



## Research paper

# Calcium adsorption on clays: Effects of mineralogy, pore fluid chemistry and temperature

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## ABSTRACT

The present study describes the calcium adsorption behavior of clays exhibiting distinct mineralogical composition. The adsorption characteristics were determined using conventional batch-equilibrium sorption method, and different theoretical models were applied to describe the equilibrium sorption isotherms. The variation in calcium adsorption capacity was determined as a function of clay mineralogy, temperature and pore fluid chemistry. Further, the thermodynamic parameters were also calculated to describe the nature of adsorption mechanisms. Significant variation in calcium adsorption potential was observed among the clays, primarily attributed to their mineralogical diversities and related unique surface charge properties. The adsorption density escalated with rise in calcium concentration, temperature and pH of the adsorption system. These observations can be attributed to surface charge modifications and mineral dissolution properties of the clays, which in turn resulted in higher electro-negativity of the clay surface and thereby enhancing the affinity for calcium ions.

## 1. Introduction

The interaction of lime (quicklime, CaO or hydrated lime, Ca[OH]<sub>2</sub>) with clayey soils causes a multitude of temporal and complex physico-chemical amendments to the soil system (Al-Mukhtar et al., 2010; Choquette et al., 1987; Keramatikerman et al., 2016; Maubec et al., 2017). The short-term clay-lime interaction involves adsorption of free calcium ions on to clay minerals, predominantly by cation exchange mechanism (Cherian and Arnepalli, 2016). Concurrently, the high pore fluid alkalinity induced by addition of lime favours the incongruent dissolution of reactive clay minerals. These dissolved mineral components (viz., silica and alumina) participate in long-term pozzolanic reactions with available free calcium to form new cementitious compounds (Cherian and Arnepalli, 2013; Di Sante et al., 2014; Pei et al., 2015; Saride et al., 2013). Therefore, the calcium adsorption properties of clays dictate the availability of excess free lime in the system for pozzolanic reactions, and hence, the optimal lime concentration required for efficient stabilization of soils (Cherian and Arnepalli, 2015). Moreover, the interfacial calcium adsorption reactions and dissolution phenomena can cause alterations of clay mineral surface charge properties and consequently influence the rate as well as the extent of cementation reactions (Bolt, 1982).

The ion adsorption behaviour and kinetics of clays are primarily functions of their inherent mineralogy and reactive nature. The clay mineral surface area and interlayer porosity have significant control on

the adsorption properties (Ammann, 2003; Deng et al., 2017). Further, the preferential adsorption of different cations can be described as a function of ionic potential and binding affinity of clay mineral surface (Bladel et al., 1993; Rytwo et al., 1996). Studies have also reported an increase in adsorption density with increasing bulk solution concentration and rise in pH (Atesok et al., 1988; Glatstein and Fransisca, 2015). Further, the thermodynamic study demonstrated that temperature variations can significantly influence the cation adsorption behaviour and kinetics (Biddappa et al., 1974; Mohamed et al., 2016; Qin et al., 2016). The thermodynamic parameters indicated that cation adsorption process can be either exothermic or endothermic in nature depending on the adsorbent and adsorbate characteristics (Abdel-Karim et al., 2016; Wang et al., 2016). Generally, the interaction between calcium ions and clay minerals exhibits a phased reaction with initially high adsorption followed by a stationary phase (Diamond and Kinter, 1966). It is inferred that the exchange of calcium ions with other positively charged ions held on the negatively charged sites of clay surface is the predominant adsorption phenomena in the acidic environment (Chan et al., 1979). However, the adsorption of CaOH<sup>+</sup> formed by pH-dependent hydrolysis of calcium primarily determines the calcium ion retention on clays in the alkaline region (Chemeda et al., 2015).

The objective of the present study was to evaluate the calcium adsorption behavior of some clays based on their surface charge modifications and mineral dissolution properties. The adsorption characteristics of calcium on clays were examined using conventional batch-

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**Nomenclature**

|             |  |            |  |
|-------------|--|------------|--|
| $pH_{H_2O}$ | natural pH of the clay   | $m$        | mass of soil solids                    |
| $\Delta G$  | Gibb's free energy   | M          | muscovite                              |
| $\Delta H$  | enthalpy change  | MIR        | middle infra-red                       |
| $\Delta pH$ | difference between natural pH of the clay and its point of zero charge | $n$        | adsorption (Freundlich) intensity      |
| $\Delta S$  | entropy change   | $pH_{pzc}$ | pH at point of zero charge             |
| AAS         | atomic absorption spectrometer   | pzc        | point of zero charge                   |
| $C_e$       | equilibrium calcium concentration                                      | pznpc      | point of zero net proton consumption   |
| $C_i$       | initial calcium concentration  | Q          | quartz                                 |
| CEC         | cation exchange capacity   | R          | universal gas constant                 |
| $C_s$       | adsorbed calcium content   | $R^2$      | regression coefficient                 |
| DDL         | diffused double layer  | SSA        | specific surface area                  |
| DTGS        | deuterated triglycine sulfate  | SS         | sodium smectite                        |
| FTIR        | Fourier transform infra-red  | SSR        | silica to sesqui-oxide ratio           |
| G           | specific gravity   | $T$        | temperature                            |
| I           | illite   | TEM        | transmission electron microscopy       |
| $K_F$       | equilibrium (Freundlich) adsorption constant                           | UATR       | universal attenuated total reflectance |
| KT          | kaolinite  | V          | volume of calcium ion solution         |
|             |  | XRF        | X-ray fluorescence                     |
|             |  | XRD        | X-ray diffraction                      |
|             |  | ZP         | zeta potential                         |

equilibrium sorption experiments, and different theoretical models were applied to describe equilibrium sorption isotherms. The variation in calcium adsorption capacity was determined as a function of inherent clay mineralogy and reactive nature, pore fluid chemistry and temperature. Further, the thermodynamic parameters were also calculated to describe the calcium adsorption mechanism.

