

# Alkaline slag is more effective than phosphogypsum in the amelioration of subsoil acidity in an Ultisol profile



Jiu-yu Li<sup>a</sup>, Zhao-dong Liu<sup>a</sup>, Wen-zhi Zhao<sup>b</sup>, M.M. Masud<sup>a</sup>, Ren-kou Xu<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, P.O. Box 821, Nanjing, PR China

<sup>b</sup> College of Resources and Environment, Yunnan Agriculture University, Kunming 650201, PR China

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## ABSTRACT

Subsoil acidity seriously inhibits the development of agriculture and forestry in southern China. However, there are few effective methods for amelioration of subsoil acidity. In order to develop low cost and efficient methods for amelioration of subsoil acidity through surface application of amendments, a column leaching experiment and an in situ field experiment were conducted to investigate the amelioration effects of surface application of alkaline slag (AS) and phosphogypsum (PG) on the soil properties in an Ultisol profile. AS increased soil pH and base saturation, and decreased exchangeable acidity of the different segments in the soil profile to different degrees. Since AS contains a high content of soluble chloride, the quick leaching of chloride ions promoted the migration of base cations in the amendments through the soil profile, the exchange of base cations with exchangeable aluminum (Al) and manganese (Mn), and the leaching of soluble Al and Mn out of the profile. Although PG could increase the soil exchangeable calcium (Ca), PG significantly increased the soluble Al and Mn in the Ultisol profile. Compared with PG, AS was more effective in decreasing soil acidity and soluble Al and Mn, and increasing exchangeable Ca and magnesium (Mg) in the Ultisol profile. Therefore, AS was superior to PG in ameliorating soil acidity in the surface soil and subsoil of this Ultisol.

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## 1. Introduction

Acid soils, such as Ultisols and Oxisols, are distributed widely in the tropical and subtropical regions in southern China and also around the world, where intense chemical weathering and leaching occur (Yu, 1997; Fageria and Baligar, 2008). Subsoil acidity is a serious constraint to crop production in these soils, since toxic levels of aluminum (Al) and manganese (Mn) and low levels of calcium (Ca) and magnesium (Mg) impair plant root development, making water and nutrients inaccessible to plants (Adams, 1984; Farina and Channon, 1988; Sumner and Noble, 2003; Tang et al., 2003). The surface application of lime has a limited effect on subsurface acidity due to the slow solubility and mobility of lime into the subsurface (Shainberg et al., 1989; Farina et al., 2000a; Liu and Hue, 2001; Conyers et al., 2003). Deep incorporation of lime can be effective but is impractical due to the lack of suitable machinery, the high cost and the negative effect on soil structure (Sumner et al., 1986; Farina et al., 2000b; Liu and Hue, 2001). Thus, it is urgent to explore some effective methods for surface application of amendments to ameliorate subsoil acidity.

The amelioration of subsoil acidity through surface application of amendments depends on transport of base cations from the surface horizon and the reaction of these cations with the acidity in the subsoil horizons. Transport is dependent on the amount of water and the concentration of cations in the leaching water; presumably the latter is dependent on concentrations of accompanying anions such as sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), chloride ( $\text{Cl}^-$ ) and  $\text{HCO}_3^-$ . The reaction of subsoil acidity depends upon the ability of the base cations in solution to displace or react with the exchangeable  $\text{Al}^{3+}$  on subsoil particle surfaces; presumably this is determined by the ratio of acidity to base cations in the incoming leachate (Pleysier and Juo, 1981; Pavan et al., 1984; Cahn et al., 1993). Gypsum has been proposed as an effective amendment for subsoil acidity (Sumner et al., 1986; Shainberg et al., 1989; Alva et al., 1990; McLay et al., 1994). Although gypsum appears to have a minimal effect on pH, it is much more soluble than lime and enables  $\text{Ca}^{2+}$  to move through the soil with  $\text{SO}_4^{2-}$  in a larger quantity and at greater speed than when supplied by lime (Sumner et al., 1986; Shainberg et al., 1989). The amelioration effect of gypsum also varies with soil properties and local precipitation. Moreover, large-scale use of gypsum depends on its cost and availability. Thus low-input alternative or complementary methods need to be developed (Sánchez and Salinas, 1981).

