

THE SORPTION BEHAVIOR OF CS & CD ONTO OXIDE AND CLAY SURFACES

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ABSTRACT

The sorption of Cs and Cd on model soil minerals was examined by complementary analytical and experimental procedures. X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance (NMR) spectroscopy were used to characterize the chemical and physical nature of Cs-reacted soil minerals. Cd and Cs adsorption isotherms for kaolinite were also measured at variable pH and temperature to establish likely reaction stoichiometries, while atomic force microscopy (AFM) was used to characterize the microtopography of the clay surface. XPS analyses of Cs-exchanged samples show that Cs is sorbed at mineral surfaces and at the interlayer site of smectite clays, although the spectral resolution of XPS analyses is insufficient to differentiate between basal, edge or interlayer sites. ^{133}Cs MAS-NMR results also show that Cs is adsorbed primarily in an interlayer site of montmorillonite and on edge and basal sites for kaolinite. Cd adsorption isotherms on kaolinite were found to be additive using $\text{Al}_2\text{O}_3 + \text{SiO}_2$ Cd binding constants. AFM quantification of kaolinite crystallites suggest that edges comprise up to 50% of the BET surface area, and are consistent with NMR and surface charge results that Cs and Cd adsorption occur primarily at edge sites.

INTRODUCTION

Effective disposal of radioactive and mixed waste in near-surface low level radioactive waste (LLW) facilities will ultimately depend upon the geochemical interactions of dissolved aqueous waste with common oxide and silicate minerals. These minerals, which range in complexity from quartz to smectite-like clays, are found in the adjacent soils, if not in the engineered waste facility. The geochemical controls for sorption of hazardous chemical and radioactive wastes onto minerals is often governed by the structure and reactivity of those mineral surfaces (1,2). A fundamental understanding of those mineral-fluid interactions is important for proper evaluation of the waste disposal and retention scenarios, as the site licensing agency must complete a performance assessment (PA) of the proposed LLW disposal site in accordance with regulations.

The key to PA is the ability to model transport and retardation of dissolved radionuclides from a LLW disposal site. Current geochemical models utilize retardation factors (K_D) to handle the uncertainties involved in radionuclide transport (3,4). These models work reasonably well when the site is well characterized, but mixing of groundwater and waste leachate may produce conditions not easily modeled by the K_D method. Although theoretical models exist for modeling sorption processes on minerals, experimental verification of those models lags, as does atomistic characterization of the retardation mechanism.

This study aims to examine the fundamental mechanisms and processes by which soil mineral phases absorb metal cations, specifically non-radiogenic Cs and Cd. Because sorption onto the surfaces of structurally and chemically heterogeneous soil minerals is complex and not very well understood, we have emphasized complementary experimental and analytical studies of metal sorption using model soil minerals. Specifically, we have employed modern spectroscopic techniques, such as X-ray photoelectron spectroscopy (XPS), solid state magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy, and atomic force microscopy (AFM), to characterize surface and bulk properties of reacting soil minerals. Adsorption isotherm measurements were also done at variable pH and temperature to establish likely reaction stoichiometries and bonding enthalpies.

METHODS

Analytical and experimental studies of the cation sorption processes were performed using both natural and synthetic soil mineral samples, including quartz (SiO_2) and corundum (Al_2O_3), gibbsite ($\text{Al}(\text{OH})_3$ from Ouro Preto, Brazil), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ from Warren Co., Georgia), and montmorillonite (Ca-interlayer clay from Apache Co., Arizona). These minerals were chosen to provide increasingly complex structures and chemical sorption sites whereby the process of metal sorption onto soil minerals might be determined. For example, quartz and corundum are simple anhydrous oxides consisting of corner-sharing Si tetrahedra or edge-sharing Al octahedra, whereas gibbsite consists of a partially-occupied Al layer which is octahedrally coordinated by hydroxyl ions. Kaolinite is a 1:1 layer type clay mineral comprised of a tetrahedral SiO_4 layer linked to an octahedral gibbsite layer (TO structure, see Fig. 1). Montmorillonite is a complex 2:1 layer type smectite clay (TOT structure), composed of an Al-deficient octahedral sheet sandwiched between two inward-pointing SiO_4 tetrahedral sheets, where interlayer cations satisfy charge balance. Characterizations of powdered minerals and reacted samples were made using standard analytical techniques (AA, DCP, EDS, ICP-MS, TEM, and XRD) in order to verify the structure of starting materials and reacted phases, and to quantify solution compositions.

