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Kaolinite properties, structure and influence of metal retention on pH

Jorge C. Miranda-Trevino[1], Cynthia A. Coles*

Faculty of Engineering and Applied Science, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X5

Abstract

The differences between kaolinite and smectite structures are notable, mainly as a result of the degree of weathering in the different compounds. Nevertheless, the kaolinite structure possesses great advantages in many processes due to its high chemical stability and low expansion coefficient. As a consequence of adsorption, the kaolinite structure and the soil solution pH will change. To analyze the adsorption behaviour of kaolinite, Pb, Zn and Cd were studied at three different concentrations (1, 2 and 3 mmol/l) and over different periods of exposure (0.1, 1, 2, 4, 8, 12 and 24 h). The kaolinite retained up to 10.0 μmol/g of Pb, 8.40 μmol/g of Zn and 6.00 μmol/g of Cd when it was mixed with the 3 mmol/l concentration of heavy metals. In each case, the adsorption eventually reduced the solution pH from 4.6 to 3.7. The changes in pH over time indicated both the release and retention of hydrogen ions by the mineral, probably involving the hydroxyl edge sites and exposed hydroxyl planes. The size of the atomic radii are 1.81, 1.71 and 1.53 Å for Pb, Cd and Zn, respectively, compared to the 0.79 Å for H. This difference, along with the differences in hydrated radii, will affect the structure of the clay causing stress in the molecule. Changes in the mechanical and chemical properties of the clay are discussed as the interactions of the heavy metal cations with the kaolinite could affect the structure of the kaolinite and influence properties such as swelling capacity, compaction capability and the double-layer behaviour. The kaolinite in this study contained some illite which may have increased the pH 7 cation exchange capacity to 17.8 mEq/100 g. Using the adsorption data, the reactions at the clay water interphase and the probable effects on the physical properties and structure of kaolinite are discussed.

Keywords: Kaolinite; Adsorption; Metals; Illite; Intercalation

1. Introduction

The importance of kaolinite is remarkable. As one of the most abundant mineral in soils and sediments, its properties are such that it interacts with other soil elements to contribute to the mechanical stability of the soil column (Huertas et al., 1999; Chen et al., 2000). Kaolinite is a 1:1 layer mineral and a product of advanced weathering processes. One layer of the mineral consists of an alumina octahedral sheet and a silica tetrahedral sheet that share a common plane of oxygen atoms and repeating layers of the mineral are hydrogen bonded together (Bear, 1965). As a consequence of this structure, the

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* Corresponding author. Tel.: +1-709-737-8704; Fax: +1-709-737-4042.

E-mail addresses: clemente@engr.mun.ca (J.C. Miranda-Trevino), ccoles@engr.mun.ca (C.A. Coles).

[1] Fax: +1-709-737-4042.

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silica/oxygen and alumina/hydroxyl sheets are exposed and interact with different components in the soil (Grim, 1968).

Frost (1998) discusses outer and the inner hydroxyl groups of the alumina hydroxyl sheet. The outer groups are situated along the unshared plane of the alumina hydroxyl sheet, while the inner groups are located along the plane that is shared with and borders on the silica oxide sheet. The movement of the inner hydroxyl plane is restricted as a result of chemical bonding between the silica and alumina sheets.

As a consequence of its well-packed structure, kaolinite particles are not easily broken down and the kaolinite layers are not easily separated. Hence, most sorption activity occurs along the edges and surfaces of the structure. Kaolinite can form a barrier that is not easily degraded and naturally occurring sediments and deposits containing an abundance of kaolinite interspersed with other minerals are effective in controlling the migration of dissolved species (Devidal et al., 1996). Clay impurities will depend on the genesis of the mineral and will affect the degree of disorder and the particle size of the clay (Balan et al., 1999).

Unlike smectites, kaolinite is non-expanding and as a result of its high molecular stability, isomorphous substitution is limited or nonexistent (Mitchell, 1993). Kaolinite is the least reactive clay (Suraj et al., 1998). However, its high pH dependency enhances or inhibits the adsorption of metals according to the pH of the environment (Mitchell, 1993), and this metal adsorption is usually accompanied by the release of hydrogen (H^+) ions from the edge sites of the mineral. Adsorption may also take place on the flat exposed planes of the silica and the alumina sheets (Spark et al., 1995).

