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Neutralizing Capacity of Basic Slag in Acid Sulfate Soils and Its Impacts on the Solubility of Basic Cations under Various Moisture Regimes

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An incubation study was conducted with the topsoils (depth: 0-20 cm) of two different series namely Cheringa (silty clay loam, pH_{water} 3.6, electrical conductivity = EC 18.5 dS m^{-1}, CEC 17.2 c mol kg^{-1}, organic matter = OM 39.1 g kg^{-1}, and Badarkhali (silty clay loam, pH_{water} 3.9, EC 19.0 dS m^{-1}, CEC 18.40 c mol kg^{-1}, OM 30.7 g kg^{-1}) acid sulfate soils to evaluate the effectiveness of basic slag (BS) for the neutralization of acidity and solubility of basic cations. These soils received BS at the rate of 0, 11, 22 and 33 t ha^{-1} under various moisture regimes (moisture at saturated condition, i.e. 100 % moisture, moisture at field condition, i.e. 50 % and wetting-drying cycles of those 50 and 100 % moisture levels). The impacts of these treatments on some selected properties and changes in water soluble bases in these soils were studied at different periods of 180 days of incubation. The application of BS was found to be increased the pH of soils from 3.6 to 5.1 for Cheringa; 3.9 to 5.2 for Badarkhali soils during the 180 days of incubation. These increments were more striking with the highest doses of BS at 33 t ha^{-1} under saturated moisture conditions in both the soils. The EC of the soils had not much influenced by the application of BS, regardless of time. The treatments were exerted significant ($p \leq 0.05$) effects on the solubility of basic cations in different periods of incubation. The maximum release of the bases were recorded during 180 days of incubation under saturated moisture condition and the findings will be supportive for planning of crop production on these soils.

Key words: *acid sulfate soils, basic cations, basic slag, incubation time, moisture regimes*

1 INTRODUCTION

Acid sulfate soils can cause severe land degradation and environmental problems. It has recently been estimated that these affect some 100 million hectares (M ha) of land world-wide (Sheeran, 2003). Among the world distributions of about 24 M ha of acid sulfate soils, about 0.7 M ha are located in coastal areas of Bangladesh. The estimate of the extent and distribution of acid sulfate soils suffer more than most from scanty field surveys, even fewer reliable laboratory data. For sustainable use of acid sulfate soils, acceptable cost effective chemical neutralization is very essential. Application of BS as agricultural lime is not well documented. Moreover, the neutralizing capacity and effectiveness of the BS for the solubility of basic cations in different acid sulfate soils are also not known but needed for its economic and sustainable budgeting for these problem soils (Khan, et al. 2002). Accordingly, agricultural limes such as BS were planned to incorporate into two acid sulfate soils under different moisture regimes. Acid sulfate soils are developed by a variety of processes and/or natural practices that result in the net addition of acidic cations and the net removal of basic cations. Some of these processes such as ‘sulfidization’ (accumulation of sulfides in soil materials), ‘sulfidation’ (processes akin to sulfidization) or ‘pyritization’ and ‘sulfuricization’ (oxidation of sulfide bearing minerals in soils) have great influence in the dynamics in acidic and basic cations of the soils. As acidic water moves downward through soils, the process of leaching tends to increase soil acidification unless loses of bases are offset by basic inputs from nutrient cycling, atmospheric deposition, or mineral weathering. Acidic cations in soil solution tend to displace basic cations until bases are largely exhausted (Schwarz, 1987). Acid induced leaching of basic cations, acidification and mineral weathering are each greatest when pH is less than 3.0 (Li, et al. 1988). Assessing soil sensitivity to acid induced leaching of basic cations has also been emphasized by McFee (1980).