After a series of Cs sorption tests, several surface-sensitive spectroscopic techniques were used to characterize the extent and site-specific control of Cs sorption onto these minerals. These techniques include X-ray photoelectron spectroscopy (XPS), which is sensitive to the near-surface ($<<20\text{\AA}$) composition and chemical state of elements, and nuclear magnetic resonance (NMR) spectroscopy, which yields structural and bonding information at the molecular level. In these tests, approximately 1 g of the mineral was reacted with 100 ml of 0.1 or 0.01 M CsCl solutions in polyethylene bottles for 5 days at 25 and 50°C. A shaking bath was used to maintain constant temperature and suspension of the sample. After the test, samples were separated by filtration.

The XPS analyses were performed under vacuum ($\sim 2 \times 10^{-9}$ torr) using a Perkin Elmer PHI 5400 instrument employing Mg K_{α} X-rays and a take-off angle of 45° . Adventitious carbon (C 1s binding energy) provided an internal standard for correcting energy shifts resulting from sample charging. The ^{133}Cs NMR spectra were collected at room temperature and at 65.5 MHz using a spectrometer with a 11.7-T superconducting magnet. Spectra for most samples were collected at room humidity, however, a few kaolinite and montmorillonite samples were collected at 100% relative humidity (RH) in order to evaluate interlayer site occupancy and exchange. Some samples were also cooled or heated in order to evaluate thermal effects upon site occupancy. The ^{133}Cs chemical shifts are reported in parts per million (ppm) relative to an external 0.1 M CsCl solution at room temperature.

Cs and Cd adsorption onto kaolinite was measured as a function of pH at 25 and 50°C . The titrant for the adsorption measurements was 0.1 M NaOH and the pH electrode was calibrated using NBS standards at the temperature of interest. Four g of kaolinite powder (BET surface area $\approx 10 \text{ m}^2/\text{g}$) were titrated in 50 mL of 0.1N NaClO_4 using a Mettler DL12 titrator. Slurries were continuously stirred and N_2 gas was pumped directly into the solution prior to and during each titration to purge CO_2 . Temperature was maintained by adjustment of a hot plate and water bath in which the reaction vessel was immersed. Certified Cs and Cd AA standards were diluted to ppm levels and used as stock solutions. A 0.1 M solution of NaClO_4 was used as the background electrolyte in these adsorption experiments because ClO_4^- complexes with neither Cs nor Cd. Total metal concentrations in sampled solutions were measured by DCP or ICP-MS analytical methods. Cs and Cd adsorption was determined by monitoring metal concentrations as the solutions were titrated to pH ~ 9 . The dissolved metal and pH data were regressed using FITEQL (5) to calculate best fit values of pK_x and site density for Cs and Cd as a function of temperature.

Relative proportions of basal and edge surface area for untreated kaolinite were determined using AFM techniques. Kaolinite was ultrasonically suspended in water for 1 minute. 50 mL of this solution was placed on freshly-cleaved muscovite and air-dried. Images were obtained in contact mode using a Park Scientific Instruments AutoProbe LS (5 mm scanner) and 0.6 mm thick Ultralevers (silicon cantilever and tip). Scanning speeds ranged from 0.5 to 2 Hz. Particle dimensions and step heights were measured on raw images of a few representative grains. These dimensions were used to calculate relative amounts of edge and basal surface area. Estimated errors for calculated surface areas are 10% based on an averaged 5% uncertainty in a single height or length measurement.

