Change in the site density and surface acidity of clay minerals by acid or alkali spills and its effect on pH buffering capacity

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Changes in the site density and surface acidity constants (i.e. pKa₁ and pKa₂) of kaolinite and montmorillonite were determined after acid or alkali spills, and pH buffering capacity was evaluated as a parameter of soil function change. Surface complexation modeling with potentiometric titrations and Fourier-transform infrared spectroscopy showed that acid or alkali spills did not significantly change the surface properties of kaolinite. In montmorillonite, however, acid spills decreased the basal site density from 832 to 737 mmol kg⁻¹ by dissolving substituted octahedral cations and decreased pKa₂ from 7.32 to 5.42 by dissolving SiOH. In response to alkali spills, the basal site density increased to 925 mmol kg⁻¹, and the edge site density increased from 84.8 to 253 mmol kg⁻¹ due to AloH and SiOH formation; thus, pKa₂ decreased to 6.78. The pH buffering capacity of acid- or alkali-spilled kaolinite at pH 6 did not significantly change, while that of acid- or alkali-spilled montmorillonite increased from 30.3 to 35.9 and 56.0 mmol kg⁻¹, respectively. Our results indicate that these spills greatly altered the surface properties of montmorillonite, but unexpectedly, increased the pH buffering capacity of montmorillonite.

As the chemical industry develops, chemical accidents occur annually, and of them, acid or alkali spills are of great concern because of their high frequency and hazard. According to the Chemistry Safety Clearing-house database, acid or alkali spills accounted for 46% of the chemical accidents in South Korea. If acid or alkali spills onto soil, most of the physicochemical properties of soil are altered, such as pH, organic matter content, base saturation, exchangeable cations, and surface area. Although neutralizers have been poured onto acid- or alkali-spilled soils for pH recovery, neutralization cannot recover nonreversible dissolution of organic matter or clay minerals and the change in cation exchange capacity (CEC) caused by the structural deterioration. Changes in these properties will alter soil functions, particularly pH buffering capacity. Because pH buffering capacity is related to soil productivity and the water quality of stream water near soil, studies of the change in pH buffering capacity of acid- or alkali-spilled soil after neutralization are needed.

For this purpose, the effects of acid or alkali spills on organic matter and clay minerals, the soil constituents that determine the pH buffering capacity of soils, should be analyzed. In the case of organic matter, acid or alkali spills desorb or dissolve it, thus, the pH buffering capacity decreases. However, the effect of these spills on clay minerals is unclear. Little attention has been paid on changes in clay minerals’ properties due to these spills. Only a few studies revealed that an acid or alkali treatment at room temperature over two weeks not only altered a crystal structure of clay minerals but also increased surface area. Instead, many studies have focused on an acid or alkali activation treating clay minerals with high concentration of acid or alkali, and its effect on clay minerals’ surface area, porosity and surface acidity. Also, there have been several studies on soil acidification phenomenon, and they revealed that the long-term acidification led to chemical weathering of clay minerals and decreased the base saturation.

However, these reaction conditions are unrealistic in natural environment after acid or alkali spills. To predict the pH buffering capacity of acid- or alkali-spilled clay minerals, clay minerals’ site density and surface reaction constants should be determined. It has been known that two major pH buffering reactions of clay minerals are protonation or deprotonation reaction of edge sites, and proton exchange reaction of basal sites. Previous studies have successfully identified the site density of surface functional groups in clay minerals and their surface.
reaction constants using surface complexation modeling\textsuperscript{25,26}. Nevertheless, a few studies exist investigating alterations of surface properties of clay minerals at ambient temperature following intensive acid or alkali treatment, which is similar to acid or alkali spills, by using surface complexation modeling. In addition, clay minerals play a significant role in the pH buffering capacity of soils with low organic matter content resulting from acid or alkali spills; thus, knowledge of the changes in clay minerals’ properties after these spills is essential to interpret the pH buffering capacity of the soils.

The goals of this study were to investigate changes in the site density and surface reaction constants of the neutralized clay minerals after acid or alkali spills and evaluate their effect on the pH buffering capacity as an indicator of soil function. Kaolinite (KGa-1b, Georgia) and montmorillonite (SWy-3, Wyoming), which are typical 1:1 and 2:1 clay minerals, respectively, were selected in this study. Three different samples (untreated, acid-spilled, and alkali-spilled) were prepared by treating with deionized water, 5 M HCl, and 5 M NaOH, respectively, and they were neutralized, and their surface properties before and after acid or alkali spills were compared. The site density and surface acidity constants were determined by a potentiometric titration using surface complexation modeling, and the change in the pH buffering capacity resulting from acid or alkali spills was investigated.

### Results and Discussion

**XRD characterization of three different clay minerals.** The XRD patterns of three different kaolinite and montmorillonite samples are shown in Fig. 1, and the results of quantitative analysis are summarized in Supplementary Table S1. The untreated kaolinite and montmorillonite were mainly composed of pure kaolinite (98%) and montmorillonite (79%), respectively. The untreated kaolinite contained an anatase (2%), and the untreated montmorillonite contained a quartz (13%) and cristobalite (8%). The results are consistent with the previous baseline study on the XRD patterns of KGa-1b kaolinite and Swy-2 montmorillonite\textsuperscript{24}.

| Clay minerals   | Condition | Concentration of Dissolved Constituent Elements (mg (g clay minerals)) | Al | Si | Fe | Mg |
|----------------|-----------|---------------------------------------------------------------------|----|----|----|----|
| Kaolinite       | Acid      | 2.67 ± 0.15                                                        | 0.74 ± 0.04 | 0.25 ± 0.01 | 0.03 ± 0.00 |
|                 | Alkali    | 21.8 ± 1.00                                                        | 25.0 ± 2.3 | 0.48 ± 0.14 | 0.02 ± 0.00 |
| Montmorillonite | Acid      | 9.09 ± 1.56                                                        | 18.8 ± 6.2 | 11.3 ± 1.19 | 1.99 ± 0.34 |
|                 | Alkali    | 1.24 ± 0.28                                                        | 104 ± 11.5 | 2.61 ± 0.16 | 0.11 ± 0.06 |

Table 1. Dissolution of the clay minerals’ constituent elements by acid or alkali spills measured by ICP-OES. The concentration of dissolved elements are the average values of triplicate experiments.