Deficiency in plant base minerals is an important factor when the reclamation and management practices are performed in acid sulfate soils (Jintaridth, 2006). Takai, et al. (1992) claimed that nutrient deficiency is an important factor for the improvement of acid sulfate soils. Dent (1986) reported that BS from the steel industry was effective in reducing the soil acidity and also economical if available locally. The application of basic slag (BS) in acid sulfate soils significantly increased soil pH, Ca and Mg with an associated decrease in Na, Fe and Al concentrations over time (Khan, et al. 2006a). This BS

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had a very high pH of 9.6 and contained 20.8 % Ca, 9.8 % Mg, and 12.8 % SiO_2 (Khan, et al. 2006b). They also added that the BS has been used on a small scale for the reclamation of ASSs in Bangladesh since 1985 and to-date there is no evidence of its harmful effect. The reclamation of these soils may be difficult but essential. Successful reclamation of the acid sulfate soils may result in the development of productive fields for crop growth. While poor soil reclamation may lead to creation of unfavorable soil conditions for crop growth and formation of actual acid sulfate soils, the real problem in the coastal tidal flat plain areas (Khan, et al. 2006b). Cook, et al. (2006) reported that the progressive oxidation of organic matters, sulfides and increasing acidity in the profile of acid sulfate soil is not only decreasing bases in the soil solution but also strongly affect the fate/mobility of metals and metalloids in groundwater, posing threat to groundwater resources and health of both terrestrial and aquatic ecosystems (Abou-Seeda, et al. 2002; Cook, et al. 2006). In acid sulfate soils, water management is the key to soil management and proper water management can limit acidification (Khan, et al. 2006b). However, the effectiveness of BS for the neutralization of acid sulfate soils and associated ion dynamics under variable soil moisture regimes and wetting-drying cycles should have much influence regarding sustainable reclamation and improvement of acid sulfate soils. Considering this background, the present study was done in order to evaluate the acid neutralizing capacity of BS under various moisture regimes and its effects on the release of basic cations in the soils.

2 METHODS AND MATERIALS

2.1 Incubation experiment

An incubation study was conducted in the laboratory of the Department of Soil, Water and Environment, University of Dhaka, Bangladesh during 2000 to 2001 for the determination of acid neutralizing capacity of the BS and its impacts on the solubility of basic cations under various moisture regimes in two acid sulfate soils. Accordingly, an experiment was carried out for 180 days (six months) under saturated soil condition (moisture=100 %), moisture at field capacity (50 %) and wetting-drying cycles of these treatments. The effects of these treatments with time were also considered for this experiment. The treatments for these experiments are presented in **Table 1**. Surface layer (Topsoils: depth 0 to 20 cm) of two different acid sulfate soils (Cheringa series and Badarkhali series) were collected from Cheringa and Badarkhali upazilas in Cox' Bazar district, Bangladesh. These soils were air-dried and grounded uniformly and passed through 2 mm (10 mesh) sieve and mixed thoroughly. Then fifty grams of each soil with respect to treatments was taken in a plastic bottle (10 cm height and 4 cm diameter). The four different doses of 0, 11, 22 and 33 t ha^{-1} of BS were considered for this study. The BS was mixed thoroughly as per treatments. The distilled water was added at saturation condition of soil (50 ml distilled water), moist at field condition (20 ml distilled water) and wetting-drying cycles (from saturation towards field capacity). In wetting-drying cycle, the soil samples in the bottles were kept open to air under saturated condition for 15 days at room temperatures (25℃ to 30℃) for natural air drying towards field capacity for the next 30 days. The wetting-drying cycle was continuously repeated within every one and half months and maintained up to the end of the incubation period of 180 days. The desired levels of moisture in the soils in each bottle were maintained by the addition of distilled water (pH 6.7, EC 0.5 dS m^{-1}) when required. The soils were sampled in order to analyze the soil pH, EC and soluble bases at 01, 15, 45, 60, 90, 105, 135, 150, 180 days after incubation. There were 9 sets of bottles and each set contained 24 bottles (2 soils X 4 treatments X 3 replications), i.e. the numbers of total bottles were 216.

Table 1 Experimental treatments for the incubation study.

AT_0M_1	BT_0M_1	A = Cheringa series; B = Badarkhali series; T_0 = Control; T_1 = Basic slag (#BS) at the rate of 11 t ha^{-1}; T_2 = BS at the rate of 22 t ha^{-1}; T_3 = BS at the rate of 33 t ha^{-1}; M_1= Saturated (Moisture at saturated condition); M_2 = Wetting - Drying cycle; and M_3 = Moist (Moisture at field condition).
AT_0M_2	BT_0M_2	
AT_0M_3	BT_0M_3	
AT_1M_1	BT_1M_1	
AT_1M_2	BT_1M_2	
AT_1M_3	BT_1M_3	
AT_2M_1	BT_2M_1	
AT_2M_2	BT_2M_2	
AT_2M_3	BT_2M_3	
AT_3M_1	BT_3M_1	
AT_3M_2	BT_3M_2	
AT_3M_3	BT_3M_3	

#**Composition of Basic slag (%)** : SiO_2 12.8, Ca 20.8, Mg 9.8, Fe 11.3, Mn 0.04, PO_4 0.03, others 44.96 and pH 9.6 (Source: Laboratory of Soil Science, Institute for Plant Nutrition and Soil Science, University of Kiel, D-24109 Kiel, Germany, 1999).

