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ORIGINAL ARTICLE

Effect of heavy metal and alkali contamination on the swelling properties of kaolinite

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Abstract One of the most important factors that determine engineering properties of soils are the type and the amount of clay present in soil. Kaolinite being a very common and non-swelling clay mineral in soil was chosen as the medium, and significance of the change in swelling property of kaolinite due to contaminant-clay interaction was investigated. The amount of change in swelling percentages of the kaolinite due to contamination with 10,000 ppm solutions of $Pb(NO_3)_2$ and $Zn(NO_3)_2$ was determined using oedometers. For uncontaminated kaolinite, the amount of swell was determined as 2.2%. For Pb-contaminated and Zn-contaminated kaolinite, these values reached to 5.8 and 5.3%, respectively. Besides heavy metals, kaolinite was also contaminated with 4 N NaOH. The biggest change in the amount of swelling was obtained from NaOH-contaminated kaolinite which is 13.9%. In addition to swelling percentages, swelling pressures were also determined. The swelling pressure of the uncontaminated kaolinite was found as 1.06 N/cm^2. For Zn and Pb-contaminated kaolinite, this value reached up to 2.0 and 2.6 N/cm^2. The NaOH-contaminated kaolinite has the greatest swelling pressure which was 230 N/cm^2.

Keywords Kaolinite · Alkali contamination · Heavy metal · Swelling properties

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Introduction

Clays are hydrous aluminum silicates (Klein and Hurlbut 1985) that have a wide range of usage owing to their special properties. They are being used as an adsorbent material because of their high specific surface area, chemical and mechanical stability, layered structure and high cation exchange capacity (Gupta and Bhattacharyya 2006) and also commonly being used in waste containment systems because of their low hydraulic conductivity. Although kaolinite has rather low cation exchange capacity and specific surface area compared to other clay minerals, it is also used for adsorption of metals from aqueous solutions (Yavuz et al. 2003) and it is one of the most commonly used soil barrier mineral in waste containment systems (Reddi and Inyang 2000).

Clays are one of the basic components of the soils which are being continuously contaminated by heavy metals with different activities (atmospheric pollution from motor vehicles, combustion of fossil fuels, agricultural fertilizers and pesticides, organic manures, disposal of urban and industrial wastes, mining and smelting process (Alloway 1990)) around the world. Although there has been much research on the heavy metal contamination of soils (Lee et al. 2006; Turer 2005; Möller et al. 2005; Turer and Maynard 2003; Gibson and Farmer 1984) there is not much research that investigates the effect of heavy metals on engineering properties of the soils. These effects can be particularly important in landfills, where clay liners are being continuously subjected to infiltration of heavy metal loaded leachate.

Kaolinite is formed by stacking of 1:1 units with strong hydrogen bonding between O^{2-} and OH^{-} of tedrahedra and octahedra, respectively. Because of the strong bonding, kaolinite does not exhibit swelling in water (Reddi and Inyang 2000). The permenant negative charge in kaolinite is produced because of isomorphic replacement of Si^{4+} by Al^{3+} in the silica tetrahedral sheet or of trivalent metal ions by divalent ions in the alumina octahedral sheet, leaving a single negative charge for each substitution (Srivastava et al. 2005). Both the alumina sheet and the crystal edges have a pH-dependent variable charge caused by protonation and deprotonation of surface hydroxyl (SOH) groups (White et al.2000). Hence, the kaolinite surface is expected to have two kinds of binding sites that could interact with metal ions (Srivastava et al. 2005). Mirand-Trevino and Coles (2003) analyzed the metal adsorption behavior of kaolinite and stated that metal adsorption is usually accompanied by release of H^+ ions from the edge sites and substitution of Pb^{2+} (a.r: 1.81 Å) and Zn^{2+} (1.53 Å) for H^+ (0.79 Å) could produce stress in the kaolinite. Also the substitution could create swelling, flocculation, decrease in shear strength and increase in hydraulic conductivity and compressibility.