Dissolution of major elements of clay minerals by acid or alkali spills. The concentrations of dissolved elements of kaolinite and montmorillonite as a result of acid or alkali spills are summarized in the Table 1.
The dissolved Al and Si concentrations of kaolinite after acid spill were 2.67 mg-Al g\(^{-1}\) and 0.737 mg-Si g\(^{-1}\), respectively, and those after alkali spill were 21.8 mg-Al g\(^{-1}\) and 25.0 mg-Si g\(^{-1}\), respectively. Kaolinite was more susceptible to alkali spill than to acid spill. In the case of montmorillonite, while the dissolved Al and Si concentrations after acid spill were 9.09 mg-Al g\(^{-1}\) and 18.8 mg-Si g\(^{-1}\), respectively, those after alkali spill were 1.24 mg-Al g\(^{-1}\) and 103 mg-Si g\(^{-1}\), respectively. While more than five times of the octahedral cations such as Al, Fe and Mg were dissolved by acid spill than by alkali spill, the tetrahedral cation, Si, was dissolved five times more by alkali spill than by acid spill. The high dissolution of octahedral cations as a result of acid spill was probably because protons preferentially attack the isomorphic substituted elements in octahedral sheet during acid treatment\(^{28}\).

**Irreversible alteration on site density and surface acidity constants resulting from acid or alkali spills.** The titration curves of three different kaolinite and montmorillonite samples under different NaNO\(_3\) concentration are shown in Fig. 2. As shown, acid or alkali spills have a greater effect on the titration curves of montmorillonite than those of kaolinite, and the background electrolytic concentration had a limited effect on the titration curves of both kaolinite and montmorillonite at pH values of 4–9. The reversibility test of three different montmorillonite samples, KH was also included in fitting parameters. The detailed procedure of parameter optimization is summarized in the Supplementary Information. *Not determined by optimization, but the average value of other research\(^{56,58–70}\).*

**Table 2.** Optimized surface properties of three different kaolinite and montmorillonite samples using FITQUEL. The Ka\(_1\), Ka\(_2\), edge site density and basal site density were fitting parameters and optimized. In montmorillonite samples, K\(_H\) was also included in fitting parameters. The detailed procedure of parameter optimization is summarized in the Supplementary Information. *Not determined by optimization, but the average value of other research\(^{56,58–70}\).*

The dissolved Al and Si concentrations of kaolinite after acid spill were 2.67 mg-Al g\(^{-1}\) and 0.737 mg-Si g\(^{-1}\), respectively, and those after alkali spill were 21.8 mg-Al g\(^{-1}\) and 25.0 mg-Si g\(^{-1}\), respectively. Kaolinite was more susceptible to alkali spill than to acid spill. In the case of montmorillonite, while the dissolved Al and Si concentrations after acid spill were 9.09 mg-Al g\(^{-1}\) and 18.8 mg-Si g\(^{-1}\), respectively, those after alkali spill were 1.24 mg-Al g\(^{-1}\) and 103 mg-Si g\(^{-1}\), respectively. While more than five times of the octahedral cations such as Al, Fe and Mg were dissolved by acid spill than by alkali spill, the tetrahedral cation, Si, was dissolved five times more by alkali spill than by acid spill. The high dissolution of octahedral cations as a result of acid spill was probably because protons preferentially attack the isomorphic substituted elements in octahedral sheet during acid treatment\(^{28}\).
Regard the surface acidity constants (i.e., pKa1 and pKa2), an acid or alkali spill did not cause meaningful changes in the kaolinite (i.e., less than a 0.5 pKa value) except the pKa2 of the alkali-spilled kaolinite increased from 5.49 to 6.34. In the case of montmorillonite, the pKa values greatly changed compared to those of the kaolinite (i.e., greater than a 0.5 pKa value) except for the pKa2 value of the acid-spilled montmorillonite. The pKa value of the alkali-spilled montmorillonite increased from −5.79 to −5.00, while the pKa2 value of the acid-spilled montmorillonite greatly decreased from 7.32 to 5.42 and that of the alkali-spilled montmorillonite decreased to 6.78. In addition, the proton exchange reaction constant of montmorillonite (pKd) changed from 1.51 to 0.72 and 1.85 as a result of an acid or alkali spill, respectively.

According to the Fig. 2, titration curves of the kaolinite and montmorillonite only slightly changed under the different concentrations of background electrolyte. In the case of kaolinite, this was probably because the edge site density was approximately five times higher than the basal site density, which was consistent with previous studies. Thus, the effect of the proton exchange reaction of the kaolinite's basal sites on the titration curve was relatively small in a range of pH 4–9 (see Supplementary Fig. S2). In contrast to the kaolinite, the basal site density of montmorillonite was approximately 5–10 times higher than its edge site density, which was consistent with previous research summarized in Bourg et al. However, the concentration of the electrolyte also had a slight effect on the titration curves of montmorillonite, and this might be because montmorillonite used in this study has a high affinity to Na+. Basal sites were saturated with Na+ at pH values of 4–9; thus, the proton exchange reaction could be negligible within this pH range (see Supplementary Fig. S2). This indicated that the pH buffering of both kaolinite and montmorillonite was largely determined by the edge site reactions rather than those of the basal sites at pH 4–9. Thus, it is reasonable that the larger change in the titration curves of the montmorillonite compared to that of the kaolinite resulting from acid or alkali spills was probably because of the greater alterations on the edge sites’ properties in the montmorillonite.