The cation exchange capacity (CEC) quantifies the soil's ability to exchange cations and retain nutrients and is a measure of the soil quality (Bear, 1965). The CEC influences the interaction of plants with nutrients but also with contaminants (Tan, 1982).

Metal adsorption by kaolinite could affect the mechanical and charge properties of soil. The substitution of Pb^{2+} (atomic radii (a.r.) = 1.81 Å), Zn^{2+} (a.r. = 1.53 Å) or Cd^{2+} (a.r. = 1.71 Å) for H^+ (a.r. = 0.79 Å) could produce stress in the kaolinite. Modification of the chemical structure and physicochemical properties of kaolinite is observed when kaolinite is subjected to static pressures or grinding (Kristof et al., 1993; La Iglesia, 1993).

2. Materials and methods

2.1. Material

The kaolinite used in the research is Hydrite flat D kaolinite from the Dry Branch Kaolin Company. They report a median particle size of ≈ 5.0 μm with < 30% of the particles having a diameter ≤ 3 μm. The particle size distribution of this kaolinite is similar to that of some soils and sediments (Coles, 1998). The metal salts used in the study are $PbCl_2$, $CdCl_2$ and $ZnCl_2$.

2.2. Experimental set-up

The pH-dependant CEC was determined following the method of Hendershot et al. (1993). A Varian SpectrAA-50/55 atomic adsorption spectrometer was used to determine all element concentrations. The specific surface area (SSA) of the kaolinite was determined according to the method of Sheldrick (1984). The Fe, Pb, Cd and Zn concentrations in the kaolinite were measured using the US EPA method "3050B—Acid Digestion of Sediments, Sludges and Soils" (American Chemical Society, 1986). Qualitative X-ray diffraction (XRD) analysis was performed on the kaolinite using a Rigaku RU200 powder diffractometer.

Determination of the point of zero charge (PZC) was as outlined by Van Raij and Peech (1972). Specifically, samples of 2 g kaolinite were placed in a 20-ml solution of NaCl (at concentrations of 1.0, 0.1, 0.01 and 0.001 M) and then agitated for 1 h. At 2-min intervals, 2 ml of 0.001-M NaOH was added to half the samples and 2 ml of 0.001-M HCl was added to the rest of the samples with the pH being measured after each addition. The PZC was taken as the pH where the titration curves intersected.

Batch equilibrium tests were conducted to measure the adsorption of metals onto the clay. The clay/solution ratio was 1:10 as suggested by Yong et al. (1992) and 1, 2 and 3 mM/l solutions of each metal were tested. Each of the clay and metal chloride solutions were agitated for 0.1, 1, 2, 4, 8, 12 and 24 h. Finally, the suspensions were centrifuged at 5000 rpm for 10 min to separate the solid and liquid phases.

3. Results

The kaolinite characterization test results are summarized in Table 1. The high concentration of Fe, which makes up about 0.125% by weight of the kaolinite, may be due to contamination of the kaolinite with illite. XRD analysis of the kaolinite revealed the presence of probably $<2\%$ illite (Ms. Maggie Piranian, Earth Sciences, Memorial University of Newfoundland, personal communication, 30 October 2002.) The presence of illite could increase the PZC, CEC and SSA of the kaolinite (Tschapek et al., 1974; Yong et al., 1992). The PZC may be slightly higher than normal for kaolinite but the results of the SSA test show that the value is still within the range of 10 to 20 m^2/g established for kaolinite (Bohn et al., 1979). The concentrations of other metals are higher than the concentrations obtained by Coles (1998) for the same type of kaolinite, but not high enough to interfere with the adsorption experiments.

The batch test results are presented in Fig. 1. The metal uptake is similar to the metal uptake for the same type of kaolinite that was studied by Coles (1998), except that in this previous study, the kaolinite contained negligible impurities, the CEC was much less and there was a good correlation between the CEC and metal uptake. The kaolinite in this study contains more impurities, the CEC is inflated and the metal uptake represents only approximately 10% of the CEC. It seems the high CEC cannot be fully accounted for by the small amount of illite present but perhaps, as suggested by Dr. Ola Karnland (Clay Technology, Sweden, personal communication, 17 October 2002), the presence of this other clay is making it difficult to obtain an accurate CEC determination.

