

# Effects of alkaline ameliorator additions on the acidic buffering abilities of aluminum-rich alfisols\*

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**Abstract**—Lime and coal flying ash applications could mitigate pollution from acid deposition and improve the buffering ability of two acidic soils sampled from Zhejiang Province. The results showed that soil alkalinity and acidified buffering capacities (QpHs) were significantly increased, especially for liming treatment; whereas, the amounts of  $\text{SO}_4^{2-}$  adsorbed by treated soils were decreased to some degrees because net negative charges of soil oxide colloidal surfaces were increased with the decrease in soil acidity, although the soil fixation abilities for adsorbed  $\text{SO}_4^{2-}$  were not reduced. These facts indicated that after the alkaline ameliorators were applied, the positive and adverse effects resulted from sulfate-type acid deposition were simultaneously existed in these soil treatments.

**Keywords**, acidic alfisol; alkaline ameliorator; acidified buffering capacity.

## 1 Introduction

With the development of industries and the increase in fuel combustion, the situation of acid deposition in southern areas of China was very serious. Being less by the content of cation exchange capacity (CEC) and level of base saturation (BS), the buffering ability and endurance of aluminum-rich alfisols, which widely developed in the east and south of China, to acid deposition were relatively lower than calcareous soils. Lime and coal flying ash acted as an alkaline amendments were applied in two acidic alfisols to mitigate the acid deposition and to improve the acidic buffering ability in this study. Attempts were made to examine the changes of sorption-desorption characteristics of  $\text{SO}_4^{2-}$ , which was main acidic component of acid rain in studied areas, and soil acidified buffering capacities ( $Q_{\text{pHs}}$ ) as well as the electric charge of soil colloidal surfaces, and to assess the positive and adverse effects possibly existed in all soil treatment by this amendments.

## 2 Materials and methods

### 2.1 Soil samples and doses of alkaline ameliorators added

The soils used in this study were sampled from the southern and northern areas in Zhe-

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jiang Province; samples were air-dried and passed through a 0.25mm sieve mesh, their properties are listed in Table 1.

**Table 1 Soil samples and physico-chemical properties**

Soil	pH <sub>H<sub>2</sub>O</sub>	OM,	CEC,	BS,	Free oxides, %		Soil particles, %	
		%	meq/100g	%	Fe <sub>2</sub>	Al <sub>2</sub>	0.05-0.001mm	<0.001mm
Red soil	5.34	1.60	18.16	26.49	3.37	0.75	51.20	36.19
Yellow								
-red soil	4.75	1.44	16.51	45.31	2.39	0.60	49.80	25.00

100 g soil samples were mixed with the different doses of two alkaline amendments and 50ml H<sub>2</sub>O were added; samples were then incubated at a constant temperature (20°C) over 3 weeks. After above retreating, samples were air-dried and grained again and were packed into plastic bottles (Table 2).

**Table 2 The doses of alkaline amendments added**

Soil Amendments	Red soil						Yellow-red soil					
	CaCO <sub>3</sub>			Coal flying ash			CaCO <sub>3</sub>			Coal flying ash		
	ck	I <sub>1-1</sub>	I <sub>1-2</sub>	II <sub>1-1</sub>	II <sub>1-2</sub>	II <sub>1-3</sub>	ck	I <sub>2-1</sub>	I <sub>2-2</sub>	II <sub>2-1</sub>	II <sub>2-2</sub>	II <sub>2-3</sub>
Doses, %	0	0.2	0.5	2.0	4.0	8.0	0	0.4	0.8	3.0	6.0	12.0

## 2.2 The test procedure and methods

### 2.2.1 Sorption-desorption of sulfate anion by treated soils

This test procedure had been described in the published literature (Wu, 1993).

### 2.2.2 Determination of electric charge of soil colloidal surfaces

The determination of positive and negative charge of soil surfaces was carried out according to the NH<sub>4</sub>Cl exchange procedure proposed by Schofield (Schofield, 1939) and Yuan (Yuan, 1985). Each of 2.5g soils samples were washed four times with 30ml aliquots of 0.2mol/L NH<sub>4</sub>Cl in preweighted centrifugal tubes, the tubes and the contents of NH<sub>4</sub>Cl residues were then reweighed. The soils were extracted four times with 0.5mol/L KNO<sub>3</sub>, after centrifuging, the supernatant were collected into 100 ml volumetric flasks. The amounts of Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup> in the KNO<sub>3</sub> extracts were then determined and followed by subtracting the contents of Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup> in the residues, the amounts of positive and negative charge that expressed as the contents of Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup> on soil surfaces could be estimated (meq/100g).

