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Effects of Amorphous $Al(OH)_3$ on the Desorption of Ca^{2+}, Mg^{2+}, and Na^+ from Soils and Minerals As Related to Diffuse Layer Overlapping

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ABSTRACT: The overlapping of the diffuse layers of the electric double layers between phyllosilicates and Fe(III) and Al(III) oxides results in compensating of some negative surface charge on phyllosilicates by the positive surface charge on Fe(III) and Al(III) oxides and thus should affect the distribution of cations in the diffuse layers on phyllosilicates. In this article, the batch experimental method was used to investigate the desorption of Ca^{2+}, Mg^{2+}, and Na^+ from an Alfisol, an Ultisol, a bentonite, and a kaolinite induced by amorphous $Al(OH)_3$ added and to evaluate the effect of the overlapping of the diffuse layers on the release of cations from the minerals and the soils. The presence of amorphous $Al(OH)_3$ was found to enhance the desorption of Na^+, Ca^{2+}, and Mg^{2+} from the soils and the minerals; the effect of amorphous $Al(OH)_3$ on the desorption of Ca^{2+}, Mg^{2+}, and Na^+ increased with its amount added. The increase of ionic strength depressed the diffuse layer and decreased the overlapping of diffuse layers and thus decreased the contribution of diffuse layer overlapping to the release of Ca^{2+} and Mg^{2+} from soils and minerals. This study suggests that the overlapping of the diffuse layers of the electric double layers of the negatively charged phyllosilicates and the positively charged $Al(OH)_3$ accelerated the release of Ca^{2+}, Mg^{2+}, and Na^+ from the soils and minerals as a result of the decrease in their effective charge density.

1. INTRODUCTION

Soil colloidal behaviors are of fundamental significance because characterizations of size, shape, surface area, surface charge density, and changes in surface charge are required for understanding the processes of adsorption, flocculation, dispersion, and transport in soils and the resultant changes in soil hydraulic properties as well as chemical migration.[1] Soils can be classified into two categories on the basis of the origin of surface charges:[2] constant charge soils with permanent surface charge and variable charge soils with a mixture of permanent and variable surface charges. The permanent surface charge of a soil originates from isomorphic substitution in internal crystal structures of phyllosilicates, which causes an increase in soil reactivity, whereas the variable surface charge develops mainly through protonation and deprotonation of surface hydroxyl groups on soil Fe(III) and Al(III) oxides.[2] Thus, variable charge soils contain two types of soil colloidal phase, that is, negatively charged particles and positively charged particles. Under normal pH conditions in variable charge soils, phyllosilicates carry net negative surface charges, while iron and aluminum oxides possess positive surface charges.[3] If these soil samples are dispersed in water, electric double layers would form both on phyllosilicates and iron and aluminum oxides. An interaction between the electric double layers on the negatively charged phyllosilicate particles and the positively charged iron and aluminum oxides (overlapping of the diffuse layers) may occur, which leads to a decrease in effective surface charge density of these charged particles in variable charge soils.

Qafoku and Sumner reported that the cations and anions of an electrolyte can be adsorbed simultaneously on variable charge soils in approximately equivalent amounts with no net release of other ions into the soil solution, but the phenomenon cannot be interpreted within the ion-exchange theory.[4] An interaction model of the electric double layers between the negatively charged phyllosilicates and the positively charged iron and aluminum oxides was proposed to explain the mechanism of simultaneous adsorption of cations and anions.[3,4] In our previous study,[5] we found that the overlapping of the diffuse layers of a kaolinite and iron and aluminum oxides decreased the effective negative charge density of the kaolinite and thus increased the zeta potential of the binary-system containing the kaolinite and iron and aluminum oxides in the suspensions. Similar results were observed in the binary systems containing a subsoil sample with net negative charge and iron and aluminum oxides, and the zeta potential of the binary-system containing soil and iron and aluminum oxide was found to be higher than the single system of the soil.[6] Tombácz et al. also observed a similar phenomenon when they investigated the interaction of montmorillonite and hematite or magnetite in suspensions.[7] These experimental observations collectively support the hypothesis of Qafoku and Sumner.[4]

When overlapping of the diffuse layers of the electric double layers occurred in binary colloidal systems, the charges of the particles on the oppositely charged colloids were balanced by each other, and thus the counterion (cations or anions) in the respective diffuse layers of the electric double layers should be removed easily from the system.[8] Therefore, the interaction between the electric double layers on oppositely charged particles would probably promote the desorption of Ca^{2+}, Mg^{2+}, and Na^+ from the surface of minerals and soils and accelerate the leaching loss of these cations from soils. To test this hypothesis, a

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Table 1. Selective Properties of Soils and Minerals

soil and mineral	pH	organic matter	CEC	exchangeable cations				free Fe_2O_3
				$1/2Ca^{2+}$	$1/2Mg^{2+}$	K^+	Na^+	
		$g\cdot kg^{-1}$	$cmol\cdot kg^{-1}$					$g\cdot kg^{-1}$
Alfisol	6.5 ± 0.04	3.67 ± 0.22	17.84 ± 0.42	12.55 ± 0.27	5.04 ± 0.16	0.27 ± 0.02	0.43 ± 0.03	22.31 ± 0.59
Ultisol	4.7 ± 0.03	3.15 ± 0.10	10.36 ± 0.21	8.22 ± 0.23	1.32 ± 0.08	0.26 ± 0.03	0.47 ± 0.04	51.05 ± 0.95
bentonite	--	--	88.73 ± 1.20	74.83 ± 1.40	13.45 ± 0.31	1.00 ± 0.01	2.62 ± 0.02	--
Na^+-saturated bentonite	--	--	88.73 ± 1.20	10.03 ± 0.18	1.30 ± 0.06	0.00	78.67 ± 1.70	--
kaolinite	--	--	6.44 ± 0.10	6.23 ± 0.15	1.13 ± 0/09	0.88 ± 0.01	1.34 ± 0.04	--