The soils were analyzed for textural class (pipette method; Day, 1965), pH (field, 1:2.5 water and 0.02 M $CaCl_2$: Jackson 1973), EC (soil : water = 1: 5; Richards 1954), organic carbon (wet combustion with $K_2Cr_2O_7$; Nelson and Somners, 1982), available nitrogen (micro-Kjeldhal method; Jackson, 1973); available phosphorus (0.02 N H_2SO_4, Spectrophotometry at 440 nm wave length; Olsen et al. 1954), water soluble ions (Jackson, 1973) such as Na, K (Flame photometry), Ca and Mg (atomic absorption spectrophotometry (Hesse, 1971), and CEC (Chapman, 1965). The level of significance of the different treatment means were calculated by Duncan's New Multiple Range Test (DMRT) and Least Significant Difference (LSD) Techniques (Zaman, et al. 1982).

3 RESULTS AND DISCUSSION

3.1 Conditions of pre- and post sampling soils

Both the Cheringa and Badarkhali soils (depth: 0-20 cm) showed a silty clay loam texture, initially low pH of 3.6 to 5.1 as determined by the different conditions for the Cheringa and 3.9 to 5.2 for the Badarkhali soils, high EC (18.5 for Cheringa and 19.0 dS m^{-1} for Badarkhali soils) and high amount of organic matter (**Table 2**). These soils were subjected to neutralize by the application of BS under different moisture regimes. The pH values in different conditions of the post sampling soils were found to be increased (IOC = increased over control, i.e. initial value) by 0.7 to 1.6 units, the EC values were decreased by 5 to 8 % in both the soils regardless of treatments (Table 2). The amounts of water soluble potassium and calcium were found to be increased by 446 to 1368 %) whereas the amounts of water soluble sodium is decreased by 3 to 57 %. The content of magnesium was found to be increased by 9 to 12 % in both the soils. The results also indicated that the acid sulfate soils were not only neutralized by the application of BS at different moisture levels but also increased the K, Ca and Mg in the soils. Such response was due to the increase in soil pH as well as release of some elements from the BS to the soils.

Table 2 Some selected properties of initial soils (depth 0-20 cm) and the average soils of all the treatments at final sampling during 180 days after incubation.

Soil properties	Cheringa soil			Badarkhali soil		
	Before use	**After use**	**% IOC**[a]	**Before use**	**After use**	**% IOC**
Texture	Silty clay loam			Silty clay loam		
Moisture at field condition (vol. %)	48	49	2	49	51	4
Soil pH (Field)	3.8	5.4	--	4	5.2	--
Soil pH (Soil:Water=1: 2.5)	3.6	4.3	--	3.9	4.6	--
Soil pH (Soil:0.02 M CaCl=1.2.5)	3.3	4.8	--	3.4	4.4	--
Electrical Conductivity (1: 5 dS m^{-1})	18.5	17	- 8	19	18	- 5
Organic matter (Wet oxidation, g kg^{-1})	39.1	41.3	5	30.7	31.5	3
Available nitrogen (1.3 M KCl, mM kg^{-1})	3.6	5.60	56	3.3	4.10	24
Available phosphorus (0.02N H_2SO_4, mM kg^{-1})	0.1	0.21	110	0.11	0.20	82
CEC (1 M NH_4Cl: cmol kg^{-1}, at pH 7.0)	17.2	18.4	7	18.5	20.1	9
Aluminium-saturation (1M NH_4Cl: %)	40.3	3.5	- 91	41.2	2.1	- 95
Iron-saturation (1M NH_4Cl: %)	8.3	4.3	- 49	7.1	2.4	- 67
Sodium-saturation (1M NH_4Cl: %)	12.4	8.2	- 34	13	8.2	- 37
Potassium-saturation (1M NH_4Cl: %)	1.4	2.3	66	1.6	2.9	81
Calcium-saturation (1M NH_4Cl: %)	1.8	12.8	613	1.9	13.5	611
Magnesium-saturation (1M NH_4Cl: %)	5.5	22.9	317	6.2	25.8	316
Water soluble ions						
Sodium (Flame photometry: cmol kg^{-1})	3.01	1.29	- 57	3.20	3.10	- 3
Potassium (Flame photometry: cmol kg^{-1})	0.30	2.75	817	0.25	3.67	1368
Calcium (AAS: cmol kg^{-1})	0.30	1.89	530	0.37	2.02	446
Magnesium (AAS: cmol kg^{-1})	3.34	3.63	9	3.43	3.84	12
Iron (AAS: cmol kg^{-1})	0.35	2.04	483	0.31	1.58	410
Sulfate ($BaCl_2$: cmol kg^{-1})	4.86	2.58	- 47	4.20	2.10	- 50

