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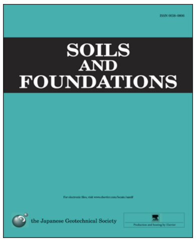

Technical Paper

Modification of the swelling characteristics and phosphorus retention of bentonite clay using alum

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Abstract

The neutralization of negatively charged clay particles using positively charged aluminum species is a well-known process. However, few studies explain the impact of the process on the Swelling Index (SWI) of clays over a wide range of alum and pH values. In this study, the SWI test was used to assess the effect of alum on the swelling characteristics of highly expansive bentonite clay and the saturation of the clay surfaces with Al species to improve the phosphorus retention characteristics of clays. The experiments included varying the pH and alum dosages and measuring the resulting SWI. When alum was not present, varying the pH was seen to have a profound impact on the swelling characteristics of the clay. Below pH 2 and above pH 11, the SWI was low because of an abundance of H^+ at low pH values and an abundance of NaOH at high pH values. Alum was effective below pH 5 in reducing the SWI from 20 mL/g without alum down to 5 mL/g using increasing quantities of alum up to 1 g of alum per 2 g of clay in 100 mL of water. Within the pH range of 5–9, alum was not effective in controlling the SWI. Above pH 11, aluminum precipitated and the SWI was low. The addition of clay competed with the availability of Al to precipitate phosphorus, and the use of modified clay coagulated with alum resulted in significant phosphorus removal. The results demonstrated the effectiveness of alum to control clay swelling and the impact of wide variations in pH on the process.

Keywords: Swelling; Bentonite clay; Alum; Phosphorus retention

1. Introduction

Clays have unique characteristics that allow their use in beneficial ways (Grim and Güven, 1978; Kahr et al., 1990; Komine and Ogata, 1999; Yong, 1999) or cause problems that require solutions. The characteristics of clays (Sarıkaya et al., 2000; Varma, 2002; Christidis et al., 1997; Komadel, 2003; Önal et al., 2002; Tan et al., 2004; Kahraman et al., 2005; Komadel et al., 1996) relate to at least four variables (Cernica, 1995), including chemical composition, layered structure, small size (less than 2 μm), and former processing and environmental exposure. Clays, especially bentonite, have high affinities for water, distribute themselves evenly throughout water, swell when they become wet and the reverse when they become dry, and have electrically active surfaces and high specific charges (charge/mass). They can electrostatically interact with ions in aqueous solutions, attracting those that carry opposite charges and fixing some of them closely on their surfaces, and have the ability to exchange ions within aqueous solutions. The above properties can be altered to generate modified clays that can be

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used beneficially or that behave in a less problematic manner. In particular, the tendency of the clays to swell can be modified to a large extent by using a variety of techniques, including the use of alum, as discussed in this article.

The surface chemistry of clay particles relates to the high specific surface area and the surface charges that allow active interaction with ions and water. The surface charge originates from substitutions in the tetrahedral and octahedral clay sheets. The surface charge can also result from broken bonds along particle edges and pH-dependent surface charge changes due to an acid–base type of behavior. Clays can form stable colloidal suspensions in water that do not settle within any reasonable time-frame. The stability concept refers herein to the poor settling properties and flocculation of clay particles due to the various forces resulting from the interactions among ions, clay particles, and water. The negatively charged clays, under normal pH conditions, attract positively charged cations close to their surfaces. When water is available, these cations become hydrated or swelled. When clays dry, the water is removed and the cations come in closer contact with the clay surfaces. The attraction of cations to clay surfaces results in a high density of cations in the spaces close to the clay surfaces. This results in diffusion forces in the solution that try to remove the cations from the clay surfaces. Consequently, cations close to the clay surfaces are pulled in two different directions. Despite these competing forces, the clay particles manage to maintain a surrounding region, called the diffuse layer, which has a high concentration of cations attracted by the negatively charged surfaces of the clay. Cations tend to be hydrated, and the more cations in the diffuse layer, the more water surrounds the clay particles in the diffuse layer, which causes swelling. When negatively charged clay particles come close to each other, their diffuse layers interact and the repulsion forces increase. Attraction forces between colloidal particles exist regardless of their surface charges, but are effective at short distances. If colloidal particles are brought sufficiently close to each other, the attractive forces will exceed the repulsive forces, which may join them together, causing them to flocculate.

Some cations are more favorably attracted to clay surfaces than others, and some of them become attached to the clay particle surfaces. Favored cations can replace less favored cations, which is typically the main mechanism in neutralizing clay particles, with the possibility of the entry of the cationic species into the internal structure of the clay (Cooper et al., 2002; Jiang and Cooper, 2003). Favoring a certain cation over others also depends on the relative availability of cations in the solution, the hydrated size of the cations, and the cation charge, with the positively charged aluminum Al^{3+} and iron Fe^{3+} cations being among the more favored cations. Fewer Al^{3+} or Fe^{3+} cations are required to neutralize the surface of a clay particle and at a closer hydrated distance than Na^{+} or Ca^{2+} cations. Accordingly, one way to reduce the thickness of the swell layer surrounding clay particles is to replace the monovalent and divalent cations with highly charged cations such as Al^{3+} or Fe^{3+}. In this study, alum [$Al_2(SO_4)_3.18H_2O$] was used to modify the electrostatic behavior of clay surfaces by providing positively charged ions to neutralize the negatively charged clay surfaces and to replace other cations (such as Na^{+} and Ca^{2+}) that may exist on the clay surfaces. The use of alum was assessed over a wide range of pH values, as described in the following section.

The neutralization of clays using alum is a well-understood and fully documented process; however, alum was used in this study to modify the clay characteristics for two purposes:

1. To assess the impact of the addition of clay on the swelling characteristics of clays, particularly applying the Swell Index (SWI) test, which is used to assess the suitability of clays to be employed as liners in landfills; and
2. To improve the phosphorus retention characteristics of clays through saturating the clay surfaces with Al species, which are suitable for the removal of phosphorus from solutions. Phosphorus is an important environmental contaminant and nutrient for plants and algae. Clays used to remove phosphorus can help clean contaminated waters and can be settled and recovered for use as soil additives.

Past studies (Yang et al., 2006; Auvray et al., 2006) have focused on the use of alum to remove phosphorus from wastewater and in the process used clays as coagulant aids or supporters to enhance the settling of phosphorus-containing particles. In this study, a different approach was used in which clays were first modified with alum, and then the modified clays were used to achieve the removal of phosphorus from wastewater. In addition, environmental studies involving phosphorus removal and geotechnical studies involving the use of alum to control swelling are typically conducted separately. In this study, however, both characteristics were studied and the relationship between the optimum geotechnical properties of the modified clays and the optimum properties of the modified clays to remove phosphorus were assessed simultaneously.

2. Materials and methods

2.1. Clay source and characteristics

The clay was obtained from a local company in the United Arab Emirates that imports clays from neighboring Iran. The clay is marketed with a claim that it contains at least 70% sodium montmorillonite, with at least 97% passing sieve number 200 (0.075 mm), and a cation exchange capacity (CEC) of 0.83 meq/g.

2.2. Swelling characteristics of raw and modified clays

The experimental work involved assessing the swelling characteristics of raw and alum-modified clays using the Atterberg limits (liquid limit, plastic limit, and plasticity index) and the clay swell index (SWI). The tests were conducted according to ASTM standards. The Atterberg limits were measured on the alum-modified clay samples prepared using an alum solution (10 g of alum in 100 mL of water) that was