Chemical processes at the surface of various clays on acid-base titration

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1. Introduction

The chemical reaction of radionuclides at the interface between groundwater and geological mineral is an important process determining their retardation of transport through groundwater flow in a nuclear waste disposal. Clay minerals are major components of soil and argillaceous rock, and some of them are considered to be important base materials in the design of high-level nuclear waste repository due to their large swelling, low-permeability, large surface area, and strong and large sorption of radionuclides. Clay materials are phyllosilicates containing accessory minerals such as metal oxides, hydroxides, oxyhydroxides. Their structures are condensed 1:1 or 2:1 layers of tetrahedral $SiO_{3/2}OH$ and octahedral $Al(OH)_{6/2}$ sheets.

An accurate knowledge about the properties of clay surface is required as a parameter for a long-term estimation of radionuclide retardation effects. Electric surface charge is a primary property determining ion exchange and surface complexation of radionuclides on its surface. The sources of electric surface charge are a permanent structural negative charge on a basal plane and a dissociable charge at an edge surface. Investigation of proton sorption is a prerequisite to the understanding of radionuclide sorption. The reactions on a permanently charged site and on an edge site are measured by an electrokinetic measurement and by potentiometric titration, respectively. However, side reactions such as complexation, proton/cation exchange, dissolution, hydrolysis, precipitation and readsorption, and the reaction of secondary minerals hinder an experimental measurement of accurate acid-base properties[1].

This presentation describes the pH change on dispersing various clays in water and adding acid, base or Eu(III) ion to these solutions, and the effect of Eu(III) ion on acid-base titration of clay solutions.

2. Experimental

Clays of kaolin KGa-1b (low-defect), kaolin KGa-2 (high-defect), palygorskite PFl-1, Ca-montmorillonite STx-1b, and Na-montmorillonite SWy-2 supplied by the Source Clay Mineral Repository (Columbia University, Missouri, USA) were used without any purification. Cation exchange capacity (CEC) and surface area were 2.0, 3.3, 19.5, 84.4 and 76.4 meq/100 g, and 10.5, 23.5, 136.35, 83.79 and 31.82 m^2/g, respectively. The clays of 0.1 g were dispersed in 0, 0.5 and 1.0 M NaCl solutions and shaken for a week. Their relative sedimentation speeds and volumes were visually compared after standing still the dispersed clay solutions. The pH change with time after dispersion of clays (0.5 g for kaolinite and 0.1 g for palygorskite and montmorillonite in 100 ml of aqueous solution of 1 mM $NaClO_4$ and 0.01 mM $HClO_4$) were measured at time intervals of 10 minutes. The dispersed clays were stored in an argon atmosphere for a week, and the pH change with time were measured after sequentially adding NaOH or $HClO_4$ solution and Eu(III) solution. Leached electrolytes from clay in demineralized water or 1 mM $NaClO_4$ of pH 4 and 8 were measured after a week of equilibration and centrifugation (16 krpm, 30 min). The clay solutions equilibrated for a week at pH 4 of 1 mM $NaClO_4$ solution in the absence or presence of 0.1 mM Eu(III) was titrated with 0.1 M NaOH. After the titration, the clay was centrifuged and dried over silica gel in a vacuum chamber and its XRD pattern was measured. Original clay and that washed with 0.1 mM $HClO_4$ were measured together for a comparison.

3. Results and discussion

3.1. Sedimentation in solution. In the case of kaolinite, sedimentation speed was independent of NaCl concentration. The sediment volume of low-defected KGa-1b was smaller than that of high-defected KGa-2. These are the result of low CEC which is related to a permanent negative charge. NaCl concentration effect on sedimentation was conspicuous for montmorillonite. The speed increased and the volume decreased with NaCl concentration. In the absence of NaCl, large portion of clay remained dispersed in aqueous phase even after all the other kinds of clay sedimented. This is understood as the result of expanding of Na-montmorillonite having large CEC. Palygoskite of fibrous clay sedimented fast and sediment volume was large due to small CEC and large surface area.

3.2. Acid-base equilibration in solution. The changing pH with time after addition of various chemicals to clay solutions were presented at Fig. 1 (in case of KGa-2 and SWy-2). After dispersing the clay powders, pH increased continuously more than 2 hours. Considering that the homogeneous reactions, such as dissociation, complexation and ion exchange, reach at equilibrium within a few minutes, the slow increase of pH would come from some slow side reactions which involve a proton/hydroxide balance. The final pH values showed a trend of Na-montmorillonite > Ca-montmorillonite > palygorskite ≫ kaolinite(KGa-1b) > kaolinite(KGa-2), which coincided with the alkali metal content in the clays. When NaOH or $HClO_4$ solution was added to clay solutions, the initial abrupt pH

change was followed by a slow pH increase indicating the presence of slow side reactions.