Table 2. Chemical Compositions of Soils and Minerals

soil and mineral	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	CaO	MgO	TiO_2	MnO
	$g\cdot kg^{-1}$								
Alfisol	668.7 ± 5.7	155.5 ± 0.4	62.3 ± 3.1	42.8 ± 3.1	15.1 ± 1.6	5.4 ± 0.1	14.6 ±	8.8 ± 0.2	0.2 ± 0.1
Ultisol	659.7 ± 2.7	176.4 ± 1.4	67.2 ± 3.8	54.8 ± 2.3	13.1 ± 0.2	0.0	7.6 ± 0.1	12.1 ± 0.1	0.5 ± 0.1
bentonite	606.8 ± 8.3	189.3 ± 2.0	33.5 ± 2.0	17.2 ± 0.7	13.2 ± 1.4	0.0	31.7 ± 0.1	2.3 ± 0.0	0.0
kaolinite	466.2 ± 1.8	385.5 ± 2.0	0.7 ± 0.0	28.6 ± 2.2.	13.9 ± 0.4	0.0	0.6 ±	1.1 ± 0.0	0.0

variable charge soil and a constant charge soil with low content of free iron and aluminum oxides and two minerals were chosen to investigate the effect of amorphous aluminum hydroxide on the desorption of Ca^{2+}, Mg^{2+}, and Na^+ from the surfaces of the soils and minerals.

2. EXPERIMENTAL SECTION

All reagents used in the experiments were of analytical (AR) grade and were purchased from the Shanghai Chemical Reagent Company (Shanghai, China).

2.1. Soils, Minerals, and Aluminum Hydroxide. A variable charge soil, the Ultisol (US Taxonomy; Haplic Acrisol in the WRB Taxonomy; located at 116° 17′ E, 28° 23′ N) and a constant charge soil, the Alfisol (US Taxonomy; Haplic Luvisol in the WRB Taxonomy; located at 118° 49′ E, 32° 3′ N) were collected from Jiangxi Province and Jiangsu Province, P. R. China, respectively, and used for the experiments. The clay minerals in the Ultisol are dominated by kaolinite and hydrous mica, and the soil also contains a certain amount of vermiculite. The clay fraction in the Alfisol is dominated by hydrous mica, vermiculite, and montmorillonite. Both soils were subsoils with low organic matter content (Table 1). The soil samples were air-dried and ground to pass a 60 mesh sieve. The kaolinite is a commercial clay mineral obtained from Shanghai Reagent Company (Shanghai, China). The bentonite was collected from the suburb area of Nanjing, Jiangsu Province, P. R. China, and the sample was air-dried and ground to pass a 60 mesh sieve. A number of properties of the soils and minerals are given in Table 1. The chemical compositions of soils and minerals used in the experiments are listed in Table 2.

The Na^+-saturated bentonite was prepared according to the method reported by Saha et al.[9] The clay fraction less than 2 μm in diameter was separated from the original bentonite by decantation, in which particles in the upper portion of the suspension were collected at fixed time intervals after stirring. The collected sample was then washed by a mixed solution containing 1.0 $mol\cdot L^{-1}$ sodium acetate and 1.0 $mol\cdot L^{-1}$ NaCl (pH 5.0) four times. The sample was then rinsed with ethanol until free of Cl^-. The Na^+-saturated bentonite clay was air-dried and ground to pass a 60 mesh sieve.

The kaolinite and the Ultisol samples were washed with 1.0 $mol\cdot L^{-1}$ $CaCl_2$ three times to saturate the samples with Ca and then these samples were rinsed with ethanol until free of Cl^-. The Ca^{2+}-saturated samples were air-dried and ground to pass a 60 mesh sieve.

The amorphous $Al(OH)_3$ was synthesized following the procedure reported earlier.[10] One liter of 0.5 $mol\cdot L^{-1}$ $AlCl_3$ was titrated gradually with 0.5 $mol\cdot L^{-1}$ NaOH to pH 7.0. The suspension was aged at room temperature for 48 h and then centrifuged. The precipitate was washed once with H_2O and then with methanol until free of Cl^-. The washed precipitate was air-dried, gently ground into powder using mortar and pestle, and then passed through a 60 mesh sieve. The X-ray diffraction analysis verified that the sample of the amorphous $Al(OH)_3$ was noncrystalline to X-ray. The Brunauer−Emmett−Teller (BET) surface area for the amorphous $Al(OH)_3$ was 31 $m^2\cdot g^{-1}$.

2.2. Experimental Method. Samples of 1.000 g of soils or minerals in duplicate were weighed into centrifuge bottles, and then various amounts of amorphous $Al(OH)_3$ [(0, 0.025, 0.05, 0.1, and 0.15) g] and 25 mL of deionized water were added into each of the bottles. The suspensions in the bottles were shaken for 2 h and then the solutions were separated from the solid phase by centrifugation at 8500 g for 15 min, followed by further filtration through a 0.22 μm pore membrane filter. The Na^+ in the solutions was determined by flame photometry; the Ca^{2+} and Mg^{2+} in the solutions were determined by the atomic absorption spectrophotometric method (AAS).