**Structural modification due to acid or alkali spills.** FT-IR spectra of the three different kaolinite and montmorillonite samples are shown in Fig. 3; the band assignments of the Clay Minerals Society’s source clay (KGa-1b kaolinite, Swy-2 montmorillonite) were used in this study. All absorption bands, particularly the Si-O of the tetrahedral sheet at 400–1100 cm⁻¹, Si-O-Si at 472 cm⁻¹, Al-O-Si of the octahedral sheet at 541 cm⁻¹, and the OH hydroxyl groups at 915, 938, and 830–3700 cm⁻¹, of the untreated kaolinite were observed and the positions of the bands were nearly the same as the reference. However, the untreated montmorillonite (Swy-3) used in this study had a similar but slightly different shape and position of bands compared to the Swy-2 montmorillonite in the reference. The absorption band assigned for Al-O-Si, found in Swy-2 at 524 cm⁻¹, was observed near 512 cm⁻¹, and the band assigned for the Si-O of the tetrahedral sheet, found in Swy-2 montmorillonite at 1041 cm⁻¹, was not observed in the untreated montmorillonite. Instead, the strong band at 1080 cm⁻¹ was observed, and it might be because the untreated montmorillonite contained some quartz and cristobalite whose bands assigned to the Si-O were observed near 1080 cm⁻¹. It is supported by the FT-IR spectra observed at 778 and 978 cm⁻¹, which are assigned to the Si-O of quartz and cristobalite, respectively. These results are consistent with the result of XRD analysis (Fig. 1 and Table S1) and the FT-IR baseline study. The other bands were similar to those of the Swy-2 montmorillonite. Absorption bands at 842, 885, and 917 cm⁻¹ were assigned to octahedral sites where isomorphic substitution occurred, and the band at 3627 cm⁻¹ was assigned to the hydroxyl groups of octahedral cations, particularly Al³⁺.

Acid or alkali spills did not significantly change the FT-IR spectra of the kaolinite. All the absorption bands were in the same position and the intensity of the bands was minimally altered. This indicated that limited structural alteration occurred. This is consistent with little changes in XRD patterns and qualitative analysis of kaolinite after an acid or alkali spill (Fig. 1 and Table S1). It is also supported by the results of the titration experiment in which surface reaction constants and site density did not appreciably change as a result of an acid or alkali spill (Table 2). In addition, previous studies revealed the similar result that kaolinite, which is one of the non-swelling minerals, is the most resistant clay mineral to acid or alkali attacks.

The acid- or alkali-spilled montmorillonite showed different FT-IR spectra compared to those of the untreated montmorillonite (Fig. 3). As a result of acid spill, the intensity of the bands assigned to the isomorphically
substituted octahedral cation sites (i.e., Al-(Mg, Fe, Al)-OH) decreased. This result was probably because of the great amount of dissolution of Fe and Mg in montmorillonite after acid spill (Table 1). It is also supported by the XRD quantitative analysis that the proportion of montmorillonite did not change by acid spills. It implied that the decrease in the basal site density of the acid-spilled montmorillonite was due to the dissolution of isomorphically substituted octahedral cation sites. In addition, acid spill decreased the intensity of the band for the Si-O-Si sites of montmorillonite, while the Si-O band at 1080 cm$^{-1}$ was shifted to 1090 cm$^{-1}$ at which the Si-O band of cristobalite was assigned\textsuperscript{31}. Together with the results of the XRD quantitative analysis (Table S1), the FT-IR spectra indicated that acid spills dissolved Si from montmorillonite and cristobalite was formed. Madejová also observed the similar trend in smectite that the amorphous silica was newly formed after acid treatment\textsuperscript{32}.

In contrast to acid spill, alkali spill increased the intensity of the band assigned to the isomorphically substituted octahedral cation sites of montmorillonite, which corresponds with the optimized basal site density in Table 2. Alkali spill increased basal site density by about 10% (Table 2), which matched with the increasing ratio of montmorillonite by alkali spills (Table S1); Thus, the possible reason for the increase can be ascribed to the enrichment of montmorillonite by alkali spill. Regarding the Si environment in montmorillonite, alkali spill decreased the intensity of Si-O bands of quartz and cristobalite at 778, and 798 cm$^{-1}$, respectively, which is consistent with the XRD results of alkali-spilled montmorillonite. The absorption band assigned to the Si-O of the tetrahedral sheet, which was not observed in the untreated or acid-spilled montmorillonite, appeared in the alkali-spilled montmorillonite at 1041 cm$^{-1}$. In addition, the intensity of the band assigned to hydroxyl group at 3627 cm$^{-1}$ increased by alkali spills, which corresponds to the increase in the edge site density of alkali-spilled montmorillonite from titration experiment (Table 2). According to Table 2, the alkali-spilled montmorillonite had different Ka values than those of the untreated montmorillonite. The results of FT-IR analysis and optimized Ka values indicate that alkali spills increased the proportion of montmorillonite by dissolving quartz and cristobalite, and also changed the surface functional groups’ properties by forming new AlOH and SiOH in montmorillonite.

FT-IR spectra demonstrated that montmorillonite was more vulnerable to acid or alkali spills compared to kaolinite, and had good agreement with the optimized site density (Table 2). This was probably because H\textsuperscript{+} and OH\textsuperscript{-} could attack not only the edges but also the swollen interlayer of the montmorillonite\textsuperscript{8,34}. The results indicated that the extent of change in the surface properties resulting from an acid or alkali spill varied with the type of clay mineral, and especially, an expandability should be carefully considered.

**Interpretation of the change in Ka\textsubscript{2} using first principle molecular dynamics results.** Experimentally derived Ka represented the average Ka of the reactive edge sites in the clay minerals. It is difficult to directly compare the Ka derived from the titration experiment to those calculated from first principle molecular dynamics (FPMD)\textsuperscript{35,36}. In addition, the interpretation of pKa\textsubscript{2}, generally less than 0, optimized from the titration experiment was inherently limited because the titration data at the pH near pKa\textsubscript{2} were meaningless because of the dissolution of the clay minerals. However, a previous study showed that the experimental Ka\textsubscript{2}, optimized by assuming one edge site with a constant capacity model, well matched the Ka calculated from FPMD\textsuperscript{37}; thus, it is possible to interpret pKa\textsubscript{2} in terms of the theoretically calculated pKa. Liu et al. compared the optimized Ka values of kaolinite and montmorillonite from various titration experiments with the theoretical values calculated based on FPMD; these values are summarized in Supplementary Table S2\textsuperscript{37,38}. The pKa values of three different kaolinite and montmorillonite samples optimized from this study coincided well with the calculated and experimentally fitted values from other references. This indicated that the edge sites detected from the titration experiments represented surface functional groups as summarized in Supplementary Table S2.