[a] IOC = Increase over control

3.2 Changes in soil pH

A significant ($p \leq 0.05$) positive increase in pH were determined with the increased rates of BS application in both the soils compared with the control where no BS was applied but the water content was maintained at field capacity **(Fig. 1)**. It is evident from the data that the initial low pHs of the soils was increased steadily with the highest doses of BS and the effects were more pronounced with the latter periods of incubation. The most striking changes in pH were obtained under the AT_3M_1 and BT_3M_1 treatments in both the soils. The pH rose from 3.6 to 5.1 in Cheringa soil and 3.9 to 5.2 in Badarkhali soil after 180 days of incubation, which revealed a wide and significant ($p \leq 0.05$) changes in soil pH were made by the application of BS in the both soils. The lower pHs were determined in the control treatments having moisture at field capacity as compared with those obtained from the saturated and wetting-drying cycle conditions. This might be due to having more oxidized conditions at field capacity than those of the other soil conditions. As the release of acidic materials occurred from the break down of pyrite in more oxidized acid sulfate soils, reflecting the requirement of more liming materials to neutralize more acidity in both the soils. In case of control, except for several initial increased trends within first 90 days, the almost unchanged values of soil pHs were found in both the soils throughout the whole period of incubation of 180 days. Application of BS was found to be increased the soil pH linearly with their increase doses regardless of water contents and soil conditions. Khan, et al. (1996) reported that the application of BS at the rate of 12 t ha^{-1} in acid sulfate soil raised the soil pH from 5.3 to 7.4. The rise of soil pH in present study also remained almost similar range, which might be due to the washout of soluble sulfate and/or in the formation of insoluble sulfate compounds like gypsum, akaganeite (Bigham, et al. 1990).

The increase in soil pH or in other way, it can be expressed in the neutralizing capacity of BS by releasing basic elements in the acid sulfate solution was found to be the highest after180 days of incubation with each of the moisture condition and treatment in both the soils. This might be due to the neutralization of produced acids with the released basic ions with the passes of time and the slow releasing state basic ions from the BS might hold the steady increments in pHs of the soils. Throughout the incubation period, it was noticed that the potentiality of BS as a liming material would be effective for neutralizing the acidity of acid sulfate soils for long time. To maintain a reasonably good conditioned soil for growing crops, the soil should be amended at saturated soil condition followed by the application of BS at 33 t ha^{-1}. The basic slag was also reported effective in increasing soil pH as well as maintained favorable soil conditions (Abbaspour, et al. 2004; Alves, et al. 2006 and Khan, et al. 2006b).

3.3 Changes in soil EC

Application of BS at different moisture regimes did not exert any remarkable changes on the electrical conductivity (EC) in both the soils. Almost similar increased and decreased trends in the EC values of the soils under various treatments were observed for Cheringa and Badarkhali soils throughout the incubation **(Fig 2)**. In both the soils, a little increment in EC values were observed initially and then steady till 180 days of incubation. The initial increments of in the EC values reflected the immediate solubility of salts from the applied BS in both the soils. The decrements in EC values were thought to be due to the formation of some insoluble compounds in the basic conditions prevailed as a result by the application BS in the acid sulfate soils. Bigham, et al. (1990) also reported almost similar findings.