When the effect of amorphous $Al(OH)_3$ on the release of Ca^{2+} and Mg^{2+} from bentonite and Alfisol at different ionic strengths was investigated, suspensions containing 1 g of bentonite (or Alfisol), various amounts of amorphous $Al(OH)_3$ [(0, 0.025, 0.05, 0.1, and 0.15) g], and 25 mL of deionized water, 0.03 $mol\cdot L^{-1}$ $NaNO_3$ or 0.3 $mol\cdot L^{-1}$ $NaNO_3$ were prepared. The suspensions

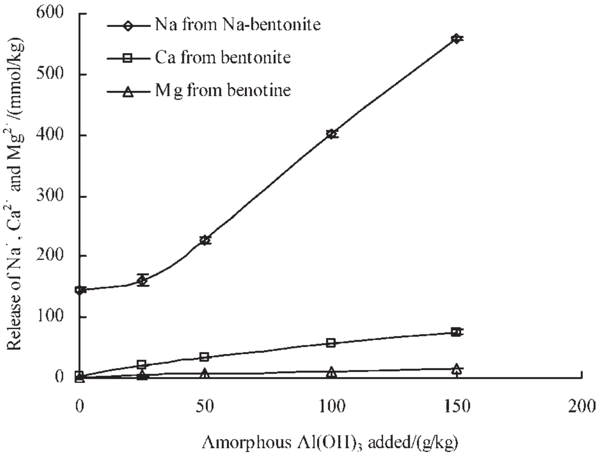

Figure 1. Effect of the amorphous $Al(OH)_3$ on the release of Na^+, Ca^{2+}, and Mg^{2+} from the Na^+-saturated bentonite and bentonite, respectively.

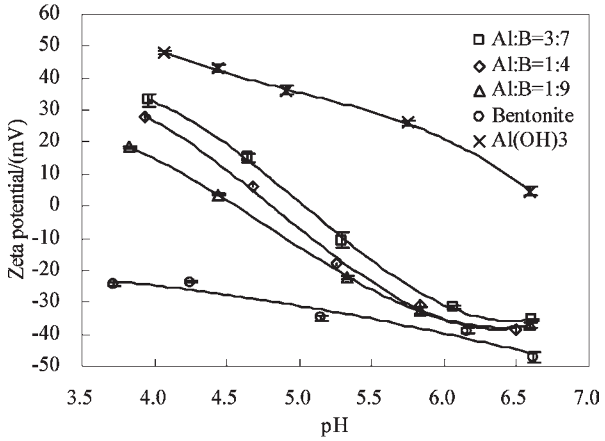

Figure 2. pH−zeta potential curves in single systems of bentonite or amorphous $Al(OH)_3$ and binary systems containing bentonite and amorphous $Al(OH)_3$. Al:B is the mass ratio of amorphous $Al(OH)_3$ to bentonite.

were stirred by a magnetic stirrer for 2 h and the pH of suspensions was measured with a pH meter (Orion 3 star, USA) with a combined electrode. Then, the solutions were separated from the solid phase by centrifugation at 8500 *g* for 15 min, followed by further filtration through a 0.22 μm pore membrane filter. The Ca^{2+} and Mg^{2+} in the solutions were determined by AAS. Soluble aluminum in the solutions was determined by the 8-hydroxyquinoline method at pH 8.3, using butyl acetate as an extractant.[11]

Similarly, a series of the same suspensions were prepared again. The pH of the suspensions was controlled at the constant value as the same with that of the suspensions with 0.15 g of amorphous $Al(OH)_3$ added by an automatic potentiometric titration system through addition of 0.025 $mol \cdot L^{-1}$ HCl under magnetic stirring. After 2 h, the solutions were separated from the solid phase, and the Ca^{2+}, Mg^{2+}, and soluble aluminum in the solutions were determined as the same methods as mentioned above.

2.3. Zeta Potential Determination. The zeta potential of colloidal systems was measured with JS94G+ microelectrophoresis apparatus made in China.[6] The colloid suspension containing 0.1 $mmol \cdot L^{-1}$ NaCl as the background electrolyte was prepared with a concentration of kaolinite, bentonite, or amorphous $Al(OH)_3$ at 0.25 $g \cdot L^{-1}$. The suspensions were dispersed ultrasonically at a frequency of 40 kHz and a power of 300 W for 45 min at 25 °C. Then the pH of the suspensions was adjusted with HCl or NaOH to the desired values, and these suspensions were shaken for 2 h at 25 °C. Further, the suspensions were equilibrated for another three days before electrokinetic potential determination. During this period the colloid suspensions were shaken manually at certain intervals. For the binary colloid suspensions, the kaolinite (or bentonite) sample and amorphous $Al(OH)_3$ were placed in the same container according to a certain mass ratio, and the rest of the procedure was adopted as similar to that for the single colloid suspension. The colloid suspensions were agitated and transferred to the electrophoresis vessel after the electrode was wetted to avoid any disturbance caused by air bubbles. The values of zeta potential were calculated using the computer with specific software.[6]

2.4. Uncertainty in the Results. In this study, all experimental treatments were duplicated, and the data in all figures and in Tables 1 and 2 are reported as means ± standard errors of the experimental duplicates and analytical replicates. The standard errors represent the uncertainties of the results obtained in this study.