There are many studies on swelling properties of expanding montmorillonite; however, the evaluation of swelling properties of kaolinite is limited (Shridharan and Rao 1973; Rao and Sridharan 1985; Sivapullaiah and Manju 2005). Shridharan and Rao (1973) suggested that volume change behavior of kaolinite is governed by shearing resistance at interparticle level. They also stated that the factors determining the shear resistance and volume change behavior of kaolinite as frictional resistance, clay fabric and attractive forces (van der Walls forces, the coulombic attractions between negative surfaces and positive edges, particle-cation-particle linkages and forces arising from hydrogen bonds) arise from physiochemical mechanisms. Among these factors, interparticle hydrogen bond which determines the kaolinite fabric and frictional forces was shown to be the most effective factor controlling volume change of kaolinite (Rao and Sridharan 1985)

Besides heavy metal, the effect of alkali contamination on the swelling properties of kaolinite was also studied, which was the focus of Rao and Rao (1994) and Sivapullaiah and Manju (2005). Rao and Rao (1994) studied a ground heave of a kaolinite-rich red soil as a result of a caustic soda solution spillage into sub-soil through cracked drains in an industrial establishment. They observed 5.05% swelling potential of the undisturbed soil by passage of 40% caustic soda solution in the oedometer test and they suggested that the notable ground heave in the vicinity of the caustic soda towers is a consequence of chemical interactions between the spilled caustic soda solution and the foundation soil.

The lower concentrations of alkali cause changes in the structure of the soil (Mitchell 1993). High concentration of alkali can produce new compounds and also effect the clay structure due to clay-alkali interaction (Sivapullaiah and Manju 2005). X-ray diffraction studies of alkali contaminated kaolinite showed that aluminum silicate hydroxide hydrate is formed by clay alkali reaction and the amount of this new compound depends on the concentration of alkali solution (Sivapullaiah and Manju 2005).

Kaolinite has been chosen as the medium because it is one of the major clay minerals in the soil. Also as kaolinite has very low swelling capacity determination of the positive results might mean greater effects in soils having swelling clays.

Material properties

The particle size analysis of the kaolinite showed that it consists of 70% silt and 30% clay size particles. The XRD analysis shows that besides kaolinite there are some illite and quartz minerals in the samples (Fig. 1).

Artificial contamination of kaolinite

The kaolinite was contaminated with 10,000 ppm solutions of $Pb(NO_3)_2$ and $Zn(NO_3)_2$ with a solid/solution ratio of 1:10. The solution was left for adsorption to take place with occasional shaking. After 2 days, the contaminated kaolinite was separated from solution by centrifuge and oven dried.

The kaolinite was also contaminated with 4 N NaOH with a 1:2 solid solution ratio. This solution was left for 2 days with occasional shaking. Then, the contaminated kaolinite was separated from solution by centrifuge and oven dried.

Determination of swelling percentages and pressures

The heavy metal and alkali contaminated kaolinites were compacted into oedometer rings ($r = 3.17$ cm) to attain 1.16 gr/cm^3 densities. The compaction process was achieved under 2 tons of load for Pb and Zn-contaminated kaolinite while it needed 25 tons of load to compact the required amount of NaOH-contaminated kaolinite to attain 1.16 gr/cm^3 density. After compaction water was added to the rings and the