When Eu(III) solution was added, the increase of pH after abrupt change were small for kaolinite solutions, while large for palygorskite and Na-montmorillonite solutions. In the case of Ca-montmorillonite, the increase of pH was observed only at near neutral solution (pH 7.8) due to small hydroxide generation. In the case of Eu(III) ion addition to the basic solution of kaolinite, the initial fast hydrolysis of Eu(III) and following adsorption with slow dehydrolysis could be assumed. However, the increase of pH was observed in the addition to acidic solutions of palygorskite or Na-montmorillonite, where hydrolysis is not expected. These slow increases of pH might reflect the existence of slow reactions following fast Eu(III) adsorption. The slow reactions interfering fast pH equilibration should be studied more.
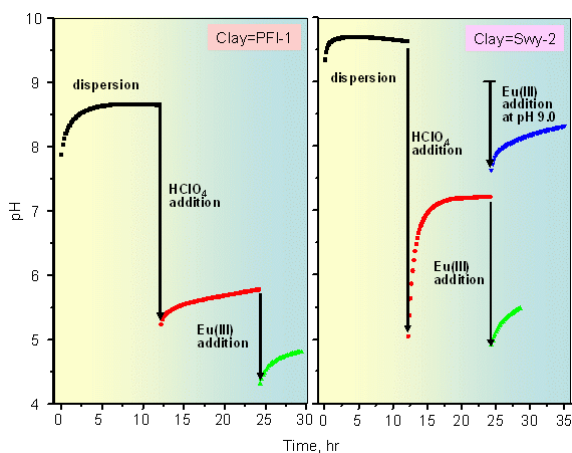

Fig. 1. Acid-base equilibration in some clay solutions.

3.3. Acid-base titration. The clay solutions with or without Eu(III) ion were titrated after equilibrating at pH 4 more than 2 days. To observe the effect of Eu(III) adsorption on a permanently charged site, ionic strength was kept as low as 1 mM NaClO$_4$. The effect of Eu(III) ion on the pH change against NaOH addition depended on clay types. The presence of Eu(III) ion decreased the pH value at the same added amount of OH$^-$. However, in the case of kaolinite, the suppression of pH by Eu(III) ion is divided into two regions, below and above pH 6, indicating different reactions at two regions. Eu(III) is adsorbed to Na-illite clay by outer sphere complex formation on a permanently charged site of basal plane at pH<4 and by inner sphere complex formation on a tetrahedral or octahedral edge site at pH>5[2]. In the case of palygorskite, adsorption type could not be divided on the pH titration curves. The effect of Eu(III) ion on the acid-base reaction of montmorillonite was smaller than that of kaolinite.

XRD pattern of clays of original, Eu(III) adsorbed and washed at pH 4 were measured and compared. Three kinds of clay showed their typical diffraction patterns. However, pretreatment of clay did not affect their XRD patterns.
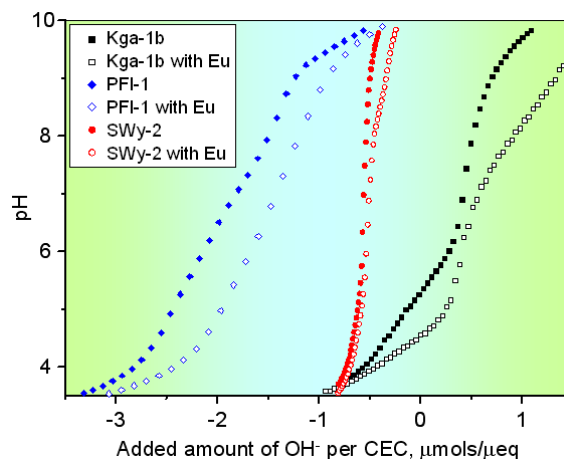

Fig. 2. Effects of Eu(III) on acid-base titration of some clay solutions.

4. Summary

The pH change on dispersing various clays in water and adding acid, base or Eu(III) ion to these solutions, and the effect of Eu(III) ion on acid-base titration of clay solutions were measured. Sedimentation behavior of dispersed clays was different in accordance with their types. Expanding montmorillonites are hard to sediment in water of low electrolyte concentration. The dispersion of clay or the chemical addition to clay solution showed slow pH change following normal fast reactions which indicates the presence of slow side reactions. The effect of Eu(III) ion on the pH change against the added volume of NaOH was different depending on the kinds of clay. In case of kaolinite, Eu(III) adsorptions by cation exchange at pH<6 and by surface complex formation at pH>6 was observed while no conspicuous division at other clays. Pretreatment of clays showed no effect on their XRD patterns.

REFERENCE

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