3. RESULTS AND DISCUSSION

3.1. Desorption of Ca^{2+}, Mg^{2+}, and Na^+ from Bentonite. Figure 1 showed that the presence of the amorphous $Al(OH)_3$ enhanced the desorption of Na^+ from the Na^+-saturated bentonite, and the amount of Na^+ desorbed increased with the increase in the amount of the amorphous $Al(OH)_3$ added. When the original bentonite was used, similar changing trends were observed for Ca^{2+} and Mg^{2+}. The addition of the amorphous $Al(OH)_3$ also led to the increase in the amounts of both Ca^{2+} and Mg^{2+} desorbed from the bentonite (Figure 1). Na^+, Ca^{2+}, and Mg^{2+} were mainly adsorbed on the negative charge sites of the bentonite surface through electrostatic attraction (Table 1). When the bentonite was dispersed in water, the electric double layers were formed on the particle surface of the bentonite, and Na^+, Ca^{2+}, and Mg^{2+} existed as counterions in diffuse layers of the electric double layers of the bentonite. From the zeta potential−pH curves for the amorphous $Al(OH)_3$, the calculated isoelectric point (IEP) was 8.4 for the amorphous $Al(OH)_3$. Therefore, under normal pH conditions, the amorphous $Al(OH)_3$ carry a positive surface charge. When the amorphous $Al(OH)_3$ was added into the bentonite system, the electrostatic attraction made the particles of the amorphous $Al(OH)_3$ reach close to the particles of the bentonite, and the diffuse layers on the positively charged amorphous $Al(OH)_3$ and the negatively charged bentonite could overlap to each other to some extent, which results in the decrease in the effective negative charge density of the bentonite and thus enhanced the desorption of Ca^{2+}, Mg^{2+}, and Na^+ from Na^+-saturated bentonite and bentonite. In this section, the desorption experiments were conducted in deionized water, and $NaNO_3$ was not added to adjust ionic strength. The effect of ionic strength on desorption of Na^+, Ca^{2+}, and Mg^{2+} can be neglected. When (25, 50, 100, and 150) $g \cdot kg^{-1}$ of amorphous $Al(OH)_3$ were added, the system pH was 5.78, 5.57, 5.47, and 5.40, respectively. The pH decreased slightly with the amount of amorphous $Al(OH)_3$ added and may contribute to the desorption of Ca^{2+}, Mg^{2+}, and Na^+. The relative contribution of H^+ and diffuse layer overlapping will be discussed in a later section of this article.

The zeta potentials of a single system of bentonite or amorphous $Al(OH)_3$ and a binary system containing bentonite and amorphous $Al(OH)_3$ as shown in Figure 2 gave some evidence to

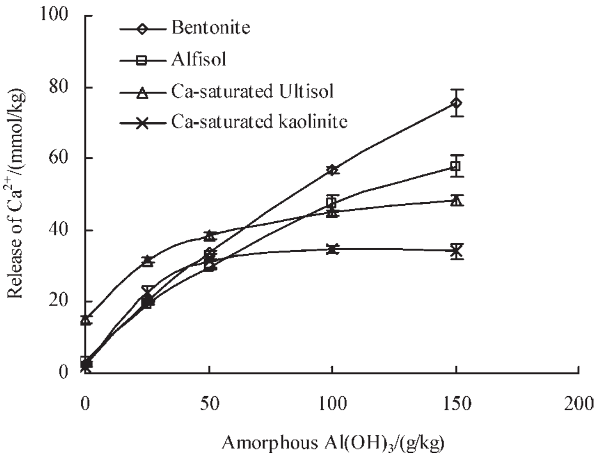

Figure 3. Effect of amorphous $Al(OH)_3$ on the release of Ca^{2+} from bentonite, Ca^{2+}-saturated kaolinite, Alfisol, and Ca^{2+}-saturated Ultisol, respectively.

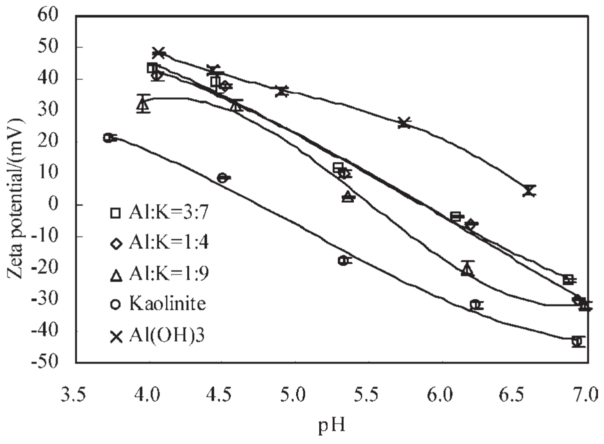

Figure 4. pH−zeta potential curves in single systems of kaolinite or amorphous $Al(OH)_3$ and binary systems containing kaolinite and amorphous $Al(OH)_3$. Al:K is the mass ratio of amorphous $Al(OH)_3$ to kaolinite.

the interpretation mentioned above. In the studied pH range from 3.7 to 6.7, the values of zeta potential for the single bentonite were negative, while the values for the single amorphous $Al(OH)_3$ were positive. These data suggested that the bentonite carries negative surface charge and the amorphous $Al(OH)_3$ has a net positive charge on its surface. The presence of amorphous $Al(OH)_3$ led to the shift of a zeta potential−pH curve of the binary system containing bentonite and amorphous $Al(OH)_3$ to a positive-value direction (Figure 2). The shift of the zeta potential−pH curve for the binary system increased with the amount of the amorphous $Al(OH)_3$ added. These results suggested that the overlapping of diffuse layers of the electric double layers on negatively charged bentonite and positively charged amorphous $Al(OH)_3$ occurred when these oppositely charged particles coexisted in the same suspension system.[5] The interaction of the diffuse layers on the oppositely charged particles made the surface charge density on the bentonite less negative compared with the single bentonite system,[12] and thus the electrostatic attraction between bentonite surface and cations decreased due to the presence of the amorphous $Al(OH)_3$. Therefore, the overlapping of the diffuse layers on oppositely charged particles caused the counterions such as Na^+, Ca^{2+}, and Mg^{2+} to exit from the diffuse layer of the bentonite and made the ions enter the bulk solution. This is the main reason why the amorphous $Al(OH)_3$ increased the desorption of Na^+, Ca^{2+}, and Mg^{2+} from the bentonite.