3.4 Changes in the solubility of ions

The amounts of water soluble ions depend on their solubility in water in the soil matrix. Some portions of absorbed cations and anions are easily dissolved in water but the remaining portions are subjected to be very ideal conditions to dissolve. The nutrition of plants mainly depends on these water soluble elements in the soil. Accordingly, the present study was conducted to evaluate the changes in the solubility of cations at various periods of incubation having different treatments under various moisture conditions in order to predict the maximum availability state and ionic balance of nutrients in the soils for plant growth.

3.5 Water soluble sodium and potassium

Application of BS and various moisture regimes regarding to the neutralization of acid sulfate soils were increased the concentration of Na and K in both the soils **(Fig 3)**. In wetting-drying cycle, when the soil was wetting then the concentration of Na and K in both the soils increased due to solubility of BS, but in drying conditions, both of these cations decreased. Under saturated conditions, all the treatments exerted a very significant ($p=\leq 0.05$) positive impacts than those of any other conditions. Sodium salts are more or less highly soluble in water. The neutralizing studies of salt affected acid sulfate soil through BS treatments showed a very high concentration of water soluble sodium in the soils

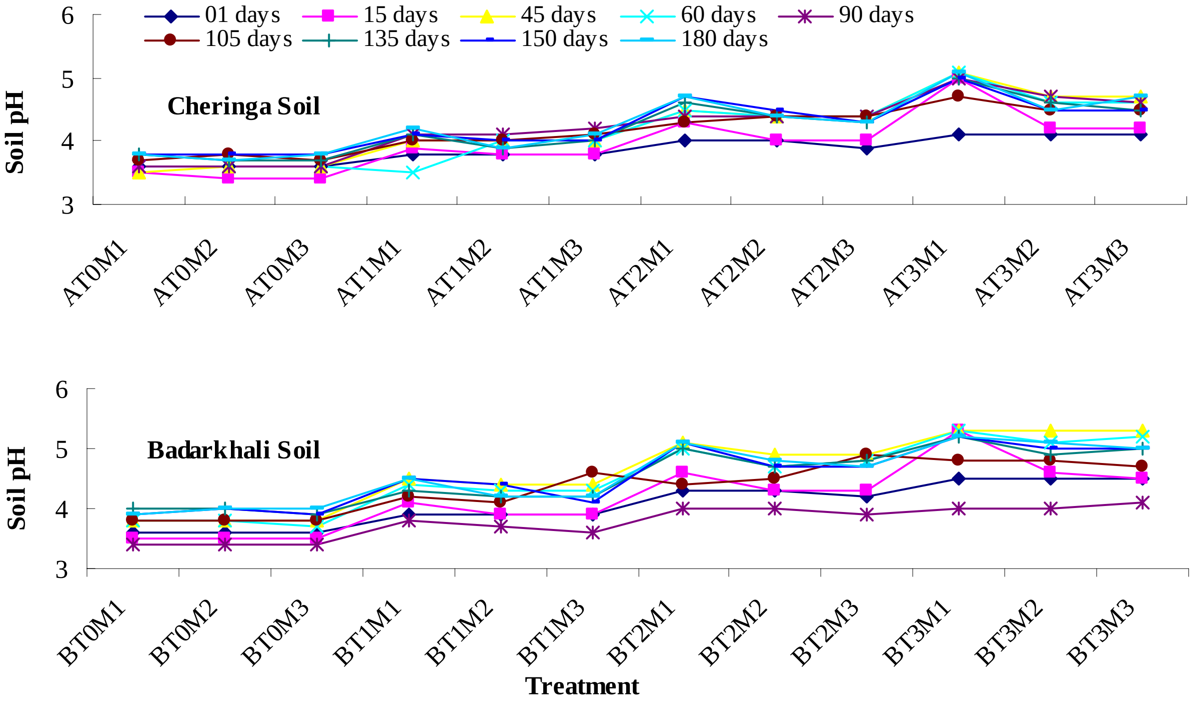

Fig. 1 Changes in soil pH as influenced by the different rates of basic slag, moisture regimes and incubation times.