RESULTS

A Cs XPS signal was not observed for any of the starting materials, although several Cs peaks were observed for all reacted samples but gibbsite. EDS analyses acquired during XPS analysis indicate that powdered corundum sorbed ~ 0.3 mole % Cs; the kaolinite slab exhibited Cs sorption at the 1 mole % level; and powdered montmorillonite sorbed ~ 2 mole % Cs. Sorbed Cs concentrations were reduced by 50-75% after Ar sputtering of the near surface. Based upon these results, the relative Cs sorption capacity for these minerals is montmorillonite \gg kaolinite \gg corundum \gg gibbsite. In addition to near-surface compositional profiles, XPS can measure shifts in the binding energy of core electrons resulting from a change in chemical environment (chemical

shift). These shifts result from a change in the nearest neighbor, oxidation state or crystal structure. We did not observe a chemical shift for Cs sorbed onto montmorillonite nor kaolinite. Multiple surface or interlayer sites for Cs could not be resolved from the single peak Cs spectra observed for clay mineral samples (Fig. 2). These same samples were also characterized by ^{133}Cs magic angle spinning (MAS)-NMR spectroscopy. There was no observed ^{133}Cs MAS-NMR spectral signal from the corundum or gibbsite samples. The NMR spectra for the montmorillonite samples contain one broad peak at -18 to -12 ppm, whereas the kaolinite samples contain multiple peaks (Fig. 2b), including a large, relatively narrow peak at a more shielded chemical shift (-40 to -25 ppm) along with several other weak peaks. Higher concentrations of Cs in the reacting solution, as well as lower temperatures and higher humidity, resulted in less shielded chemical shifts. There was increased peak broadening for kaolinite and montmorillonite with decreasing temperature, although separate peaks were unresolved even at -80°C.

Cs and Cd adsorption measurements onto a kaolinite clay substrate show that metal binding is favored at high pH, although Cd is more strongly bound to kaolinite relative to Cs (Fig. 3). Generally, association of metals with hydroxylated mineral surfaces parallels metal-hydroxyl association at high pH in aqueous solutions. The weak binding of Cs relative to Cd therefore, arises from its proportionally weaker tendency to hydroxylate. Potentiometric titrations were done on Al_2O_3 (6) and SiO_2 (7) to resolve pH-dependent surface charge and calculate Al and Si surface site acidities. Adsorption measurements were subsequently done with Cd and regressed to calculate metal binding constants for each oxide. Potentiometric titration measurements were also made with kaolinite slurries at 25 and 50°C to evaluate the pH-dependence of multi-site surface charge as a function of temperature. Proton donor-acceptor reactions were found to occur simultaneously on the Si and Al sites exposed at basal planes and edges. We found that the Si site acidity at the kaolinite-solution interface differs minimally from that of pure SiO_2 , whereas Al sites became appreciably more acidic with substitution into the kaolinite matrix. Increasing temperature causes both Al and Si sites to become more acidic, the Si sites more so than the Al sites. Calculated site densities increase with increasing temperature suggesting appreciable surface roughening. The combination of increasing site acidity and density points to kaolinite having a greater sorptive potential at higher temperatures.

Particles of untreated kaolinite ranges from 0.1 to 0.8 mm in diameter and 100 to 1200 Å in total thickness. Edge to basal surface area ratios range from 15 to 50%. Edge surface area from small steps on the surface (Fig. 1b), typically 1 to 10 unit cells high (7 to 70 Å), increases the edge area obtained from the gross shape of the grain by a minimum of 10%. The additional contribution of step edge area depends on the number of and average height of the steps. The potentiometric titration results require a site density of 2.25 sites/nm² to explain the amount of adsorption assuming that the entire BET surface area sorbs hydrogen or hydroxyl ions. Crystallographic site densities are estimated to be 3 to 6 sites/nm². Therefore, if adsorption occurs only at edge sites where the density of charged sites is highest, then a minimum of 38% of the BET surface area must be edge surface. This amount of edge surface is approximately the median of the range gleaned from limited AFM observations.

DISCUSSION

One of the primary goals of this study is to identify the specific sites for metal adsorption.