The Na-saturation percentage in the Na^+-saturated bentonite was higher than the Ca-saturation and Mg-saturation percentages in the original bentonite, and Na^+ was found to be easier to be desorbed from the negative charge surface sites than Ca^{2+} and Mg^{2+};[2] thus, the amount of Na^+ desorbed from the Na^+-saturated bentonite was much greater than the amount of Ca^{2+} or Mg^{2+} desorbed from the original bentonite as shown in Figure 1. The increase in the amount of the amorphous $Al(OH)_3$ added led to a stronger interaction of the electric double layers of the oppositely charged particles and resulted in more cations desorbed from the bentonite (Figures 1 and 2).

3.2. Release of Ca^{2+} and Mg^{2+} from Minerals and Soils.

The effect of the amorphous $Al(OH)_3$ on the desorption of Ca^{2+} from minerals and soils was presented in Figure 3. The presence of the amorphous $Al(OH)_3$ also resulted in the increase of the desorption of Ca^{2+} from the Ca^{2+}-saturated kaolinite. When the amount of the amorphous $Al(OH)_3$ added was increased from (0 to 50) $g \cdot kg^{-1}$, the release of Ca^{2+} from the Ca^{2+}-saturated kaolinite increased sharply from 1.8 $mmol \cdot kg^{-1}$ to 32.0 $mmol \cdot kg^{-1}$. The desorption of Ca^{2+} then increased to a less extent with the further increase of aluminum hydroxide. This may be because the interaction of the electric double layers between the kaolinite and the aluminum hydroxide was weaker than that for the bentonite systems when the amount of the aluminum hydroxide added was high as a result of a low CEC of the kaolinite as shown in Table 1. The results of zeta potentials in single kaolinite system and binary-system containing kaolinite and amorphous $Al(OH)_3$ as shown in Figure 4 supported this hypothesis. Similar to the binary system containing bentonite and amorphous $Al(OH)_3$, the presence of the amorphous $Al(OH)_3$ also led to the shift of zeta potential−pH curves to the positive-value side. The shift of zeta potential−pH curves increased with the amorphous $Al(OH)_3$ added from its percentage of 10 % (mass ratio of amorphous $Al(OH)_3$ to kaolinite = 1:9) to 20 % (mass ratio of amorphous $Al(OH)_3$ to kaolinite = 1:4). However, when the percentage of amorphous $Al(OH)_3$ increased from 20 % to 30 % (mass ratio of amorphous $Al(OH)_3$ to kaolinite = 3:7), the zeta potential−pH curves for the binary system no longer changed. This result suggested that the overlapping extent of the diffuse layers between kaolinite and amorphous $Al(OH)_3$ did not increase with the further addition of the amorphous $Al(OH)_3$ from its percentage of 20 % to 30 %, which was consistent with the change of Ca^{2+} desorption from Ca^{2+}-saturated kaolinite with the amount of the amorphous $Al(OH)_3$ added as shown in Figure 3.

A similar desorption experiment to these for the bentonite and kaolinite was also conducted for the Alfisol with a high Ca-saturation percentage and similar changing trends for the desorption of Ca^{2+} and Mg^{2+} were observed for the soil (Figures 3 and 5). Therefore, the interaction of the electric double layers of the negatively charged soil and positively charged Al hydroxide also enhanced the desorption of cations from the soil. The Ultisol used in this study was acidic and had a higher Al-saturation percentage and a low Ca^{2+}-saturation percentage. Therefore, the soil was washed with $CaCl_2$ to make it Ca^{2+}-saturated, and then the desorption of Ca^{2+} from the Ca^{2+}-saturated Ultisol sample as influenced by the amorphous $Al(OH)_3$ was investigated. The

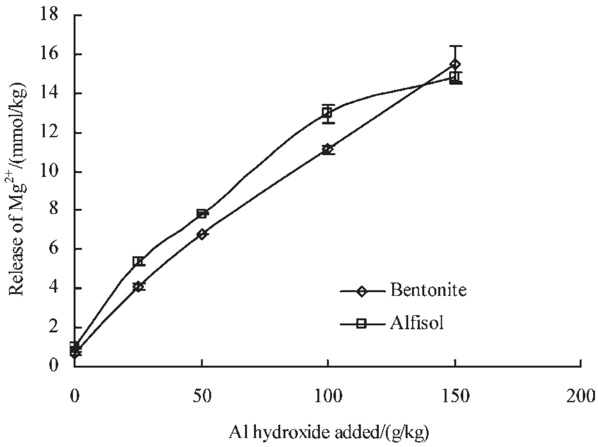

Figure 5. Effect of amorphous $Al(OH)_3$ on the release of Mg^{2+} from bentonite and Alfisol.