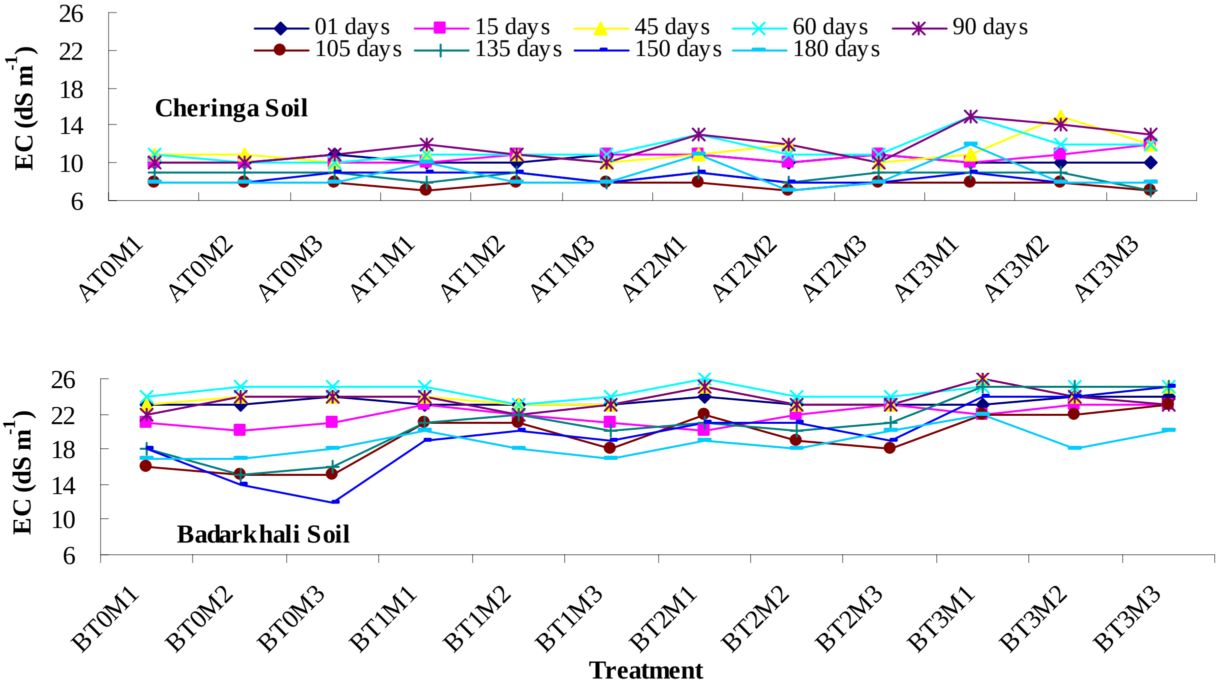

Fig. 2 Changes in electrical conductivity (EC) of soil as influenced by the different rates of basic slag, moisture regimes and incubation times.