Table 1
Kaolinite properties

CEC (mEq/100 g)	PZC pH	SSA (m^2/g)	Metal concentrations (mg/kg)			
16.63, pH 3.8	4.7	16.41	Fe	Zn	Pb	Cd
18.41, pH 8.4			1247	70	14.9	10

According to Fig. 1a, b and c, the adsorption stabilizes after 12 h for Zn, and after 8 h for Pb. For Cd, there is initial stability during the first 12 h as also observed by Taylor and Theng (1995), but between 12 and 24 h, there is a considerable drop in the metal adsorbed, and this could be related to the drop in the pH of the solution (Fig. 1c). An additional 48-h test with Cd (not shown) confirmed that there was no further change in pH between 24 and 48 h, and that the final stabilization of pH for Cd was at 24 h. For Zn, the adsorption is almost stabilized after 1 h, but there is a small decline at 2 and 4 h for the 1 and 3 mmol/l concentrations, respectively. On average, Pb tends to be adsorbed the least at 0.1 h, and this is most noticeable for the 3 mmol/l concentration. The adsorption of Pb appears to progress the most slowly initially, but after equilibrium, the adsorption of Pb is the greatest.

Fig. 1d, e and f show the amounts of H^+ ions released from the kaolinite as a result of metal adsorption. The behaviour of Zn and Pb is similar between 2 and 12 h because there is generally a marked increment in the amount of H^+ ions released into solution. With Cd, there is a decrement in H^+ ions released into solution between 2 and 12 h, and then between 12 and 24 h the release of H^+ ions increases noticeably. In this study of kaolinite, the metal adsorption selectivity is Pb>Zn>Cd. During the first 12 h of adsorption, the most noticeable peaks in release of H^+ ions from the kaolinite surfaces follow the same order of Pb>Zn>Cd. Therefore, there appears to be a correlation between the metal adsorption and the displacement of H^+ ions.

The final pH of the solutions is approximately 3.7 for the three metals. Once the pH of the solutions has stabilized, the predominant hydration state of the metal cations and their hydrated radii remain constant (Bowden et al., 1980). This information could be important if the sites where the metals react are limited by their spherical sizes. The adsorption of heavy metals could affect properties such as swelling capacity, compaction capabilities and the diffuse dou-