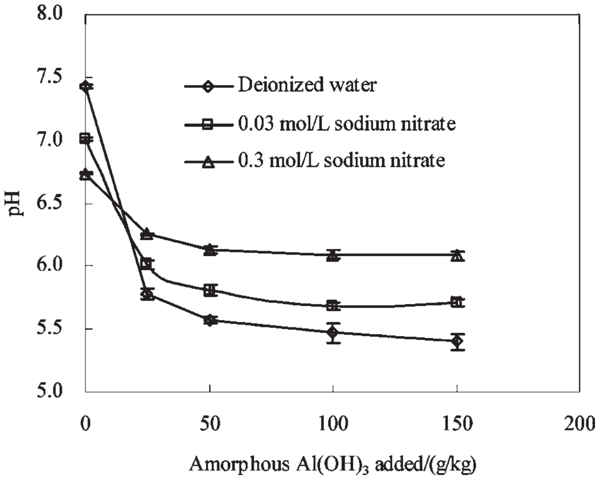

Figure 6. Effects of amorphous $Al(OH)_3$ and ionic strength on the pH of benonite suspensions.

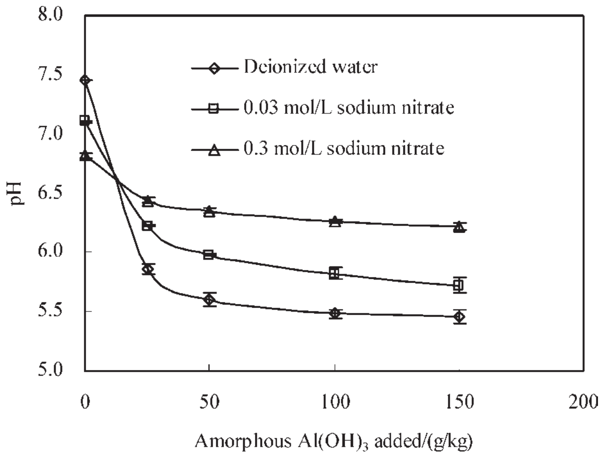

Figure 7. Effects of amorphous $Al(OH)_3$ and ionic strength on the pH of Alfisol suspensions.

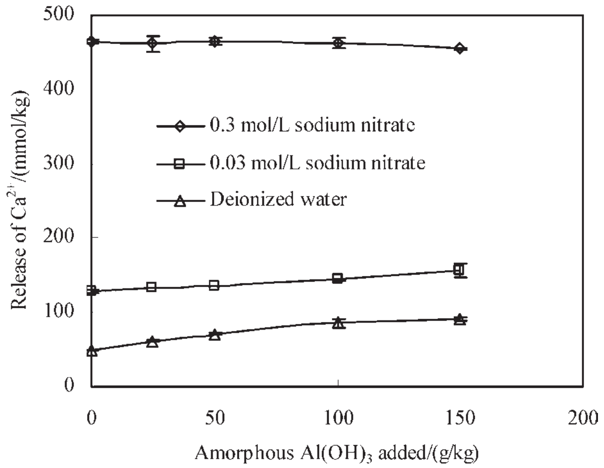

Figure 8. Effects of amorphous $Al(OH)_3$ and ionic strength on the release of Ca^{2+} from bentonite at constant pH of 5.37 for the systems of 0.3 $mol \cdot L^{-1}$ $NaNO_3$, 0.03 $mol \cdot L^{-1}$ $NaNO_3$, and deionized water.

results were also shown in Figure 3. The amount of Ca^{2+} desorbed was found to increase sharply when the aluminum hydroxide added was increased from (0 to 50) $g \cdot kg^{-1}$ and then increased gradually with the further addition of the aluminum hydroxide. This is similar to that observed for the kaolinite system and may be due to the same reason for the case of the kaolinite, that is, because of a lower CEC (Table 1). The kaolinite is a dominant clay mineral in the soil. While the desorption of Ca^{2+} and Mg^{2+} from the Alfisol induced by the Al hydroxide was similar to that observed for the bentonite system (Figures 3 and 5), this is because that the dominate clay minerals in the soil are hydrous mica, vermiculite, and montmorillonite, and thus the soil has a higher CEC.

3.3. Effects of pH and Ionic Strength on the Release of Ca^{2+} and Mg^{2+}.

It is possible that the amorphous $Al(OH)_3$ added induced the decrease in suspension pH of soils and minerals and thus enhanced the desorption of cations of Ca^{2+}, Mg^{2+}, and Na^+ through the exchange of H^+ with the adsorption phase of these cations. The effect of amorphous $Al(OH)_3$ added on suspension pH of bentonite and Alfisol at different ionic strengths was shown in Figures 6 and 7. In controls without amorphous $Al(OH)_3$ added, the addition of $NaNO_3$ induced the release of H^+ from bentonite and Alfisol and thus decreased their suspension pH. This suggested that some exchangeable H^+ was present on the surfaces of Alfisol and bentonite. The addition of amorphous $Al(OH)_3$ led to more H^+ release from Alfisol and bentonite and thus a larger decrease in suspension pH in the deionized water system compared with $NaNO_3$ system. The high ionic strength lowers the activity of H^+; therefore, the decrement of pH due to the addition of amorphous $Al(OH)_3$ decreased with the increase in ionic strength.

To distinguish the contribution of H^+ and overlapping of diffuse layers to the enhancement on the desorption of Ca^{2+} and Mg^{2+}, constant pH experiments were conducted, and results were presented in Figures 8 to 11. The release of Ca^{2+} and Mg^{2+} in the controls without amorphous $Al(OH)_3$ and $NaNO_3$ added was ascribed to the contribution of H^+. With the increase in the amount of amorphous aluminum hydroxide added, the amount of Ca^{2+} and Mg^{2+} released from bentonite and Alfisol in deionized water increased. This was attributed to the overlapping of diffuse layers on amorphous $Al(OH)_3$ and bentonite and Alfisol. The difference of the amount of Ca^{2+} and Mg^{2+} between