Some gypsum-containing by-products, such as phosphogypsum (PG), appear to be practical approaches to the worldwide

\* Corresponding author. Tel.: +86 25 86881183; fax: +86 25 86881000.

E-mail address: [rkxu@issas.ac.cn](mailto:rkxu@issas.ac.cn) (R.-k. Xu).

problem of subsoil acidity and infertility. PG has a gypsum content of 85–93% and has a similar ameliorating effect to gypsum on subsoil acidity and fertility (Alcordero and Rechcigl, 1993,b; Wang et al., 1999a,b). However, PG is highly acidic and often lowers pH of surface soils. Thus, more attention is being given to alternatives. Many other industrial by-products containing Ca and  $\text{SO}_4$  can also act as alternative amendments (Alva et al., 1990; Alcordero and Rechcigl, 1993; Garrido et al., 2003; Illera et al., 2004; Peregrina et al., 2007). Alkaline slag (AS) is a by-product from ammonia-alkali production of sodium carbonate, contains high contents of calcium sulfate and calcium carbonate, and has proved very effective in correcting surface soil acidity in indoor incubation and field experiments (Li et al., 2010, 2014; Wang et al., 2012). The heavy metal contents in AS constitute a limited environment hazard at the rates normally used in agriculture (Li et al., 2010). However, the effect of AS on subsoil acidity has received little attention under the conditions of both indoor and field. Thus, the amelioration effect of AS on soil acidity and fertility in an Ultisol profile was investigated in a column leaching experiment and an in situ field experiment under natural conditions, with PG included for comparison. The main objective of the present study is to develop low cost and efficient methods for amelioration of subsoil acidity through surface application of amendments.

## 2. Materials and methods

### 2.1. Soil sample and amendments

The Ultisol used for the leaching study was collected from cropland at Langxi County (119°08'E, 31°06'N), Anhui Province in the south of China, where the mean annual temperature and precipitation are 16.0 °C and 1290 mm, respectively. Soil was taken from the top layer (0–30 cm), air-dried and ground to pass a 2-mm sieve. The soil was a strongly acidic Ultisol (U.S. Soil Taxonomy) derived from a Quaternary red earth, with dominant clay minerals being kaolinite, hydrous mica, chlorite, vermiculite and a small quantity of gibbsite, hematite and goethite as determined by X-ray diffraction (XRD). The soil has a sandy clay texture with particle size distribution of 41, 26 and 33% for <2  $\mu\text{m}$  (clay), 2–50  $\mu\text{m}$  (silt) and >50  $\mu\text{m}$  (sand). Soil pH was 3.92, as determined in a 1:2.5 soil: water suspension. Soil organic matter was 16.1  $\text{g kg}^{-1}$ , its CEC was 9.4  $\text{cmol}_c \text{kg}^{-1}$  and its exchangeable  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Al}^{3+}$  were 19.2, 2.6, 3.6, 1.4 and 60.1  $\text{mmol}_c \text{kg}^{-1}$ , respectively.

AS is the waste obtained from ammonia-alkali production of sodium carbonate, using the raw materials limestone and sea salt. PG is generated in the wet-acid production of phosphoric acid through treatment of rock phosphate with sulfuric acid. Both the AS and PG were collected from China Petrochemical Corporation Nanjing Chemical Industrial Co., Ltd. The AS and PG were passed through a 1-mm sieve before use. AS and PG were subjected to XRD using Cu  $\text{K}\alpha$  radiation generated at 40 kV and 20 mA with a Rigaku X-ray diffractometer equipped with an incident beam graphite monochromator. The results indicated that the main minerals in AS are gypsum and calcite, and gypsum and calcium sulfate hydrate in PG (Fig. 1). The major chemical components are calcium sulfate, calcium carbonate and calcium chloride in AS and calcium sulfate