The pKa\textsubscript{2} of the untreated and acid-spilled kaolinite (5.49 and 5.94) was similar to calculated pKa of AlOH sites of kaolinite (5.7), while that of the alkali-spilled kaolinite (6.34) was near the average value of calculated pKa of AlOH and SiOH sites of kaolinite (6.3). However, considering little changes in kaolinite samples’ titration curves, XRD, and FT-IR, the differences in pKa values were just theoretically generated during the optimization process. In case of montmorillonite, the pKa\textsubscript{2} of the untreated montmorillonite (7.32) was similar with the average value of calculated pKa of SiOH and AIOH sites of montmorillonite (7.87), while that of the acid-spilled montmorillonite (5.42) was near the calculated pKa of AIOH sites of montmorillonite (approximately 5.5). It indicated that acid spills decreased SiOH sites of montmorillonite and this is consistent with FT-IR spectra results that acid spills dissolved Si from the untreated montmorillonite and formed the cristobalite. Because theoretical pKa of edge sites was calculated from pure clay minerals, the formation of cristobalite would make pKa of the acid-spilled montmorillonite further different from the untreated montmorillonite. Also, decrease in substituted octahedral sites of the acid-spilled montmorillonite might affect pKa\textsubscript{2}, because isomorphic substitutions increased the adjacent edge sites’ pKa\textsuperscript{39,40}. In the case of the alkali-spilled montmorillonite, pKa\textsubscript{2} (6.78) was between that of the untreated and acid-spilled montmorillonite. Both SiOH and AIOH increased after alkali spills (Fig. 3); thus pKa\textsubscript{2} changed less than the acid-spilled montmorillonite. These results indicated that changes in pKa\textsubscript{2} by acid or alkali spills was primarily because of dissolution or formation of surface functional groups, which have different theoretical pKa values.

**Effect of acid or alkali spills on pH buffering capacity.** The pH buffering capacity was the reciprocal of the slope of the titration curve, and it was calculated from the following Equation (1):

\[
\text{pH buffering capacity at pH} = \left( \frac{\text{TOTH}_{\text{pHx}} + 0.1}{\text{TOTH}} \right) / 0.1
\]

where, TOTH\textsubscript{pHx} (mol L$^{-1}$) is the total amount of proton added to the suspension of clay minerals during the titration until the suspension pH reaches a value of x. Because the initial pH of the suspension of all the clay minerals ranged from 5.5 to 6.5, the pH buffering capacity at pH 5.5, 6.0 and 6.5 was calculated from the titration curves predicted by using surface complexion modeling under 0.001 M NaNO\textsubscript{3} condition (Fig. 4).
Acid or alkali spills slightly decreased the pH buffering capacity of the kaolinite at pH 5.5, 6.0, and 6.5 from 19.2, 17.6, and 14.6 mmol kg$^{-1}$ to 17.6 or 18.2, 15.8 or 16.6, and 14.2 or 14.6 mmol kg$^{-1}$, respectively. In the case of montmorillonite, these spills increased the pH buffering capacity at pH 5.5, 6.0 and 6.5 from 37.7, 30.3 and 27.9 mmol kg$^{-1}$ to 44.5 or 63.2, 35.9 or 56.0, and 32.7 or 55.8 mmol kg$^{-1}$, respectively. Because the surface reaction constants and site density determined the pH buffering capacity, the pH buffering capacity of montmorillonite, of which the surface properties were greatly altered by the acid or alkali spills compared to those of kaolinite, was more affected by these spills than kaolinite.

Acid or alkali spills do not result in meaningful changes in the pH buffering capacity of kaolinite, but, unexpectedly, increased the pH buffering capacity of montmorillonite. It indicated that acid or alkali spills do not have an adverse effect on the pH buffering capacity of clay minerals, which is the indicator of soil functions, after neutralization. However, in reality, soils contain not only clay minerals, but also organic matter; thus, the pH buffering capacity of acid- or alkali-spilled soils could change in a different manner from that of a single clay mineral alone. Organic matter is known as the most important component determining pH buffering$^2$, and it may have a pH buffering capacity 300 times higher than that of kaolinite$^3$. Because acid or alkali spills would decrease organic matter contents via desorption and dissolution$^{14-16}$, these spills might cause a decrease in the pH buffering capacity of acid- or alkali-spilled soils despite an increase in the pH buffering capacity of single clay minerals. Nevertheless, the results of the pH buffering capacity of clay minerals in this study clearly show that the pH buffering capacity was not deteriorated, but rather increased in montmorillonite after acid or alkali spills.

Conclusions

In this study, we investigated the change in surface properties of clay minerals due to acid or alkali spills and its effect on the pH buffering capacity as an indicator of soil functions. Surface complexation modeling indicated that acid or alkali spills did not significantly change the site density of surface functional groups and their surface acidity constants in kaolinite. In contrast, acid or alkali spills greatly changed the site density and surface acidity constants of montmorillonite. Acid spills dissolved isomorphically substituted octahedral cations and SiOH sites in montmorillonite. In addition, alkali spills dissolved the quartz and cristobalite and edge sites such as AlOH and SiOH sites were newly formed in montmorillonite. Regarding the pH buffering capacity of clay minerals, acid or alkali spills did not have an adverse effect on it, but rather increased in montmorillonite. Soil generally contains organic matter, which plays a significant role in pH buffering, and thus further research with field soil is needed to delineate the effect of acid or alkali spills.