Two spectroscopic techniques were employed to characterize Cs-sorbed minerals. XPS surface spectra of reacted montmorillonite samples suggests almost complete exchange of cesium for the original interlayer calcium. Mineral structures without exchangeable cation sites yielded spectra characterized by the presence of strong Cs signals, indicative of Cs sorption on mineral surfaces and along grain boundaries. The presence of single, unresolvable XPS peaks also suggests that the chemical shifts associated with Cs adsorption on edge or basal sites are not very strong. NMR spectra obtained from Cs reacted montmorillonite indicate the presence of a range of interlayer sites that are dynamically averaged at temperatures above approximately 20°C. Room temperature ^{133}Cs MAS-NMR spectra for the kaolinite samples, however, show the presence of as many as four distinct sites. The bulk of these sites are thought to be edge and basal plane sites, in addition to some smectite-like 'exchangeable layer' sites. The latter probably result from the presence of small quantities of smectite-like layers on the kaolinite crystallites. Given the sheetlike structure of kaolinite (see Fig. 1), exposed Si and Al sites at the crystal's edge would provide likely sorption sites suggested by the ^{133}Cs NMR spectra.

We also sought to determine if soil clay K_D 's could be estimated from simple oxide component reactivities. Cd sorption onto kaolinite at 25°C is shown in Fig. 3b as a function of pH. The line through the results was independently calculated from the Cd binding constants measured on the single oxides Al_2O_3 and SiO_2 . The quality of this fit is exciting because it suggests that metal binding on clay minerals is additive from the oxide components. Note that metal adsorption isotherms have already been measured on the most important (hydr)oxides in soils. The goodness-of-fit of the two-site model suggests that, of the four sites indicated by the NMR work, only two dominate the overall sorptive capacity of kaolinite. However, interlayer cations and multivalent cations commonly found in smectite clays will probably pose special problems when predicting additive adsorption properties for those minerals given the compositional and surface charge variability of expandable 2:1 layer clays. We are, therefore, in the process of extending our efforts to specifically account for these effects. The end result of this work will, ideally, be a methodology by which K_D 's can be predicted for soils.

AFM examination of the untreated kaolinite demonstrates that edges may comprise over 50% of the available sorbing surface. It is known that metal sorption onto clay surfaces is a function of the charge distribution on the surfaces as well as the absolute proportions of exposed planes of differing surface charge. Although total surface areas can be measured using routine BET methods, the best way to determine proportions of edge and basal surface is to use an imaging technique where all three dimensions can be determined on individual particles. The easiest method for doing this is AFM (8,9). Basal kaolinite surfaces often contain numerous steps of one to a few unit cells in height. AFM examination of a few kaolinite grains revealed at least a 10% increase of edge surface area from such steps beyond that estimated from average particle dimensions. Better statistical characterization of surface area proportions could affect significantly the interpretation of both NMR and experimental adsorption data.

CONCLUSION

XPS analyses of Cs-reacted soil minerals show that Cs is sorbed on the surfaces of corundum, kaolinite, and montmorillonite, but not on gibbsite. The XPS spectra suggest that Cs is sorbed on the interlayer site of montmorillonite and possibly on kaolinite, although the spectral resolution of

XPS analyses is insufficient to differentiate between basal, edge or interlayer sites. ^{133}Cs MAS-NMR results demonstrate that Cs is adsorbed in a motionally-averaged interlayer site of montmorillonite. For kaolinite, most of the adsorbed Cs is found on edge and basal sites. Measured sorption isotherms for Cd were found to be additive for simple mixed-oxide clays, suggesting a potential mechanism for predicting the sorptive capacities of other clays. A physicochemical rationale for component oxide acidity shifts in multi-oxide silicates remains an important obstacle. Quantification by AFM of edge and basal surface area for kaolinite showed that edges can comprise as much as 50% of the total BET surface area. This is consistent with interpretation of H^+/OH^- adsorption occurring primarily at charged edge sites. By implication, the combined AFM and NMR results suggest that Cs and Cd adsorption also occur primarily at edge sites. These results provide a generalized and systematic method for evaluating adsorption of metals on soil minerals, and could lead to innovative techniques promoting the fixation of the metal (radionuclide) species.

ACKNOWLEDGMENTS

This work was supported by the U.S. Nuclear Regulatory Commission and the U.S. Department of Energy under Contract No. DE-AC04-94AL85000 to Sandia National Laboratories.