## 2. Materials and methods

### 2.1. Selection and characterization of clays

For experimental analysis, two commercial clays, kaolin and bentonite, and a raw clay collected from the lake bed situated at Indian Institute of Technology Madras campus, Chennai, Tamilnadu, India, were selected. The preliminary characterization of the clays was carried out for determining the physico-chemical, mineralogical and molecular properties. The specific gravity (G) was determined as per ASTM D5550 (2014), and the percentage of clay-size fraction was obtained according to ASTM D422 (2007). The specific surface area (SSA) and cation exchange capacity (CEC) were determined as per the procedure described in Cerato and Lutenegeger (2002) and ASTM D7503 (2010), respectively. The chemical composition of clays was determined by using X-ray fluorescence (XRF) analysis, with the aid of X-ray analytical microscope (Horiba XGT-2700, Japan).

Further, the mineralogical composition of clays was assessed by performing powder X-ray diffraction (XRD) analysis. The X-ray diffractometer (PANalytical X'pert Pro, Netherlands) equipped with Cu-K $\alpha$  source of wavelength 1.54 Å, monochromator, nickel filter and X'celerator detector was used for this analysis. The goniometer used a fixed divergent slit of 0.87° and 10 mm wide beam mask in front of the X-ray tube. It had soller slits of 0.02 radians and anti-scattering slits of 2° on both source and detector sides. The samples were scanned between 5° and 70° (2 $\theta$ ) with a step size of 0.02° (2 $\theta$ ) and time per step of 20 s, at working conditions of 45 mV and 30 mA.

In view of identifying the major functional groups in the clays which contribute to calcium adsorption, Fourier transform infra-red spectroscopy (FTIR) analysis was performed in middle infra-red (MIR) spectral range (550–4000 cm<sup>-1</sup> wave number). The FTIR instrument (Perkin Elmer Spectrum 100, USA) equipped with deuterated triglycine sulfate (DTGS) detector and universal attenuated total reflectance (UATR) accessory was used for this analysis. The data was collected from the integration of 128 scans and scan resolution was 4 cm<sup>-1</sup>.

### 2.2. Determination of surface charge properties

The variations in the surface charge properties of clays was assessed in terms of zeta potential (ZP) and point of zero net proton consumption (pznpc) measurements, as a function of pH and initial calcium concentration of aqueous solution. For this purpose, clay-calcium ion solutions of varying calcium concentrations up to 1000 mg L<sup>-1</sup> were prepared by using analytical grade calcium chloride (CaCl<sub>2</sub>) salt. The soil suspensions were prepared at a liquid to solid ratio of 20. In addition, clay-lime solutions corresponding to lime saturation pH of 12.6 were prepared by using hydrated lime in order to assess the ZP variation. All solutions were prepared in triplicate and equilibrated for 24 h to ensure proper particle-solution interactions. After equilibration, the ZP was determined based on the principle of electrophoresis, by employing the particle size analyzer (Horiba nano partica SZ 100, Japan). The pH was measured using a glass-pH electrode connected to a pH meter (Elico PE 138, India). Further, the pznpc (a category of point of zero charge, pzc) value corresponding to zero net proton consumption was determined for the clays by salt titration method (Alvarez-Silva et al., 2010). For this purpose, clay-CaCl<sub>2</sub> solutions of 0.1 molarity were prepared at a liquid to solid ratio of 20 over wide range of pH. Later, the equilibrium pH was measured after an interaction period of 24 h. Further, the molarity of calcium ions in the solutions was increased and the subsequent equilibrium pH was measured. Based on the experimental results, a titration curve was plotted between the change in pH (denoted as  $\Delta pH$ ) as ordinate and corresponding equilibrium pH as abscissa. The pH value at the cross over point of the titration curve with zero ordinate (i.e.,  $\Delta pH = 0$ ) was determined as pznpc.

### 2.3. Determination of mineral dissolution properties

The mineral dissolution properties of the clays were evaluated as a function of solution pH and temperature. The wide range of pH representing acidic to highly alkaline environments was considered, along with two different temperatures of 25 °C and 40 °C. The solution pH was adjusted by adding mild acid (HCl) or base (NaOH), and the liquid to solid ratio was maintained as 20. The prepared clay solutions were thoroughly mixed and conditioned for 96 h in temperature controlled environmental chamber with orbital shaking facility. Later, the solutions were centrifuged and the decanted filtrate was analyzed using atomic absorption spectrometer, AAS (ICE 3500, Thermo Scientific, USA) to determine the variations in total dissolved silicon (Si) and aluminium (Al) concentrations. In addition, the field emission gun

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