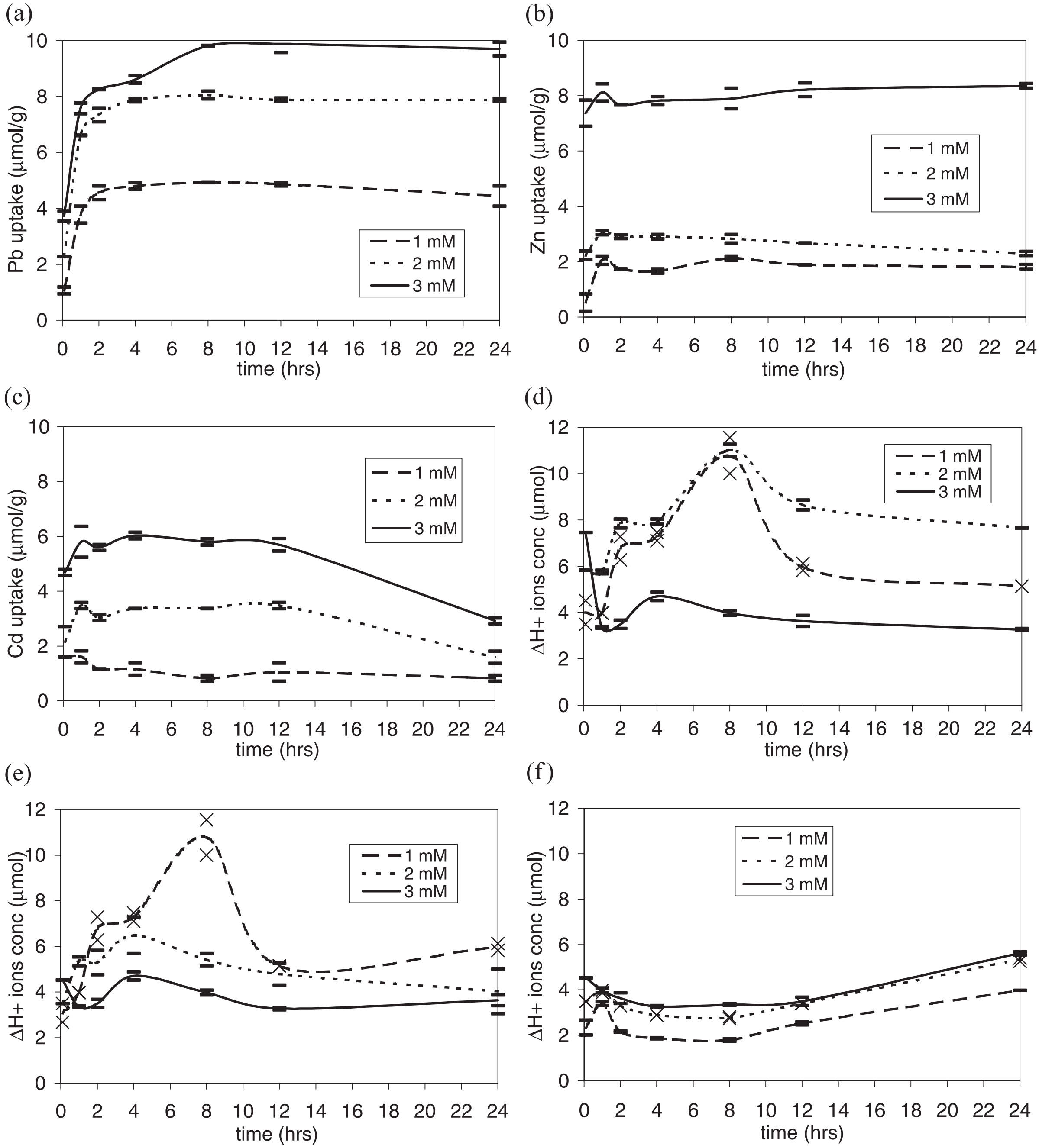

Fig. 1. Metal uptake as a function of time for (a) Pb, (b) Zn and (c) Cd, and change in solution H^+ ion concentration as a function of time for (d) Pb, (e) Zn and (f) Cd. The points represent the experimental values and the line is the mean value. The pH of the kaolinite of 4.6 was taken to be the initial pH of the metal and kaolinite mixtures.

ble layer (DDL) behaviour, as discussed in the following section.

4. Discussion

The presence of illite may cause structural modifications to the kaolinite in the same way Balan et al. (1999) suggest that the interactions of Fe oxides with kaolinite cause structural modification to clay. The presence of illite with kaolinite will have a direct effect on the CEC of the kaolinite (Ma and Egglenton, 1999) and the PZC and the SSA will also be affected, although the amount of illite is too small to influence these properties to any great extent.

The adsorption of Cd appears to be more dependent on kaolinite's edge charge as influenced by pH. Cd is the least successful at displacing H^+ ions, and during the last 12 h of the batch tests, the Cd adsorption and the pH are both decreasing. The reduced solution pH at 24 h may be causing less Cd to be retained (Ziper et al., 1988). Unlike Cd, the data for Pb and Zn may be suggesting that some adsorption of these two metals is also taking place along the outer hydroxyl plane described by Frost (1998) and, therefore, releasing the H^+ ions located there although the H^+ ions at these sites may not be as easily exchanged as those on the broken edges of the kaolinite (Ma and Egglenton, 1999). Desorption studies of Farrah and Pickering (1978) show that the percentages of Pb desorbed from kaolinite are around 90% or higher, confirming that the metals are attached by ion exchange mechanisms. The H^+ ions that are displaced at about 8 h during adsorption of Pb and Zn appear to be subsequently readsorbed by the kaolinite (or the Fe oxides).