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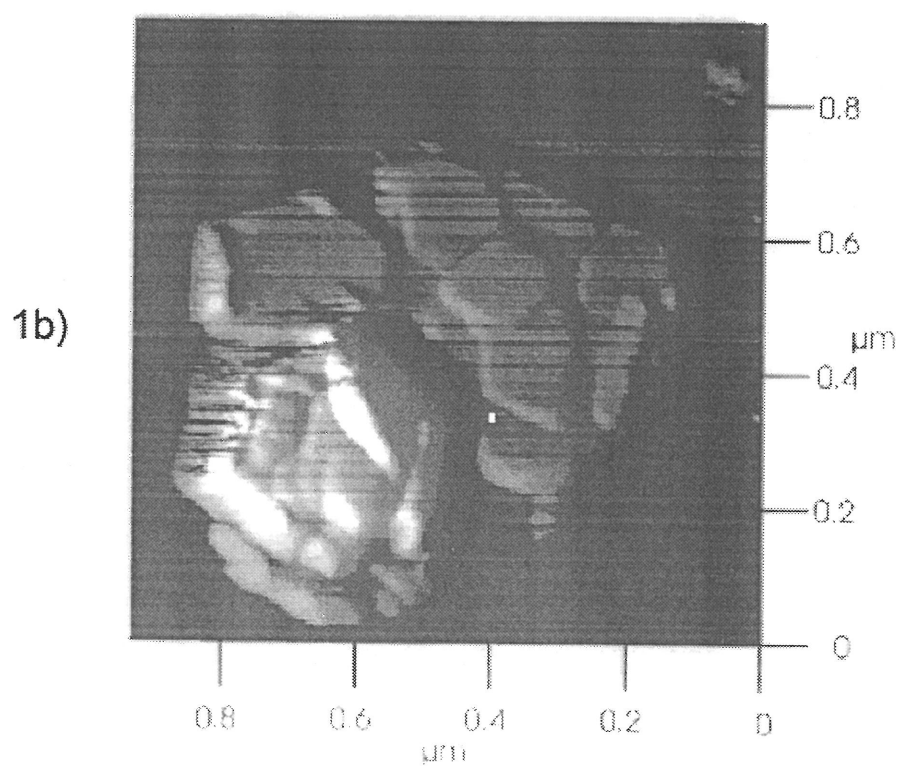
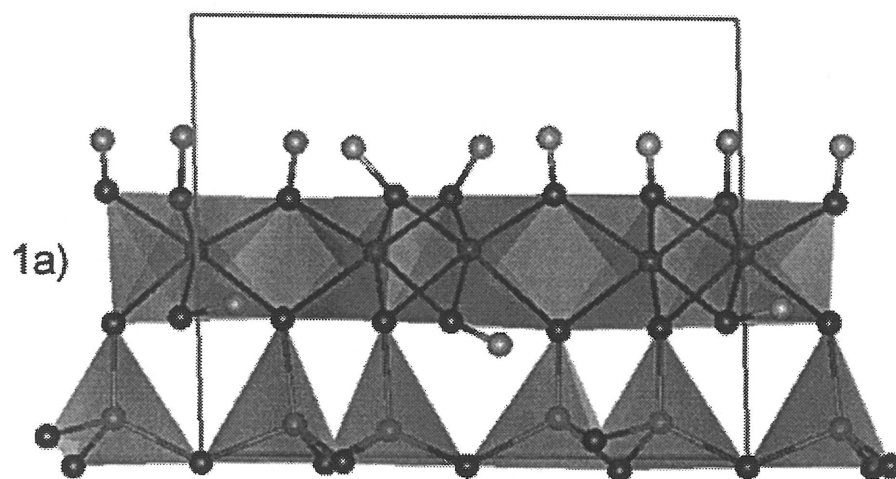