Materials and Methods

Preparation and characterization of clay minerals. KGa-1b kaolinite (Georgia) and SWy-3 montmorillonite (Wyoming) were purchased from the Clay Minerals Society’s Source Clays Repository. All chemicals used in this study were of extra pure or reagent grade. The clay minerals were prepared following a similar procedure to the best practices for analyzing surface properties of montmorillonite reviewed by Duc et al.$^{40-43}$. Thirty grams of kaolinite and montmorillonite was dispersed in 1 L of deionized water with a specific resistance of 18.2 MΩ m (Millipore, Bedford, Ma, USA) for 4 h. Prior to the size separation, the pH value of the kaolinite suspension was adjusted to 9.5 by adding NaOH (98%, Daejung, Korea) to facilitate a dispersion. The <2-μm fraction of each clay mineral was collected via centrifugation (119 g, 5 min). This fraction was washed with 1 M NaNO$_3$ (99%, Daejung, Korea) and HNO$_3$ (60%, Daejung, Korea) solution at pH 3 and the supernatant was decanted after centrifugation. This decarbonating procedure was repeated until the supernatant pH reached 3$^{41,42,44-46}$. The clay minerals were then collected via centrifugation and washed three times with 1 M NaNO$_3$ solution to change the clays to a Na$^+$ form. Although three washing cycles with NaNO$_3$ might not be enough to make clay minerals homoionic$^47$, this pretreatment was chosen to allow for closer comparisons to previous studies, which determined clay minerals’ Ka and site density through surface complexation modeling$^{30,44,48}$. Excess Na$^+$ was removed by washing five times with deionized water, and the final pH was in the range from 6 to 7. The collected clay minerals were freeze-dried, and the clay minerals are referred to as untreated kaolinite and montmorillonite, measured ammonium ion through the ammonium acetate method$^{49}$, was 44 and 832 mmol kg$^{-1}$, respectively. The specific surface areas of the untreated kaolinite and montmorillonite, 10 and 12 m$^2$ g$^{-1}$, were freeze-dried, and the clay minerals are referred to as untreated kaolinite and montmorillonite.

Acid spills dissolved isomorphically substituted octahedral cations and SiOH sites in montmorillonite. In addition, alkali spills dissolved the quartz and cristobalite and edge sites such as AlOH and SiOH sites were newly formed in montmorillonite. Regarding the pH buffering capacity of clay minerals, acid or alkali spills did not have an adverse effect on it, but rather increased in montmorillonite. Soil generally contains organic matter, which plays a significant role in pH buffering, and thus further research with field soil is needed to delineate the effect of acid or alkali spills. 

Figure 4. pH buffering capacity of three different kaolinite and montmorillonite samples at pH 5.5, 6.0, and 6.5. Open and cross-hatched bars represent kaolinite and montmorillonite, respectively, and black, red, and blue bars represent untreated, acid-spilled, and alkali-spilled kaolinite or montmorillonite, respectively.
montmorillonite, obtained using N$_2$- Brunauer–Emmett–Teller (BET) analysis (ASAP2020, Micromeritics, USA) through adsorption (32 points) and desorption (23 points) isotherms (see in Supplementary Fig. S4)$_{50,51,52,53}$, were 12.10 and 33.75 m$^2$ g$^{-1}$, respectively. These values were used as parameters for the surface complexation modeling$_{50,51,52,53}$. 

**Acid or alkali spill and neutralization.** HCl (35%, Daejung, Korea) and NaOH were selected as the strong acid and alkali, respectively, based on their frequency of chemical accidents and amount of use$_{54}$. One gram of the untreated kaolinite or montmorillonite was placed in a 50-mL conical tube and 45 mL of 5 M HCl or NaOH was added to simulate an extreme acid or alkali spill situation. Whole reactions were conducted in a rotating shaker at 25 °C and 40 rpm for two days. The suspension was centrifuged and the supernatant solutions were filtered through a 0.22-μm filter (Whatman, UK). After acid or alkali spill experiments, the treated solutions were analyzed by using inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 7400, Thermo Fisher Scientific, USA) to determine the dissolution of the major structural constituents of kaolinite and montmorillonite such as Al, Si, Fe, and Mg.

Separated or acid-montmorillonite were washed with deionized water five times to remove excess salts and dissolved ions. A neutralization process was needed because excess H$^+$ and OH$^-$ remaining after washing and decanting could affect the titration experiment. Thus, the washed kaolinite or montmorillonite were neutralized by adding HNO$_3$ or NaOH until the supernatant pH reached a neutral pH range. The suspensions were centrifuged and decanted and then residual clay minerals were washed three times with 1 M NaNO$_3$ to make them homocionic. These clay minerals were washed five times with deionized water, and then freeze-dried. The concentrations of Al and Si in the suspensions were measured by ICP-OES to check the remaining ions’ concentration, and they were below one mg kg$^{-1}$. The whole experiments of acid or alkali spills and neutralization were carried out in triplicates. The XRD analysis was conducted to analyze the mineral identity of the acid- or alkali-spilled clay minerals. The CEC of acid- or alkali-spilled kaolinite was 4.7 cmol kg$^{-1}$, while that of acid- or alkali-spilled montmorillonite was 737 and 925 mmol kg$^{-1}$, respectively. The specific surface area of the acid- or alkali-spilled kaolinite was 13.60 and 14.14 m$^2$ g$^{-1}$, respectively, while that of the acid- or alkali-spilled montmorillonite was 34.88 and 19.32 m$^2$ g$^{-1}$, respectively (see in Supplementary Fig. S4).

**Potentiometric titration.** Potentiometric titration has been used to quantify the density of active reaction sites of clay minerals and determine the surface acidity constants (Ka) of those sites$_{55,56,43,44,46,54-57}$. The protonation behaviors of three different kaolinite or montmorillonite (untreated, acid-spilled, and alkali-spilled) were investigated using an automatic potentiometric titrator (G10S, Mettler-Toledo, Switzerland). Duc et al. recommended the best experimental conditions for the titrations to analyze the acid-base properties of montmorillonite$_{55,56,57}$, and we adapted the procedure with some modifications as follows.