### 2.2.3 Determination of soil acidified buffering capacities(QpHs)

0.5g soil samples were mixed with 250 ml of 0.005 mol/L NaCl solution, the original pH values of the suspension were measured; a graded volume of 0.5mol/L H<sub>2</sub>SO<sub>4</sub> solution ( $n \pm n \times 10 \mu\text{l}$ ) were added using microinjectors, and the pH values of the acidified soil suspension were then separately determined. This test was stopped when the pH value of soil

solution was dropped down to 4.0. The volume of  $H_2SO_4$  added ( $\mu l$ ) by each time and the corresponding pH values of acidified soil solution were recorded, the amounts of  $H^+$  consumed by unit weight of soils acidified to given pH values ( $H^+$  mmol/100g) also could be calculated.

#### 2.2.4 Method of physical and chemical analysis

Soil pH, organic matter, texture, CEC and  $Cl^-$ ,  $NH_4^+$  were determined by conventional analysis method (Institute of Soil Science, Chinese Academy of Sciences, Nanjing, 1978). The contents of active Fe and Al oxides ( $Fe_d$ ,  $Al_d$ ), extracted by a DCB reagent, were determined using a DCP spectrophotometer. The amounts of  $SO_4^{2-}$  in the supernatant were detected using a 721-type spectrophotometer, after displacing the  $CrO_4^{2-}$  by equivalent  $SO_4^{2-}$  in the excessive volume of  $BaCrO_4$  suspension added, the optimum detective concentration of  $SO_4^{2-}$  was 10–120mg/L.

### 3 Results and discussion

#### 3.1 Variation of both soil pH values and the amounts of $SO_4^{2-}$ adsorbed

After two alkaline amendments were applied, the pH values of treated soils rose in some degrees, except for small dose of coal flying ash application (2%) in red soil sample, especially in the liming treatments; however, at the same initial concentration of  $SO_4^{2-}$  (1000  $\mu g/ml$ ) in the adsorption mediums, the adsorption amounts and rates of  $SO_4^{2-}$  by treated soils synchronously decreased (Table 3). The relationship between the increases of soil alkalinity and the decreases of adsorbed  $SO_4^{2-}$  amounts was very close ( $r = 0.98$ ), and the results also agreed with the same tested results reported by Korentajer (Korentajer, 1983), Bolan (Bolan, 1988) and their coworkers.

Table 3 Variation of pH values and amounts of  $SO_4^{2-}$  adsorbed by treated soils

Soil Amendments	Red soil						Yellow-red soil					
	CaCO <sub>3</sub>			Coal flying ash			CaCO <sub>3</sub>			Coal flying ash		
	ck	I <sub>1-1</sub>	I <sub>1-2</sub>	II <sub>1-1</sub>	II <sub>1-2</sub>	II <sub>1-3</sub>	ck	I <sub>2-1</sub>	I <sub>2-2</sub>	II <sub>2-1</sub>	II <sub>2-2</sub>	II <sub>2-3</sub>
pH	5.34	6.65	7.80	5.32	5.57	5.85	4.75	7.35	8.11	5.23	5.41	5.95
Adsorbed, $\mu l/g$	1003.3	779.5	605.1	1051.4	954.2	849.9	1354.3	1223.6	1181.2	1163.2	1118.6	792.9
Adsorption rates, %	18.8	14.6	11.5	19.9	18.0	16.1	25.4	22.8	22.0	21.7	20.9	14.8

\*  $C_0 = 1000 \mu g SO_4^{2-}/ml$

The increases of alkalinity of treated soils were favorable to strengthen the ability of neutralization for acid input and the adverse effect of acid deposition on soil acidification was then reduced. On the other hand, the decline of the binding capacity of  $SO_4^{2-}$  expressed as the decrease of  $SO_4^{2-}$  adsorbed also would be beneficial to increase the migration of  $SO_4^{2-}$  added, which may be gave rise to leach and remove the bases and nutrient ions out of the soil profiles.

#### 3.2 The changes of desorption characteristics of adsorbed $SO_4^{2-}$

The desorption amounts and rates of adsorbed  $\text{SO}_4^{2-}$  by both  $\text{H}_2\text{O}$  and 1.0mol/L NaCl desorbents are listed in Table 4.