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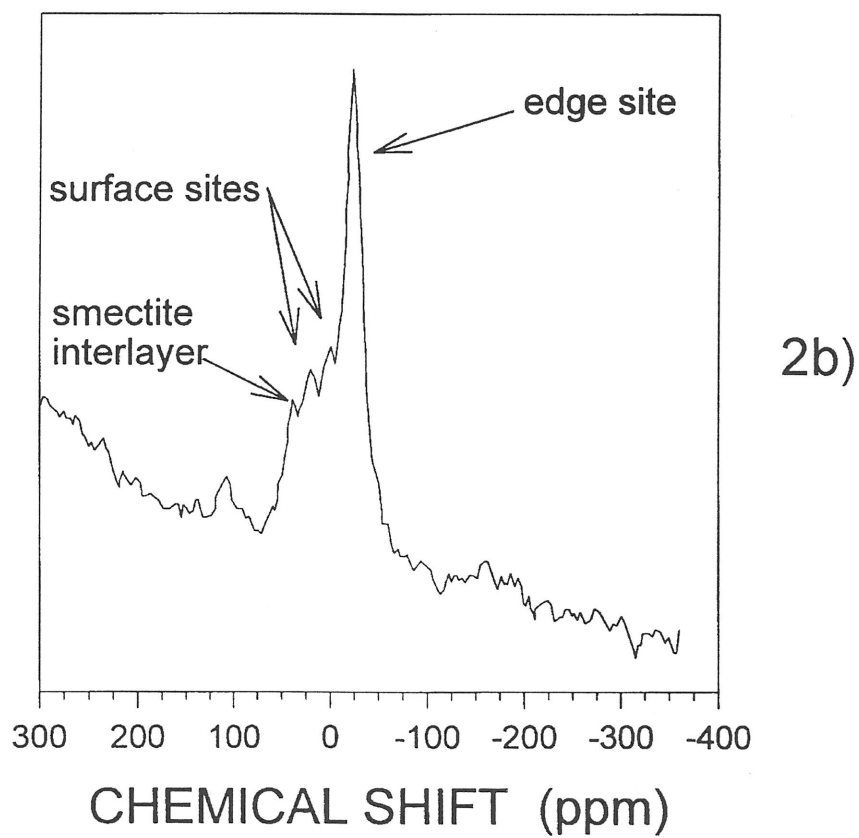
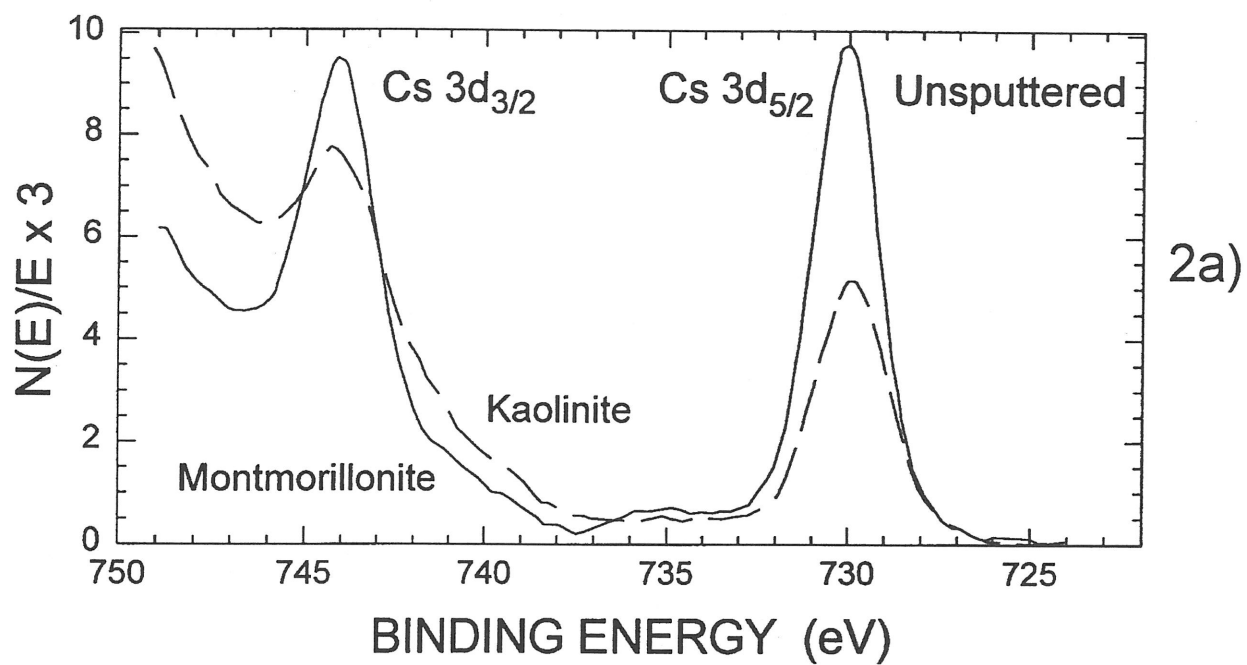
FIGURE TITLES