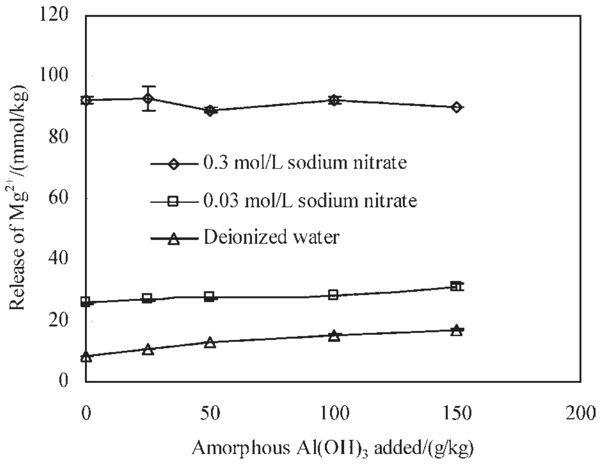

Figure 9. Effects of amorphous $Al(OH)_3$ and ionic strength on release of Mg^{2+} from bentonite at constant pH of 5.37 for the systems of 0.3 $mol \cdot L^{-1}$ $NaNO_3$, 0.03 $mol \cdot L^{-1}$ $NaNO_3$, and deionized water.

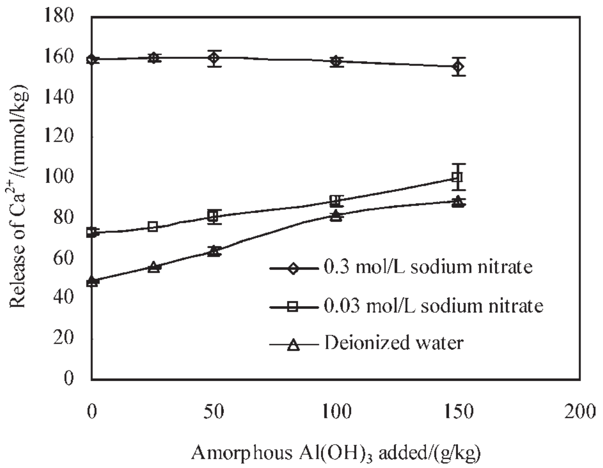

Figure 10. Effects of amorphous $Al(OH)_3$ and ionic strength on release of Ca^{2+} from Alfisol at constant pH of 5.34 for the systems of 0.3 $mol \cdot L^{-1}$ $NaNO_3$, 0.03 $mol \cdot L^{-1}$ $NaNO_3$, and deionized water.

the systems with amorphous $Al(OH)_3$ added and the controls represents the contribution of the diffuse layer overlapping to the release of both cations. The amount of Ca^{2+} and Mg^{2+} released from bentonite by H^+ was (49.2 and 8.4) $mmol \cdot kg^{-1}$. When (25, 50, 100, and 150) $g \cdot kg^{-1}$ of amorphous $Al(OH)_3$ were added, the amount of Ca^{2+} released from bentonite was (11.7, 21.9, 36.1, and 42.4) $mmol \cdot kg^{-1}$ due to the diffuse layer overlapping, respectively; the corresponding data were (2.3, 4.4, 7.2, and 8.8) $mmol \cdot kg^{-1}$ for Mg^{2+}. From surface of the Alfisol, the amount of Ca^{2+} and Mg^{2+} released by H^+ was (48.7 and 11.9) $mmol \cdot kg^{-1}$. When (25, 50, 100, and 150) $g \cdot kg^{-1}$ of amorphous $Al(OH)_3$ were added, the amount of Ca^{2+} released from the Alfisol was (7.1, 15.3, 33.0, and 39.6) $mmol \cdot kg^{-1}$ due to the diffuse layer overlapping, respectively; the corresponding data were (1.3, 4.1, 7.5, and 9.7) $mmol \cdot kg^{-1}$ for Mg^{2+}. Therefore, both H^+ and the diffuse layer overlapping have significant contributions to the release of Ca^{2+} and Mg^{2+} from bentonite and Alfisol.

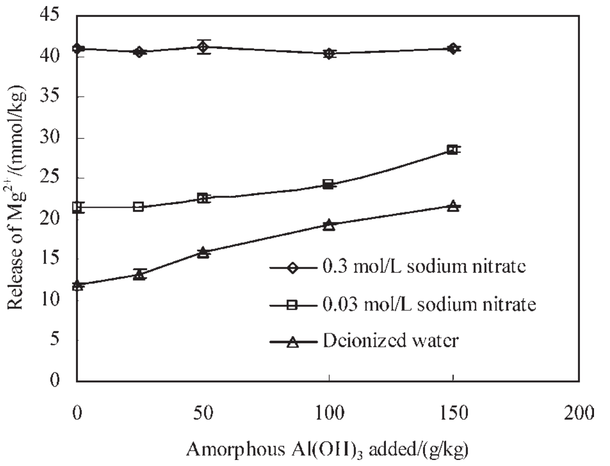

Figure 11. Effects of amorphous $Al(OH)_3$ and ionic strength on release of Mg^{2+} from Alfisol at constant pH of 5.34 for the systems of 0.3 $mol \cdot L^{-1}$ $NaNO_3$, 0.03 $mol \cdot L^{-1}$ $NaNO_3$, and deionized water.

The presence of soluble Al(III) in suspensions may also induce the release of Ca^{2+} and Mg^{2+} from bentonite and Alfisol through the competition of aluminum ions for negative charge sites with the both cations. The soluble Al(III) in suspensions of bentonite and Alfisol with and without amorphous $Al(OH)_3$ added was presented in Table 3. The results indicated that the contents of soluble Al(III) in all systems with deionized water and 0.03 $mol \cdot L^{-1}$ $NaNO_3$ were lower than 0.05 $mmol \cdot kg^{-1}$ and much lower than the contents of Ca^{2+} and Mg^{2+} in the corresponding systems. Therefore, the enhancement of soluble Al(III) on the release of Ca^{2+} and Mg^{2+} from bentonite and Alfisol can be neglected.

