

TEST REPORT #7: Contaminant Attenuation by Freshwater AquaBlok® Formulations

Clay minerals are natural and essentially inert, with physical and chemical properties that are well understood. They have long been used in the environmental industry to contain or isolate various hazardous substances, primarily because of their relatively low permeability to aqueous solutions. In particular, bentonite, which is a geologic deposit rich in smectite clays, has been used extensively as an integral component of drilling fluids, in landfill liner and capping systems, and in slurry walls for diverting ground water flow. Bentonite is a principle component of typical freshwater formulations of AquaBlok™ (Test Report #1) and not only has substantial merit as a hydraulic barrier (Test Report #3), but as a chemical barrier as well.

Because of its mineralogical and surface-charge configuration, montmorillonite – typically the major component of bentonite - has an inherently large surface area compared to other commonly occurring “plate-like” clay minerals (Table 1). This high surface area, in combination with water’s affinity for montmorillonite’s negatively charged surfaces, results in significant physical expansion of the clay upon its hydration (Test Report # 6). The high surface area and negatively charged surfaces also account for the clay’s ability to sorb or exchange relatively large quantities of dissolved cations (Table 1).

Table 1. Physical and Chemical Properties of Montmorillonite and Other Selected Phyllosilicate Minerals (from Bohn et. al., 1979).

Clay	Surface Area (m ² /g)	Expands Upon Hydration?	Cation Exchange Capacity(meq/100g)
Montmorillonite	600 - 800	Yes	80 – 120
Mica	20 - 40	No	70 – 120
Kaolinite	10 – 20	No	1 – 10

Table 2. Heavy Metal Sorption from Solution onto Montmorillonite and Bentonite (from Bereket et. al., 1997¹ and Lothenbach et. al., 1997²).

Heavy Metal	Bentonite ¹ (initial solution pH = 5)	Montmorillonite ² (pH between ~ 4 and 7)
----- Percent of Metal Removed from Solution -----		
Lead	82	20 – 100
Copper	56	20 – 100
Zinc	34	20 – 40
Cadmium	71	15 – 20
Nickel	No data available	15 – 20

Published research indicates that naturally occurring montmorillonite and bentonite can not only sorb innocuous base-metal cations like calcium, magnesium, and sodium, but can also sorb - or attenuate – potentially toxic heavy metal cations onto clay surfaces, effectively minimizing concentrations of such metals in bulk solution phase of pore and surface waters. Batch-shaking and flow- through column studies typically indicate significant removal of dissolved metal cations like lead, copper, zinc, cadmium, and nickel from solution onto montmorillonite and bentonite (Table 2).

The degree of metal attenuation by montmorillonite and bentonite differs between charged metal species and also with system variables including: pH, competition between metals for exchange or sorption sites, total salt concentrations in solution, oxidation-reduction potential, presence of dissolved organic substances, and speciation of metal ions in solution.

For example, lead and copper typically sorb more strongly to most clay mineral surfaces, including montmorillonite, than do zinc and cadmium, and metal sorption is usually greater, overall, in higher-pH systems. Published research also generally indicates that, despite such systematic factors affecting ion sorption, heavy metal

cations are held more strongly to montmorillonite and bentonite than are mono- and divalent base-metal cations. Additionally, a relatively greater degree of metal sorption occurs to montmorillonite than to other, lower surface-area clays like kaolinite. In many situations, oxides of iron, manganese, or aluminum can accentuate heavy metal sorption to clay rich substrates.

In light of demonstrated abilities for metal sorption/attenuation under controlled laboratory conditions, montmorillonite and bentonite have both been used in different capacities in the environmental industry to: immobilize heavy metals in contaminated soils and sediments, remove metals from landfill leachates, and remove metals from waters and wastewaters. Due to its low permeability and radionuclide-sorbing capabilities, bentonite is also commonly considered for use as an environmental buffer material during disposal of radioactive wastes. Such remedial uses of these clay and clay rich materials will likely increase, as should development and use of chemically modified versions of montmorillonite and bentonite clays for selective attenuation of organic pollutants.

Specially engineered cation-like compounds, such as quaternary ammonium ions, can be used to physically displace base cations, like sodium, from exchange sites of montmorillonite clays. The use of tetramethylammonium (TMA⁺) ions is one example (Figure 1).

Reactive surfaces of these “organoclays” or organobentonites are more organophilic in nature (compared to non-modified clays) and, as a result,

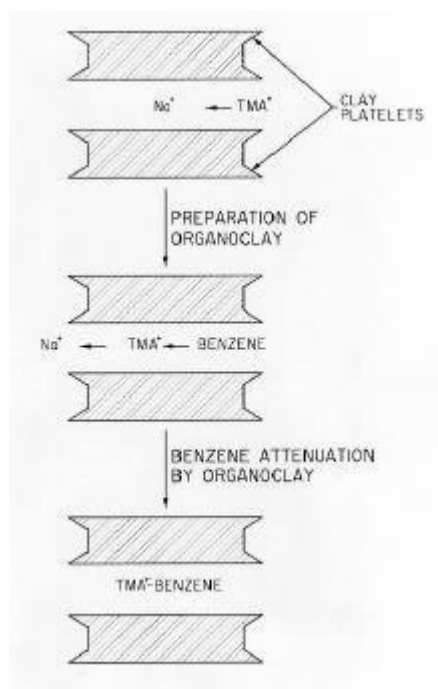


Figure 1. Contaminant Attenuation by Organoclays

have a relatively greater affinity for charged and non-charged organic pollutants. Published research indicates that organoclays can selectively remove a variety of organic pollutants including non-polar, nonionic BTEX compounds, phenols and chlorinated hydrocarbons, and pesticides (Figure 1). As with metal-clay interactions, the degree of attenuation by organoclays is dependent on factors like pH and competition for clay sorption sites.

Organoclays have been used commercially in water and wastewater treatment systems for the removal of organic pollutants from contaminated ground waters and industrial waste streams (including oils and greases). Organoclays have also been tested for use in the solidification/stabilization of phenolic-contaminated soils.

The bentonite component of typical freshwater AquaBlok formulations, either in bentonite’s natural or modified form, can effectively reduce concentrations of heavy metals and organic pollutants in the bulk solution phase. However, other types of clay minerals, hydrous oxides, and/or other reactive materials can also be used in conjunction with bentonite to develop special AquaBlok formulations designed to address site-specific needs, including sediment capping in saline environments.

In summary, AquaBlok and AquaBlok-based caps can minimize the migration of toxic, harmful compounds from moving into ground water, or into floral or faunal communities inhabiting overlying deepwater or wetland ecosystems. AquaBlok’s inherently low permeability accentuates its ability to isolate pollutants from such environments. Therefore, AquaBlok not only acts as a relatively cohesive, physical and hydraulic barrier between contaminated sediments and water resources, but can also be mineralogically and compositionally tailored to maximize chemical attenuation of specific metal or organic pollutants, depending on site-specific conditions and needs.

References

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