Fig. 1. Kaolinite clay ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$): 1a) Schematic of kaolinite structure along (100); note that the SiO_4 tetrahedral layer is apically bonded to a gibbsite-like octahedral layer; the basal spacing is 7.1 Å; 1b) AFM image of kaolinite crystallites with (001) orientation; note the well-developed hexagonal habit. Particle at upper right contains surface steps ~800 Å in diameter. Step thicknesses average 7-8 unit cells in height; average particle thickness excluding surface steps is 290 Å. Assuming particle is hexagonal in shape and that similar steps occur on both basal surface, the total edge surface area is 0.048 mm²; total basal area is 0.325 mm².

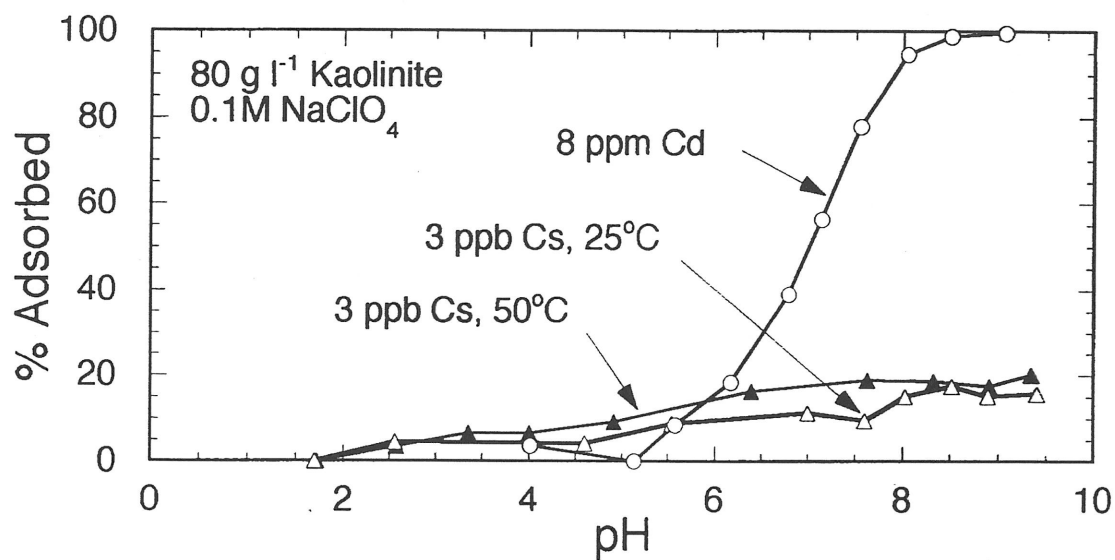
Fig. 2. XPS and NMR spectra: 2a) High resolution XPS spectra for unspattered kaolinite and montmorillonite after reaction with 0.1 N CsCl solution at 50°C for 120 hours; the single peaks do not identify the presence of multiple surface or interlayer sorption sites; 2b) ¹³³Cs MAS NMR spectrum for kaolinite after reaction with 0.1 N CsCl solution at 25°C for 5 days; one broad and three minor peaks have been assigned to edge, surface and 'interlayer' Cs sorption sites.

Fig. 3. Adsorption isotherms for Cs and Cd onto kaolinite: 3a) Measured Cs and Cd adsorption isotherms as a function of pH; note the strong sorption of Cd at high pH relative to the weak binding of Cs; 3b) Adsorption isotherm of Cd (solid line) calculated from Cd binding constant of SiO_2 and Al_2O_3 is plotted against Cd adsorption measurements (filled circles) at 25°C.





3a)



3b)