All titration experiments were performed within a pH range of 4–9 at 25 ± 1 °C under an N$_2$-purging condition. Deionized water was boiled to remove CO$_2$ before making clay suspensions and the base titrant. Kaolinite (0.1 g) or montmorillonite (0.05 g) was dispersed in 50 mL of background electrolyte (NaNO$_3$) solution, and the suspensions were purged with N$_2$ for 1 h to exclude CO$_2$. The suspensions were continuously stirred and purged with N$_2$ during each titration. Titrations of each clay suspension were conducted at three different concentrations of NaNO$_3$ (0.1, 0.01, and 0.001 M) to investigate the effect of the background electrolytic concentration. Titrant solutions of 0.1 M HNO$_3$ or NaOH, also purged with N$_2$, were added to the suspensions as 5–10-μL increments every 5 min, and the pH was automatically recorded. Previous research has demonstrated that a short time interval between successive increments of titrant, generally less than 10 min, is reasonable to minimize mineral dissolution$_{58,59,60}$. Drifts in the measured potential were less than 1 mV min$^{-1}$ in all titration experiments. Two independent titrations of each clay suspension, from initial pH to pH 4 and from initial pH to pH 9, were conducted and combined to obtain one titration curve ranging from pH 4 to 9. This pH range was selected because it is known that the dissolution of kaolinite and montmorillonite is negligible in this pH range$_{61,62,63}$. In addition, to check the reversibility of titration experiments, titrations from pH 4 to pH 9 were conducted at 0.01 M NaNO$_3$ condition.

**X-ray diffraction measurement.** X-ray diffraction (XRD) pattern of the samples of kaolinite and montmorillonite was measured with a X-ray diffractometer (D8 ADVANCE with DAVINCI, Bruker, German) using Cu Kα radiation with a λ of 1.5418 Å and a Lynxeye-XE detector operating at 40 kV and 40 mA at a scan rate of 2.4° min$^{-1}$ from 5° to 80°. The TOPAS Rietveld analysis of XRD patterns was used to quantify the content of mineral components of kaolinite samples. Since it is not precise and difficult to quantify montmorillonite by Rietveld analysis due to the stacking disorder$_{64,65}$, the fraction of constituents was analyzed semi-quantitatively by comparing the integrated intensities of the diffraction peaks of each constituent$_{66}$. 

**Fourier-transform infrared spectroscopy.** Fourier-transform infrared (FT-IR) spectroscopy was used to investigate the mineralogical and chemical structure and active surface sites of clay minerals for surface acidity$^{32}$, Clay samples were dried at 110°C overnight to minimize water adsorption. KBr pellets were prepared by mixing kaolinite (1.5 mg) or montmorillonite (1 mg) with 240 mg of KBr powder at a pressure of 10 tons. The FT-IR spectra of the pellets with kaolinite or montmorillonite were recorded using an FT-IR spectrometer (Nicolet 6700, Thermo Scientific, USA) with 32 scans at a resolution of 4 cm$^{-1}$ within the range of 400–4,000 cm$^{-1}$. 

**Surface complexation modeling.** A constant capacitance model with permanent negatively charged sites on basal plane and variable charged sites on the mineral edges was chosen to model the surface properties of the kaolinite and montmorillonite$_{30,37,44}$. The former was referred to as basal sites, while the latter as edge sites. A proton exchange reaction occurred on the basal sites of the clay minerals, while a protonation or deprotonation reaction occurred on the edge sites of them. The least square fitting program FITEQL 4.0 was used to optimize the site densities of the kaolinite and montmorillonite and their surface reaction constants from the titration
experiment. The CEC of the kaolinite and montmorillonite was used as the total site density of the kaolinite and the basal site density of the montmorillonite, respectively. Surface properties were optimized from titration data at three different concentrations of background electrolyte (0.1, 0.01, and 0.001 M NaNO₃). FITQUREL failed to converge without fixing the equilibrium constant of the proton exchange reaction probably because the titration curves of the kaolinite could be well described without considering the basal sites’ proton exchange reaction. Thus, $pK_a$ of the kaolinite’s proton exchange reaction constant was assumed to be $-2.9$ (Table 2), which is an averaged value from references. Detailed descriptions of the surface complexation modeling used in this study and the optimization process are explained in the Supplementary Information.

Data Availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

References

1. Kleindorfer, P. R. et al. Accident epidemiology and the RMP rule: learning from a decade of accident history data for the US chemical industry. The Wharton School of the University of Pennsylvania and Office of Emergency Management US Environmental Protection Agency (2007).

2. Chemistry safety clearing-house (CSC) database: http://csc.me.go.kr (2018).

3. Shin, D. et al. The current status of strong acids production, consumption, and spill cases in Korea. Journal of Soil and Groundwater Environment 19, 6–12, https://doi.org/10.7857/jseg.2014.19.6.006 (2014).

4. A study on the method of environmental impact investigation by accident of acidic chemicals; Highlights of NIER-RP2013-235; Ministry of Environment: Seoul, 2013; http://www.ndsl.kr/ndsl/commons/utlnd/ndslOriginalView.do?dltm=TRKO&cn=TRKO20170008369&nr=8&pageCode=PG18 (2013).

5. Dai, Z., Liu, Y., Wang, X. & Zhao, D. Changes in $pH$, CEC and exchangeable acidity of some forest soils in southern China during the last 32–35 years. Water, Air, and Soil Pollution 108, 377–390 (1998).

6. Jardine, P., McCarthy, J. & Weber, N. Mechanisms of dissolved organic carbon adsorption on soil. Soil Science Society of America Journal 53, 1378–1385 (1989).

7. Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B. & Matzner, E. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Science 165, 277–304 (2000).

8. Jozefaciuk, G. & Bowanko, G. Effect of acid and alkali treatments on surface areas and adsorption energies of selected minerals. Clays and Clay minerals 50, 771–783 (2002).

