characteristics of the 2:1 clays have been shown to be the most useful for these purposes. However, specific 2:1 clays are better suited than others.

The smectites are one of the 2:1 clays that have been used extensively for adsorption purposes. The smectites overlap categories and can contain both trioctahedral and dioctahedral types. Smectite is, in fact, a general term that groups several clay minerals together.

The montmorillonite family falls within the smectite category and is the most common of the 2:1 clay family. The name montmorillonite comes from the village of Montmorillon in France, where this type of clay was first chemically described in 1863.

In general, montmorillonite clays contain plate-shaped particles that are approximately 1 μm in diameter and about 1 nm in thickness (Figure 1).

The two most common types of montmorillonite are generally referred to as sodium montmorillonite and calcium montmorillonite (Table 1).

Sodium montmorillonite is so named because it has sodium as the predominant exchange cation and results in a swelling clay. Sodium montmorillonite has high cation exchange ability with thin and flexible crystallites. These characteristics produce a rapid dispersion in water, high aqueous viscosities and exceptional film-forming abilities. This type is the least common form of the montmorillonites.

Calcium montmorillonite, with calcium as the predominant exchange cation, does not possess the same adsorbent qualities as sodium montmorillonite. However, the calcium cation can be replaced by sodium if the sodium ion is available.

The affinity of the montmorillonite clays to attract and bind certain mycotoxins has been well established in the literature. Mycotoxins bound by montmorillonite are those that can physically enter into the interlayer space. The width of the interlayer space is 0.25-0.7 nm in the dry state and 1 nm in the hydrated state. Aflatoxins and ochratoxins can enter into this space, but the other mycotoxins are too large to be able to enter (Table 2). Therefore, the use of the typical montmorillonite clay has limited applicability as a mycotoxin binder.

Nanoclay development

Nanotechnology uses the world's most advanced molecular technology to improve the physical characteristics of compounds. The prefix "nano" is used to describe microscopic sizes of materials.

Nanotechnology has already been used to improve a variety of products worldwide, including filtration systems for wastewater, reduction of glare on surfaces and in the development of medical devices.

Montmorillonite clays possess several qualities that make them an excellent base for manipulation through nanotechnology. These qualities include stability, an interlayer space, high hydration and swelling capacity and a high chemical reactivity.

Researchers at Olmix in France have developed a technique where the ulvans (a polysaccharide) contained in seaweed are used as pillars to increase the interlayer space of the montmorillonite clay by 10 times. This increase in the interlayer space allows even the larger-sized mycotoxins to

enter, providing protection to the animal. This new product is called Amadite and has been patented worldwide (Figure 2).

Research trials performed by the independent laboratory TNO in the Netherlands have shown the efficacy of nanoclay as a wide-spectrum mycotoxin binder. The binding ability of the nanoclay to the mycotoxins was maintained as the product passed through the stomach and small intestine. Studies showed that the new product reduced the level of DON (1 part per million) by 40% compared to control and of fumonisin B1 (2 ppm) by 50-60% when compared to control.

Low inclusion rates of 1 kg per ton were used to obtain these adsorption levels, which add to the practical and economic usefulness of the product. In addition, the trials showed the inability of the nanoclay to adsorb carbohydrates, proteins and water-soluble vitamins, a concern with the use of other clay products. Additional field trials have been performed confirming the ability of the product to improve productivity, and others are currently under way.

Conclusions

Over the years, the scientific understanding of what clays can do to improve animal health has increased. With Europe banning the use of antibiotics, the development of other products to improve animal health has flourished. As these products become more widely available, the benefits for the producer and consumer will be evident.

The newest technology is now being used in the animal industry to improve the natural qualities of clay, leading the way to healthier and more productive animals. It is time to take a new look at what clays can do to improve your bottom line.

1. Common montmorillonite clays	
Sodium montmorillonite (also called low-charge or Wyoming type)	$\text{Na}_{0.3}\text{Al}_{1.7}\text{Mg}_{0.3}\text{Si}_4\text{O}_{10}(\text{OH})_2$
Calcium montmorillonite (also called high-charge or Cheto type)	$\text{Ca}_{0.3}\text{Al}_{1.6}\text{Mg}_{0.3}\text{Si}_4\text{O}_{10}(\text{OH})_2$

2. Size of mycotoxin molecules (nm)		
	H*	L*
Aflatoxin	0.8	2.0
Ochratoxin	0.7	3.0
Zearalenon	2.0	1.5
Fumonisin	2.0	6.0
Trichothecens	1.5	2.5-4.0
H* The approximate dimension of the molecule in a potentially adsorbable position.		
L* The approximate dimension of the molecule rotated 90° from position H.		