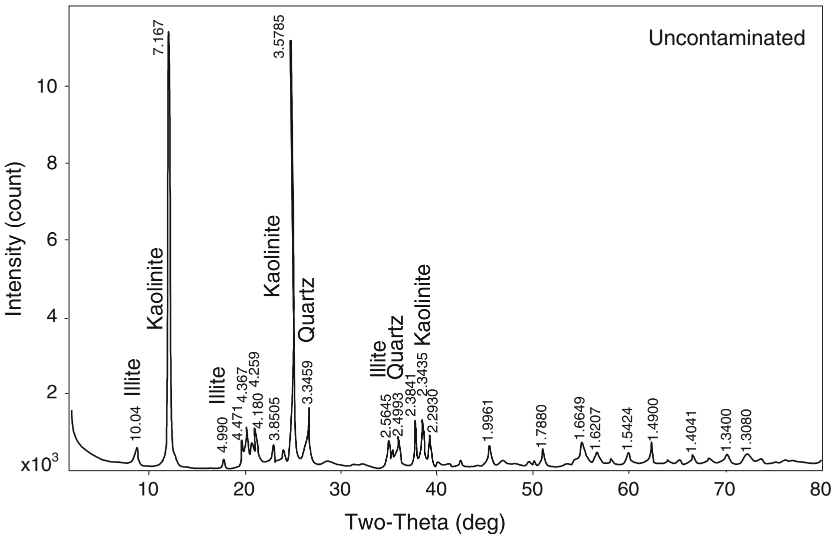


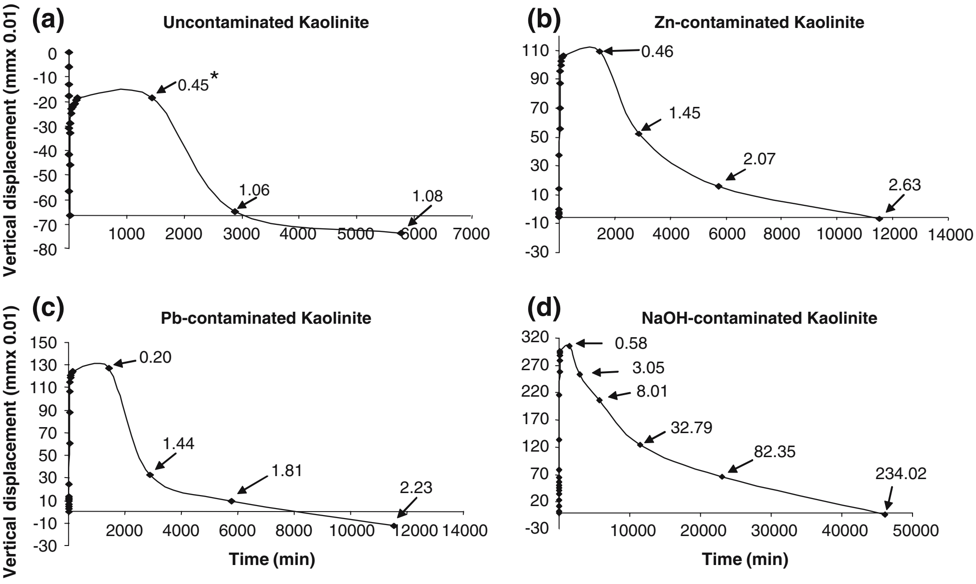
Fig. 1 XRD analysis of the Kaolinite

samples were left to swell until no more change in elevation was observed, the amounts of swell for the kaolinites were calculated using the difference between the height that it started to swell and the final height that it reached. To determine the swelling pressures of the kaolinites, the loads were added to the oedometer rings until the height, at which the swelling started, was reached.

Results

With the addition of water to the oedometer ring having uncontaminated kaolinite inside, vertical displacement occurred in a negative direction (0.66 mm). Then it started to swell but did not reach its original height (Fig. 2a). The amount of swell calculated in vertical direction was 2.2%. For Zn-contaminated and Pb-contaminated kaolinite, the amount of swell was calculated as 5.3 and 5.8%, respectively (Fig. 2b, c). Zn-contaminated kaolinite showed a negative displacement of 0.06 mm with the addition of water. The greatest change in the amount of swelling has been obtained in NaOH-contaminated kaolinite, which is 13.9%.

The swelling pressure of the uncontaminated kaolinite was determined as 1.06 N/cm^2 (Fig. 3a). For Zn and Pb-contaminated, this value reached up to 2 and



*: Load (N/cm^2)

Fig. 2 Vertical displacement versus time graphics

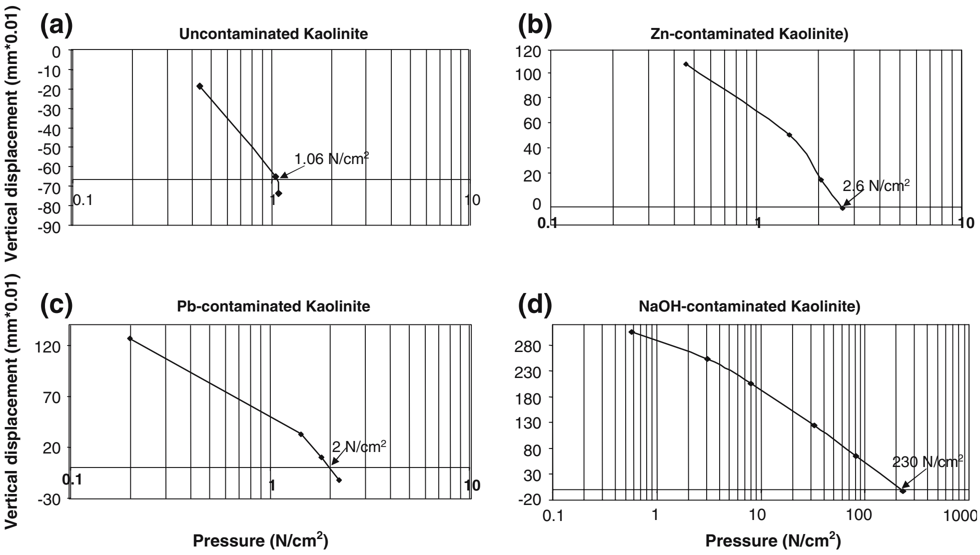


Fig. 3 Vertical displacement versus pressure diagrams

2.6 N/cm^2, respectively (Fig. 3b, c). The NaOH-contaminated kaolinite has the greatest swelling pressure which is 230 N/cm^2 (Fig. 3d).