9. Fenn, M. E. et al. Status of soil acidification in North America. Journal of Forest Science 52, 3–13 (2006).

10. Kastman, K. H., Ghalib, S. & Zagula, S. In-situ remediation of a hydrochloric acid spill. In Proceedings of the Industrial Waste Conference (USA) (1992).

11. Protopopov, N., Serediná, V. & Molokova, L. In Contaminated Soil 2000: Seventh International FZK/TNO Conference on Contaminated Soil (Thomas Telford Ltd), 1–671 (2000).

12. Goulding, K. W. Soil acidity and the importance of liming agricultural soils with particular reference to the United Kingdom. Soil Use and Management 32, 390–399, https://doi.org/10.1111/sunm.12270 (2016).

13. Jiang, J. et al. Responses of soil buffering capacity to acid treatment in three typical subtropical forests. Science of the Total Environment 563–564, 1068–1077, https://doi.org/10.1016/j.scitotenv.2016.04.198 (2016).

14. Weng, L., Van Riemsdijk, W. H., Koopal, L. K. & Hiemstra, T. Adsorption of humic substances on goethite: comparison between humic acids and fulvic acids. Environmental Science and Technology 40, 7494–7500 (2006).

15. Ulrich, B. & Sumner, M. E. Soil acidity (Springer Science & Business Media 2012).

16. Chen, H., Koopal, L. K., Xiong, J., Avena, M. & Tan, W. Mechanisms of soil humic acid adsorption onto montmorillonite and kaolinite. Journal of Colloid and Interface Science 504, 457–467, https://doi.org/10.1016/j.jcis.2017.05.078 (2017).

17. Ravichandran, J. & Sivasankar, B. Properties and catalytic activity of acid-modified montmorillonite and vermiculite. Clays and Clay Minerals 45, 854–858 (1997).

18. Bhattacharyya, K. G. & Gkiriou, S. S. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. Advances in Colloid Interface Science 140, 114–131, https://doi.org/10.1016/j.cis.2007.12.008 (2008).

19. Palková, H., Hronský, V. & Madejová, J. The effect of acid treatment on the structure and surface acidity of tetraalkylammonium-montmorillonites. Journal of Colloid and Interface Science 395, 166–175 (2013).

20. Aleksseeva, T., Aleksseev, A., Xu, R. K., Zhao, A. Z. & Kalinin, P. Effect of soil acidification induced by a tea plantation on chemical and mineralogical properties of Alfisols in eastern China. Environmental Geochemistry and Health 33, 137–148, https://doi.org/10.1007/s10653-010-9337-5 (2011).

21. Nakao, A., Funakawa, S. & Kosaki, T. Hydroxy-Al polymers block the frayed edge sites of illitic minerals in acid soils: studies in southwestern Japan at various weathering stages. European Journal of Soil Science 60, 127–138, https://doi.org/10.1111/j.1365-2389.2008.01097.x (2009).

22. Van Der Salm, C. & De Vries, W. Soil acidification in loess and clay soils in the Netherlands. Water, Air, and Soil Pollution 120, 139–167 (2000).

23. Attken, R., Moody, P. & McKinley, P. Lime requirement of acidified Queensland soils I. Relationships between soil properties and pH buffer capacity. Soil Research 28, 695–701 (1990).

24. Spósito, G. The chemistry of soils (Oxford university press, 2008).

25. Bourg, I. C., Spósito, G. & Bourg, A. C. Modeling the acid-base surface chemistry of montmorillonite. Journal of Colloid and Interface Science 312, 297–310, https://doi.org/10.1016/j.jcis.2007.03.062 (2007).

26. Tournassat, C., Davis, J. A., Chiaberge, C., Grangeon, S. & Bourg, I. C. Modeling the acid-base properties of montmorillonite edge surfaces. Environmental Science and Technology 50, 13436–13445, https://doi.org/10.1021/acs.est.6b04677 (2016).

27. Chipera, S. J. & Bish, D. L. Baseline studies of the clay minerals society source clays: powder X-ray diffraction analyses. Clays and Clay Minerals 49, 498–499 (2001).

28. Theng, B., Lagaly, G. & Bergaya, F. Handbook of clay science (Elsevier, 2006).

29. Szelekeres, M. & Tombácz, E. Surface charge characterization of metal oxides by potentiometric acid–base titration, revisited theory and experiment. Colloids and Surfaces A: Physicochemical and Engineering Aspects 414, 302–313, https://doi.org/10.1016/j.colsurfa.2012.08.027 (2012).

30. Gu, X. & Evans, L. J. Surface complexation modelling of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) adsorption onto kaolinite. Géochimica et Cosmochimica Acta 72, 267–276, https://doi.org/10.1016/j.gca.2007.09.032 (2008).

31. Madejová, J. & Komadel, P. Baseline studies of the clay minerals society source clays: FTIR techniques in clay mineral studies. Vibrational Spectroscopy 31, 1–10 (2003).
33. Vicente-Rodriguez, M. A., Suarez, M., Bañares-Muñoz, M. A. & de Dios Lopez-Gonzalez, J. Comparative FT-IR study of the removal of octahedral cations and structural modifications during acid treatment of several silicates. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **52**, 1685–1694 (1996).

34. Jozefaciuk, G. Effect of acid and alkali treatments on surface-charge properties of selected minerals. *Clays and Clay Minerals* **50**, 647–656 (2002).

35. Tazi, S., Rotenberg, B., Salanne, M., Sprik, M. & Sulpizi, M. Absolute acidity of clay edge sites from ab-initio simulations. *Geochimica et Cosmochimica Acta* **94**, 1–11 (2012).

36. Bickmore, B. R., Rosso, K. M., Nagy, K. L., Cysgan, R. T. & Tadano, C. J. Ab initio determination of edge surface structures for diocahedral 2:1 phyllosilicates: implications for acid-base for reactivity. *Clays and Clay Minerals* **51**, 359–371 (2003).