Table 4 The desorption amounts and rates of adsorbed  $\text{SO}_4^{2-}$

Code	Adsorbed, $\mu\text{g/g}$	Desorbents	Desorbed, $\mu\text{g/g}$	Desorption rates, %
Red soil				
ck	1018.84	$\text{H}_2\text{O}$	468.16	45.95
	997.03	NaCl	759.82	76.21
I <sub>1-1</sub>	768.60	$\text{H}_2\text{O}$	314.00	40.85
	790.43	NaCl	634.53	80.28
I <sub>1-2</sub>	619.51	$\text{H}_2\text{O}$	274.15	44.25
	597.94	NaCl	575.81	96.30
II <sub>1-1</sub>	835.65	$\text{H}_2\text{O}$	388.34	46.47
	1159.32	NaCl	972.99	83.93
II <sub>1-2</sub>	941.34	$\text{H}_2\text{O}$	536.56	57.00
	967.28	NaCl	826.54	85.45
II <sub>1-3</sub>	911.08	$\text{H}_2\text{O}$	572.70	62.86
	727.69	NaCl	640.01	87.95
Yellow-red soil				
ck	1354.32	$\text{H}_2\text{O}$	900.24	66.47
	1354.31	NaCl	1196.67	88.36
I <sub>2-1</sub>	1223.62	$\text{H}_2\text{O}$	485.15	39.65
	1223.62	NaCl	778.55	63.63
I <sub>2-2</sub>	1245.52	$\text{H}_2\text{O}$	578.76	46.47
	1213.38	NaCl	902.53	74.38
II <sub>2-1</sub>	1305.58	$\text{H}_2\text{O}$	262.72	20.12
	1262.87	NaCl	483.76	38.31
II <sub>2-2</sub>	1091.89	$\text{H}_2\text{O}$	257.36	23.57
	1145.29	NaCl	388.01	33.88
II <sub>2-3</sub>	878.34	$\text{H}_2\text{O}$	194.30	23.11
	707.49	NaCl	386.52	54.63

The results could be described as follows:

When the amounts of adsorbed  $\text{SO}_4^{2-}$  were approximately equal, the desorption amounts and rates by 1.0mol/L NaCl were larger or greater than that by  $\text{H}_2\text{O}$ , despite of two alkaline amendments whether or not were applied. The neutral salt solution (NaCl) could remove some or most amounts of adsorbed  $\text{SO}_4^{2-}$ , which meant the predominant mechanism of sulfate adsorption by soils seemed to be a reversible electrostatic ion exchangeable reaction. This phenomena was also expressed by our previous study(Wu, 1993).

By comparison with the control, the differences of desorption rates of adsorbed  $\text{SO}_4^{2-}$  in the treated red soils by two desorbents were smaller ( $\pm 10\%$ ); but the decrease of desorption rates were significant in the treated yellow-red soils, especially in the treatment of coal flying ash applications. This results could be shown that when this alkaline materials were incorporated in soils, although the binding capacity of  $\text{SO}_4^{2-}$  by soils was reduced due to the increase of soil alkalinity, but the soil fixation ability for adsorbed  $\text{SO}_4^{2-}$  was not decreased and so far as to increase in some degree in the treated yellow-red soils, indicating the positive and negative effects by the alkaline amendment additions to withstand the sulfate-type acid deposition were simultaneously existed in this instance.

### 3.3 The variation of electric charge on the soil surfaces

The stoichiometric amounts of charge on the oxide colloidal surfaces were depended on the changes of the soil acidity. After the alkaline amendments were added, the amounts of positive and negative charge on the oxide colloidal surfaces were decreased and increased respectively, due to the soil alkalinity was increased, which induced the increase of the amounts of net negative charge on soil surfaces. This tendency was even more significant in the liming treatments (Table 5).