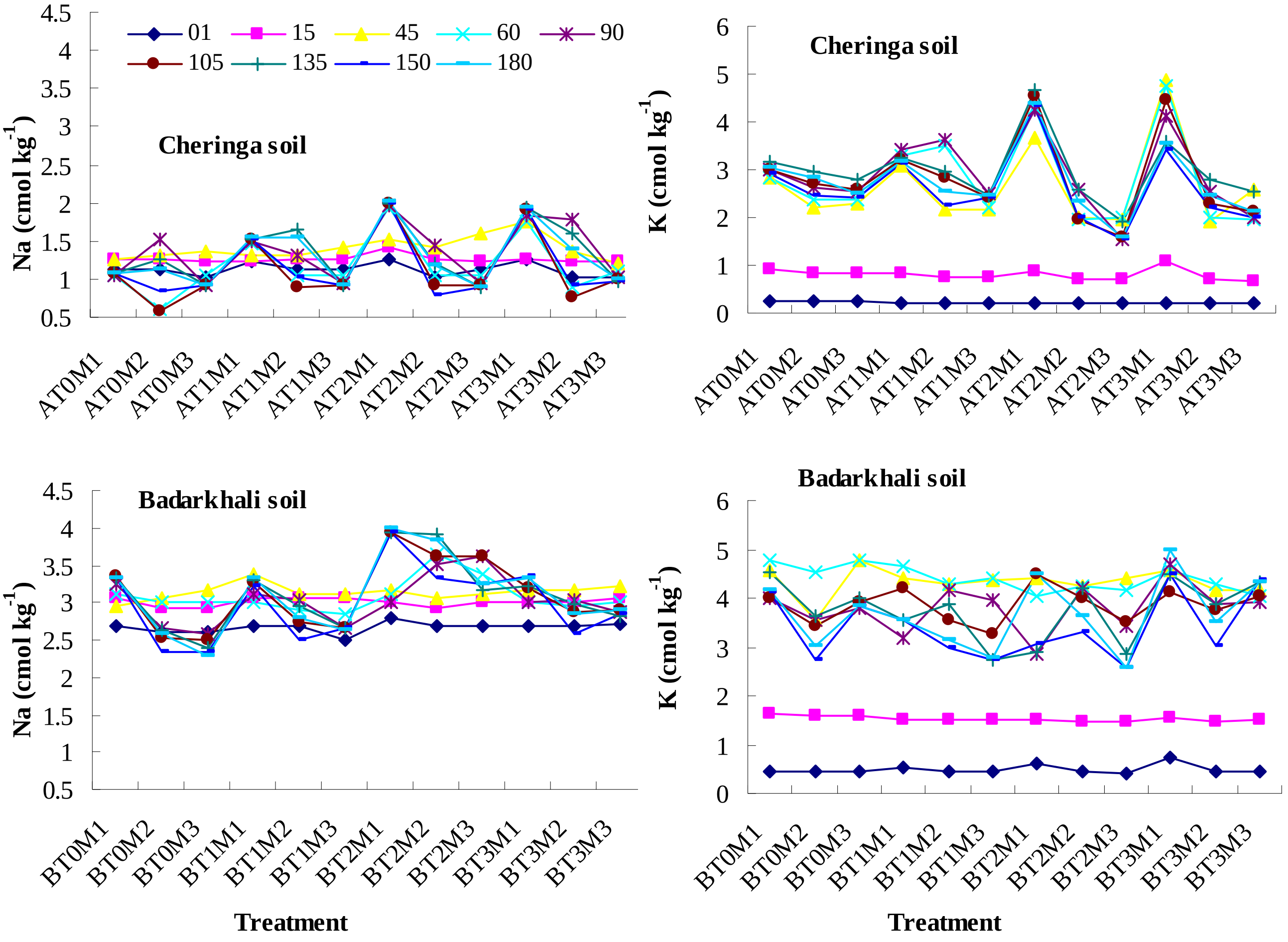

Fig. 3 Effects of basic slag, moisture regimes and incubation times on the solubility of sodium and potassium in the soils.