Results in Figures 8 to 11 indicated that the amount of Ca^{2+} and Mg^{2+} from bentonite and Alfisol also increased with the increase in the concentration of $NaNO_3$, while the contribution of the diffuse layer overlapping to the release of the both cations changed oppositely. For example, when the amount of amorphous $Al(OH)_3$ was 150 $g \cdot kg^{-1}$, the release of Ca^{2+} and Mg^{2+} due to the diffuse layer overlapping was (27.7 and 5.2) $mmol \cdot kg^{-1}$ for bentonite and (27.2 and 7.1) $mmol \cdot kg^{-1}$ for Alfisol in 0.03 $mol \cdot L^{-1}$ $NaNO_3$ systems, which were lower than the corresponding data in the deionized water systems. When the concentration of $NaNO_3$ was increased to 0.3 $mol \cdot L^{-1}$, the amounts of Ca^{2+} and Mg^{2+} released from bentonite and Alfisol were much higher than the corresponding data in deionized water and 0.03 $mol \cdot L^{-1}$ $NaNO_3$, but the amount of both cations released did not change with the addition of amorphous $Al(OH)_3$. These results suggested that the extent of diffuse layer overlapping decreased with the increase in ionic strength and thus its effect on the release of Ca^{2+} and Mg^{2+} from soils and minerals. In 0.3 $mol \cdot L^{-1}$ $NaNO_3$, the effect of diffuse layer overlapping on the release of Ca^{2+} and Mg^{2+} was completely inhibited. It is well-known that the thickness of diffuse layer of electric double layers on colloidal particles decreased with the increase in ionic strength of medium. The increase in ionic strength and the decrease in thickness of colloidal diffuse layer caused the reduction of overlapping of the diffuse layers between amorphous $Al(OH)_3$ and bentonite or Alfisol (Li and Xu, 2008) and thus decreased the enhancement of the diffuse layer overlapping on the release of Ca^{2+} and Mg^{2+} from soils and minerals in the presence of amorphous $Al(OH)_3$. The results further confirmed that the overlapping of the diffuse layers on positively charged amorphous $Al(OH)_3$ and negatively charged soils

Table 3. Release of Aluminum during the Interaction between Alfisol (or Bentonite) and Amorphous $Al(OH)_3$ under Different Ionic Strengths at Constant pH[a]

	Alfisol			bentonite		
$Al(OH)_3$ addition	water	$0.03\ mol\cdot L^{-1}\ NaNO_3$	$0.3\ mol\cdot L^{-1}\ NaNO_3$	water	$0.03\ mol\cdot L^{-1}\ NaNO_3$	$0.3\ mol\cdot L^{-1}\ NaNO_3$
$g\cdot kg^{-1}$	$mmol\cdot kg^{-1}$					
0	0.03	0.04	0.07	0.01	0.02	0.03
25	0.04	0.04	0.06	0.01	0.02	0.03
50	0.04	0.04	0.07	0.02	0.02	0.04
100	0.05	0.05	0.07	0.03	0.01	0.05
150	0.05	0.05	0.09	0.03	0.02	0.04

[a] The pH is 5.34 for the Alfisol with $0.3\ mol\cdot L^{-1}\ NaNO_3$, $0.03\ M\ NaNO_3$, and deionized water and 5.37 for the bentonite with $0.3\ mol\cdot L^{-1}\ NaNO_3$, $0.03\ mol\cdot L^{-1}\ NaNO_3$, and deionized water, respectively. The uncertainties of the measurement are in the range of ± $0.01\ mmol\cdot kg^{-1}$.

and minerals enhanced the release of Ca^{2+}, Mg^{2+}, and Na^{+} from soils and minerals at low ionic strength.

4. CONCLUSIONS

The overlapping of the diffuse layers on oppositely charged particles made the effective surface charge density on kaolinite and bentonite and soils less negative; thus, the ability of these negatively charged surface to adsorb cations declined. Therefore, the addition of amorphous $Al(OH)_3$ accelerated the desorption and release of Ca^{2+}, Mg^{2+}, and Na^{+} from soils and minerals used. The higher the charge density on the colloidal particles, the stronger the interaction of the electric double layers between them. Thus, the larger desorption of cations from the bentonite and the Alfisol by the greater amount of amorphous $Al(OH)_3$ added was mainly ascribed to the larger value of negative surface charge on the soil and mineral and the stronger interaction of the electric double layers between oppositely charged particles compared with the systems of the kaolinite and the Ultisol. The content of soluble Al(III) in the systems was much lower than that of Ca^{2+} and Mg^{2+}; thus, the effect of soluble Al(III) on the release of Ca^{2+} and Mg^{2+} can be neglected. However, H^{+} in the systems has a significant contribution to the release of cations through the cation exchange reaction in addition to diffuse layer overlapping. The increase in ionic strength decreased the overlapping of diffuse layers and thus the enhancement of diffuse layer overlapping on the release of Ca^{2+} and Mg^{2+} from soils and minerals in the presence of amorphous $Al(OH)_3$.

The results in this study suggested that the intensive weathering and leaching led to an accumulation of aluminum oxides in the variable charge soils, and the interaction of the electric double layers between the phyllosilicates and the aluminum oxides probably enhanced the desorption of the cations from the soils and accelerated the further leaching loss of Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} from the soils.

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