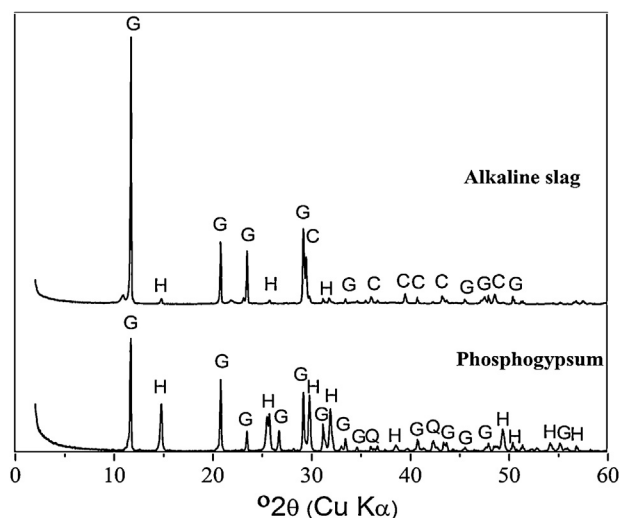


Fig. 1. X-ray diffraction patterns of alkaline slag and phosphogypsum (G: gypsum; C: calcite; H: calcium sulfate hydrate; Q: quartz).

in PG (Table 1). Compared to PG, AS contained a similar content of Ca; higher contents of Mg, sodium (Na) and Cl; and lower contents of phosphorus (P) and sulfur (S) (Table 1). The contents of heavy metals in AS and PG were lower than the background of the Ultisol except for Cu in AS (Table 2). The detail determination procedures of compositions and heavy metals in AS and PG were presented in our previous study (Li et al., 2010).

### 2.2. Column leaching experiment

Leaching columns were made of rigid polyvinyl chloride of 36.0 cm long and 20.0 cm inside diameter (Fig. 2). A hole of 0.5 cm diameter was made on the side wall of the bottom-end for drainage. The column bottom-end was filled with a 2.5-cm layer of acid-washed silica sand, underlain by a fine-sized nylon net to hold the soil in place. After that, each column was separately filled with four soil segments and each segment had 2.85 kg of Ultisol with 7.5 cm depth and bulk density of 1.21  $\text{g cm}^{-3}$ . Only the first segment (0–7.5 cm) was amended with AS or PG in seven treatments: (1) control with no amendment; (2) AS of 4  $\text{g kg}^{-1}$  (AS<sub>1</sub>); (3) AS of 8  $\text{g kg}^{-1}$  (AS<sub>2</sub>); (4) PG of 4  $\text{g kg}^{-1}$  (PG<sub>1</sub>); (5) PG of 8  $\text{g kg}^{-1}$  (PG<sub>2</sub>); (6) AS and PG each of 2  $\text{g kg}^{-1}$  [(AS+PG)<sub>1</sub>]; and (7) AS and PG each of 4  $\text{g kg}^{-1}$  [(AS+PG)<sub>2</sub>] (the application ratios with 4 or 8  $\text{g kg}^{-1}$  surface soil equivalent to 3375 or 6750  $\text{kg ha}^{-1}$  for the 30-cm depth soils, respectively, which were commonly used in the field). In the second and fourth segments, a Rhizon soil moisture sampler (<http://www.rhizosphere.com/>) was embedded in the middle part of each segment. The soil moisture sampler was made of inert polymer with no ion exchange properties; its size is 2.5 mm in diameter and 10 cm long. Once used, it can frequently extract small volumes of pore water from soil in an easy, non-destructive way. Each time, one 40 mL syringe was connected with the soil moisture sampler to extract soil solution twice, and the total volume is more than 50 mL. The soil solution extracted is clean and can be directly

Table 1  
Chemical compositions and pH of alkaline slag (AS) and phosphogypsum (PG).

	pH	ANC <sup>a</sup> ( $\text{mol kg}^{-1}$ )	$\text{SiO}_2$ ( $\text{g kg}^{-1}$ )	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	CaO	MgO	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{P}_2\text{O}_5$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{F}^-$
AS	8.48	8.22	44.	16.3	8.4	243	59.3	0.03	39.2	0.6	121	60	2.0
PG	2.12	-0.25	56.8	5.0	3.6	242	2.0	0.08	1.7	27.8	417	0.1	1.6

Source: adapted from Li et al. (2010).

<sup>a</sup> Acid neutralization capacity.

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