Table 5 Variation of electric charge of treated soil surface

Code	pH	Electric charge, meq/100g		Net negative charge, meq/100g
		+	-	
Red soil				
ck	5.34	7.96	8.65	0.69
I <sub>1-1</sub>	6.65	7.90	9.77	1.87
I <sub>1-2</sub>	7.80	5.96	11.81	5.85
II <sub>1-1</sub>	5.32	8.12	9.13	1.01
II <sub>1-2</sub>	5.57	7.60	9.43	1.83
II <sub>1-3</sub>	5.85	6.34	10.12	3.78
Yellow-red soil				
ck	4.75	5.93	7.45	1.52
I <sub>2-1</sub>	7.35	5.66	7.72	2.06
I <sub>2-2</sub>	8.11	5.27	11.62	6.35
II <sub>2-1</sub>	5.23	5.83	8.02	2.19
II <sub>2-2</sub>	5.41	4.96	9.18	4.49
II <sub>2-3</sub>	5.95	3.80	10.60	6.80

The main mechanism of sulfate adsorption on the soil oxide surfaces belonged to the attraction between the positive and negative charged particles by electrostatic binding force mentioned above. With the increase in both soil pH and the amounts of net negative charge, the repulse for sulfate anion then would be increased on the colloidal surfaces, which could

result in the decrease in adsorption amounts of  $\text{SO}_4^{2-}$ . The statistical analysis based on the tested results also demonstrated that the amounts of adsorbed  $\text{SO}_4^{2-}$  were directly and adversely correlated with the amounts of positive ( $r=0.92-0.93$ ) and negative charge ( $r=-0.85-0.96$ ) on the soils surfaces, respectively. These results were also in agreement with the research of the charge relationships of sulfate adsorption and leaching of acidic soils reported by March (March, 1987), Bolan (Bolan, 1988) and their coworkers.

### 3.4 The changes of soil acidified buffering capacities (QpHs)

Soil acidified buffering capacity could be defined as, "during the soil was artificially acidified by the procedure of acid titration, the volume of acid consumed at the soil pH values were dropped down to given levels and the corresponding holding capacity of  $\text{H}^+$  by unit weight of soils ( $\text{H}^+$  mmol/100g)", which could be used to compare the magnitude of the strength of acidic buffering capacity of different soil types and predict quantitatively the tendency of soil acidification by acid deposition. This results adopted in this study could compare the difference of the improvemental extent of soil acidic buffering ability by two alkaline ameliorator additions. The tested results are expressed in Fig. 1.

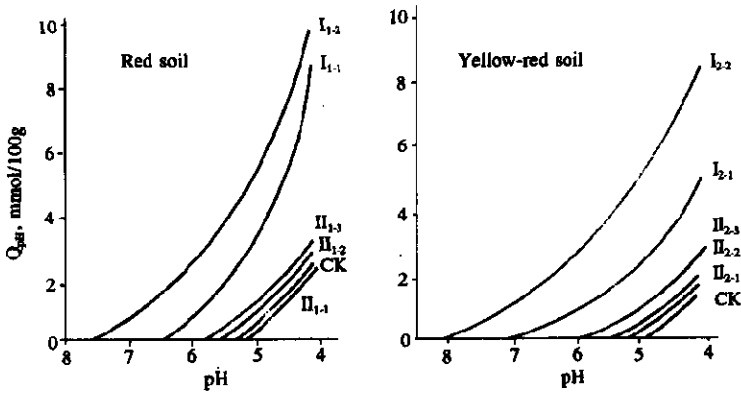


Fig. 1 Illustration of acidified buffering capacities of treated soils

As comparison with the control, the holding capacity of  $\text{H}^+$  used to drop down the soil pH to same given levels increased significantly, especially in the liming treatments, indicating that the improvement of soil acidic buffering ability by liming additions was more effective than that by coal flying ash applications.

## 4 Summary

After the lime and coal flying ash acted as an alkaline amendments were applied in the acidic alfisols, not only could be improved the physical and chemical properties as well as the nutrient-supplying abilities, but also the endurance and acidic buffering abilities acted to mitigate the acid deposition would be increased, the latter expressed as the increase in both soil alkalinity and acidified buffering capacities (QpHs), this functions by liming treatments were

more effective than that by coal flying ash additions. Whereas, the adsorption amounts and rates of  $\text{SO}_4^{2-}$  by two treated soils were decreased to some degrees due to the repulse to sulfate anion was increased with the increase in both soil alkalinity and the amounts of net negative charges on the oxide colloidal surfaces, which may be given rise to increase the migration and leaching of  $\text{SO}_4^{2-}$  and other nutrient components out of the acidic soil profiles.

In order to reduce above adverse effects, it was necessary to control the doses of the alkaline amendment applications. Based on the tested results described above, the appropriate application rates of lime and coal flying ash were of the order of 0.2% (5t/h) and 5% (130t/h), respectively; the detection and control the amounts of the harmful substances such as nuclide, BaP and so on, which mainly existed in the fractions of coal flying ash, in the farm land seemed to be need and requisite.

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