According to Thompson et al. (1992), dry grinding of kaolinite with NaCl, followed by the addition of distilled water and subsequent drying by heating, may result in 95% intercalation with NaCl between the hydrogen-bonded layers of kaolinite. This intercalation changes the structure of the kaolinite and swells the mineral, increasing the space between adjacent layers by as much as 7.8 Å, but the process is reversible in excess water. The forces that hold the kaolinite layers together are hydrogen bonding and attractive van der Waals forces. Metal adsorption on the broken edges of the kaolinite may change the van der Waals attractive forces, but exactly how they are changed is not known. In general, the interlayer bonds in kaolinite are weak, and so it may be possible that during agitation of the kaolinite and metal solutions, some intercalation of the Pb and Zn is occurring, which would cause swelling, but further tests would be required to verify this. The adsorption of the heavier cations of Pb, Zn and Cd by the kaolinite may also cause stress to the kaolinite.

With the adsorption of divalent cations of Pb, Zn and Cd, the DDL thickness decreases, repulsive forces decrease and flocculation, porosity and the hydraulic conductivity of the kaolinite increase (Yong et al., 1992; Mitchell, 1993; Chen et al., 2000). Kaolinite has greater shear strength than other clays because of its compact structure, but the shear strength and friction angle of kaolinite will be reduced if intermolecular spaces are enlarged and swelling occurs (Mitchell, 1993). The structure of the polluted kaolinite could be partially modified, there could be a larger plastic stage and the material could be softer, with molecules having more freedom to move into empty spaces.

Although kaolinite normally has a low compressibility due to its well-packed structure, the adsorption of the divalent metal cations may cause swelling of the kaolinite. The empty spaces that are developed between the molecules absorb the external pressure and the compression index increases (Mitchell, 1993; Grim, 1968; Chen et al., 2000). However, Chen et al. (2000) note that this effect is most pronounced for slurries, as when kaolinite is subjected to an overburden pressure of 300 kPa, the swelling forces are overcome, rebound hardly occurs and the mechanical strength of the kaolinite becomes important. Swelling, hydraulic conductivity, shear strength and compressibility of the kaolinite may be affected by the adsorption of Pb, Zn and Cd, but the use to which the kaolinite is eventually put will determine whether these effects will be important.

5. Conclusion

By studying the kinetics of metal adsorption by kaolinite and the exchange of H^+ ions, it is possible to observe differences in the retention of Pb, Zn and

Cd. Although more Pb than Zn or Cd is retained at 24 h, the amount of Pb that is retained at 0.1 h is generally less than the amount Zn or Cd retained, showing that Pb may initially move more slowly to be adsorbed by the kaolinite. The uptake of Cd is generally different and less than the uptake of Pb and Zn, suggesting that the uptake of Pb and Zn may also be taking place at sites not available to the Cd. Cd adsorption also appears to be more susceptible to changes in pH.

The reason for the high CEC value is not clear. A high CEC at low pH and only a small increase in CEC with increasing pH suggests a major source of permanent charge, as occurs with illite (Bohn et al., 1979). In addition, Ma and Egglenton (1999) found a significant increase in the readings of CEC in kaolinites polluted with smectites. However, the amount of illite present in the sample is minimal and it is not believed to be completely responsible of the high readings of CEC of kaolinite. Nevertheless, the variation in charge with pH is reasonable and it is possible that some interference or error is being uniformly introduced into the CEC measurements.

The structure of kaolinite will be affected by the adsorption of heavy metals, but how important the effect will be depends on how the kaolinite is to be used. The displacement of H^+ ions and the adsorption of the cations of Pb, Zn or Cd could create swelling, internal stress in the molecule, flocculation, a decrease in shear strength and an increase in hydraulic conductivity and compressibility. In addition, the substitution of H^+ ions for metal ions could change the van der Waals forces within the kaolinite structure. Changes in the properties listed above indicate the creation of empty spaces in the clay structure. Similar spaces could also be produced if the adsorption of metal ions produces a reduction in the van der Waals forces between the elements in kaolinite, but it is not certain exactly how the these forces are affected. Future studies would be required to give further insight into the modification of the properties of kaolinite as a consequence of heavy metal adsorption.

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