37. Liu, X. et al. Acidity of edge surface sites of montmorillonite and kaolinite. *Geochimica et Cosmochimica Acta* **117**, 180–190, https://doi.org/10.1016/j.gca.2013.04.008 (2013).

38. Liu, X., Cheng, J., Sprik, M., Lu, X. & Wang, R. Surface acidity of 2:1-type dioctahedral clay minerals from first principles molecular dynamics simulations. *Geochimica et Cosmochimica Acta* **140**, 410–417, https://doi.org/10.1016/j.gca.2014.05.044 (2014).

39. Baeyens, B. & Bradbury, M. H. A mechanistic description of Ni and Zn sorption on Na-montmorillonite. *Geochimica et Cosmochimica Acta* **66**, 2325–2334 (2002).

40. Schindler, P., Liechti, P. & Westall, J. Adsorption of copper, cadmium and lead from aqueous solution to the kaolinite/water interface. *Environmental Science and Technology* **52**, 4023–4030, https://doi.org/10.1021/acs.est.7b05443 (2018).

41. Scholberg, C. & Simon, R. Determination of exchange capacity and exchangeable bases in soil—a monomineral acid method. *Soil Science* **59**, 13–24 (1945).

42. Brunauer, S., Emmett, P. H. & Teller, E. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society* **60**, 309–319 (1938).

43. Maria D. A. Surface complexation model: hydrous ferric oxide (John Wiley & Sons, 1990).

44. Krael, A. M., Keller, K. & More, F. M. On the acid—base chemistry of permanently charged minerals. *Environmental Science and Technology* **32**, 2829–2838 (1998).

45. Bradbury, M. H. & Baevens, B. A mechanistic description of Ni and Zn sorption on Na-montmorillonite Part II: modelling. *Journal of Contaminant Hydrology* **27**, 223–248 (1997).

46. Bradbury, M. & Baevens, B. Sorption of Eu on Na-and Ca-montmorillonites: experimental investigations and modelling with cation exchange and surface complexation. *Chem Geol* **66**, 2325–2334 (1998).

47. Schindler, P., Liechti, P. & Westall, J. Adsorption of copper, cadmium and lead from aqueous solution to the kaolinite/water interface. *Netherlands Journal of Agricultural Science* (Netherlands) (1987).

48. Brady, P. V., Cysgan, R. T. & Nagy, K. L. Molecular controls on kaolinite surface charge. *Journal of Colloid and Interface Science* **183**, 356–364 (1996).

49. Baevens, B. & Bradbury, M. H. A mechanistic description of Ni and Zn sorption on Na-montmorillonite Part I: Titration and sorption measurements. *Journal of Contaminant Hydrology* **27**, 199–222 (1997).

50. Tournassat, C., Grenache, J. M., Tisserand, D. & Charlet, L. The titration of clay minerals I. Discontinuous backtitration technique combined with CEC measurements. *Journal of Colloid and Interface Science* **273**, 224–233, https://doi.org/10.1016/j.jcis.2003.11.021 (2004).

51. Tertre, E., Castet, S., Berger, G., Loubet, M. & Giffaut, E. Surface chemistry of kaolinite and Na-montmorillonite in aqueous electrolyte solutions at 25 and 60 °C: Experimental and modeling study. *Geochimica et Cosmochimica Acta* **70**, 4579–4599, https://doi.org/10.1016/j.gca.2006.07.017 (2006).

52. Komarek, M., Koutsky, C. M., Stephen, K. J., Alessi, D. S. & Chastny, V. Competitive Adsorption of Cd(II), Cr(VI), and Pb(II) onto nanomagnemite: a spectroscopic and modeling approach. *Environmental Science and Technology* **49**, 12851–12859, https://doi.org/10.1021/acs.est.5b03063 (2015).

53. Liu, Y. et al. Acid-base properties of kaolinite, montmorillonite and illite at marine ionic strength. *Chemical Geology* **483**, 191–200, https://doi.org/10.1016/j.chemgeo.2018.01.018 (2018).

54. Liu, X., Thomas, F. & Gaboriaud, F. Coupled chemical processes at clay/electrolyte interface: a batch titration study of Na-montmorillonite. *Journal of Colloid and Interface Science* **300**, 616–625, https://doi.org/10.1016/j.jcis.2006.04.081 (2006).

55. Rozalen, M., Brady, P. V. & Huertas, F. J. Surface chemistry of K-montmorillonite: ionic strength, temperature dependence and dissolution kinetics. *Journal of Colloid and Interface Science* **333**, 474–484, https://doi.org/10.1016/j.jcis.2009.01.059 (2009).

56. Ufer, K. & Raven, M. D. Application of the Rietveld method in the Reynolds cup contest. Clays and Clay Minerals **65**, 286–297 (2017).

57. Louter, L., Volkolinski, M., Wedn, H.-R., Banupradahy, K. & Vanorio, T. Texture analysis of a turboplastic disordered Ca-montmorillonite. *American Mineralogist* **95**, 98–103 (2010).

58. Liu, D. et al. Quantitative characterization of the solid acidity of montmorillonite using combined FTIR and TPD based on the NH₃ adsorption system. *Applied Clay Science* **80**, 407–412 (2013).

59. Herbelin, A. L. & Westall, J. C. FITEQ: A computer program for determination of chemical equilibrium constants from experimental data. *Version 4*, 99–01 (1999).

60. Angove, M. J., Johnson, B. B. & Wells, J. D. Adsorption of cadmium(II) on kaolinite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **126**, 137–147 (1997).

61. Ikhsan, J., Johnson, B. B. & Wells, J. D. A comparative study of the adsorption of transition metals on kaolinite. *Journal of Colloid and Interface Science* **217**, 403–410 (1999).

62. Srivastava, P., Singh, B. & Angove, M. Competitive adsorption behavior of heavy metals on kaolinite. *Journal of Colloid and Interface Science* **290**, 28–38, https://doi.org/10.1016/j.jcis.2005.04.036 (2005).
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