Discussion

Pb-contaminated kaolinite had a higher amount of swell than Zn-contaminated kaolinite. This can be related to the atomic radius of the Pb which is larger than Zn and the result of letting more water in the mineral structure.

NaOH-contaminated kaolinite swelled 13.9% which is much higher than what it was for heavy metal contaminated kaolinites. The results of XRD analysis showed that the reason for this high amount of swell is the formation of a new compound which has a much higher ability to swell. The new compound has been determined as Sodium Aluminum Silicate Hydroxide. In Sivapullaiah and Manju (2005), the newly formed compound was named Sodium Aluminum Silicate Hydroxide Hydrate, depending upon the peaks formed in XRD analysis (Fig. 4). They also checked change in swelling properties of the alkali-contaminated kaolinite using free swell index and determined the free swell index for uncontaminated kaolinite as 1.4 and 1.6 cc/g for NaOH-contaminated kaolinite.

Rao and Rao (1994) also used an oedometer to determine the effect of caustic soda seepage on the volume change behavior of kaolinite-rich red soil. For this purpose an undisturbed kaolinite-rich red soil (in situ void ratio = 0.67, bulk density = 1.96 Mg/m^3, water content = 21%) was set up in an oedometer cell and was inundated with water under the seating load of 6.25 kPa and stepwise loaded to 25 kPa. Under the overburden of 25 kPa, the soil sample was permeated with 40% caustic soda solution. At the end of the test a 5% increase in the height of the sample was observed. As the soil sample had its original moisture content and was also left to swell under 25 kPa, it swelled only 5%. Also in the present study the kaolinite was first contaminated with NaOH then oven dried and then saturated with water in an oedometer cell. Therefore, the amount of swelling during the addition of NaOH was not determined, and the amount of swelling determined presents information about how the ability of kaolinite to swell was changed by the newly formed compound.

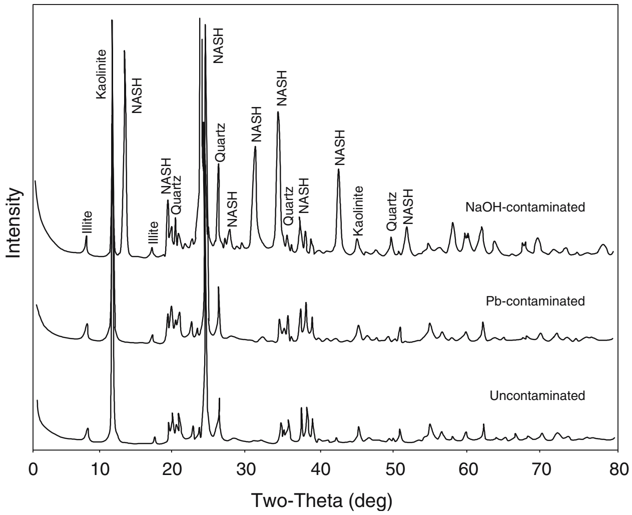


Fig. 4 Comparison of XRD patterns of uncontaminated and contaminated kaolinites

Conclusion

Contamination of the kaolinite with 10,000 ppm solutions of $Pb(NO_3)_2$ and $Zn(NO_3)_2$ caused 5.8 and 5.3% swelling while it was 2.2% for uncontaminated kaolinite. The greatest change in the swelling amount, however, comes from 4 N NaOH-contaminated kaolinite, which is 13.9%.

The swelling pressure of kaolinite before and after the contamination was also determined. It was 1.06 N/cm^2 for uncontaminated kaolinite while it was 2 and 2.6 N/cm^2 for Zn and Pb-contaminated kaolinites, respectively. The NaOH-contaminated kaolinite had the greatest swelling pressure, which was 230 N/cm^2.

These results showed that the swelling capacity of the kaolinite can significantly change as a result of contamination and further studies need to be carried out on different clay types for different types of contaminants for a thorough understanding of the contaminant effect.

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