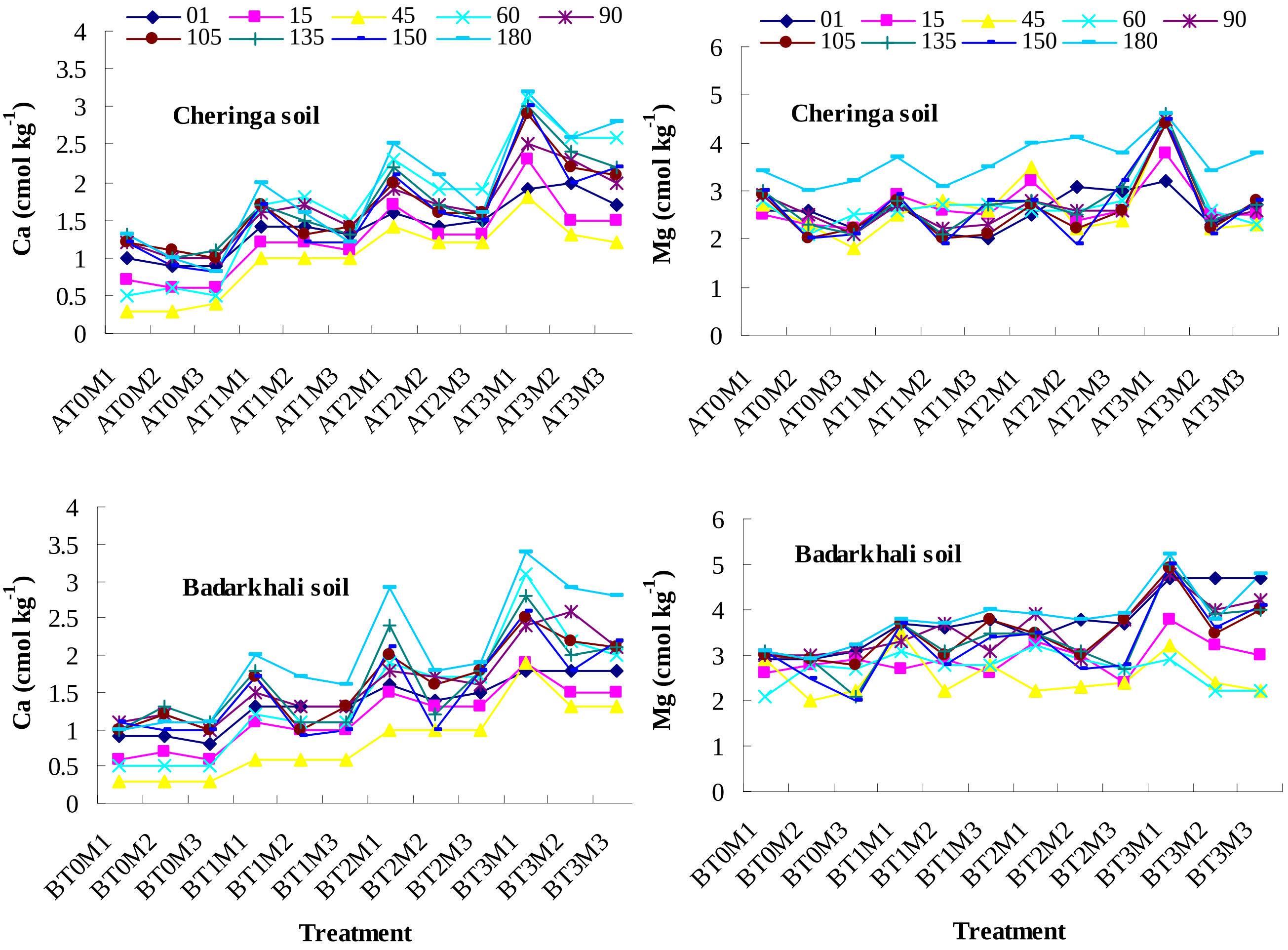

Fig. 4 Effects of basic slag, moisture regimes and incubation times on the solubility of calcium and magnesium in the soils.

throughout the incubation time. The second highest dose (22 t ha $^{-1}$) of BS was found to be increased the water soluble sodium at the highest level in saturated conditions followed by wetting-drying cycle in Cheringa soil and similar role played for Badarkhali soil. The increment of sodium might be because of the quick solubility of Na from the saline-acid sulfate soils as well as from the BS. Badarkhali soil showed the higher contents of water soluble Na compared to Cheringa soil, which might be due to the initial high content of Na in the soil. Water soluble K showed the similar trends as that observed for water soluble sodium in Cheringa the soil, while in Badarkhali soil the highest dose (33 t ha $^{-1}$) played the similar role. Application of BS at different moisture regimes did not exert any remarkable changes on K up to 15 days and then the contents of K were increased in a few cases during the incubation. About 0.33 to 4.88 and 0.25 to 4.68 c mol kg $^{-1}$ of K were found to be increased by the highest dose of BS (33 t ha $^{-1}$) treatments under saturated conditions at Cheringa and Badarkhali soils, respectively. The initial high contents of water soluble K in the soil might be attributed to the disintegration and dissociation of BS and clay particles in the soils. And the decrease of water soluble K after 90 days in a few cases might be due to fixation and release characteristics under variable moisture levels/conditions as well as variations in chemical reactions. Thus, BS application helps to improve the availability of K, making the soils more favorable for crop production.

3.6 Water soluble calcium and magnesium

Application of BS increased the concentration of Ca and Mg in the soil solution (**Fig 4**). The increase in Ca and Mg concentration in the soil solution was due partly to the addition of Ca and Mg from BS undergoing dissolution. Under saturated moisture condition showed better response to the increment of Ca and Mg in both the soils than any other conditions. However, a slight decreased trend was observed in a few cases with the passes of time, which might be attributed to the formation of insoluble compounds of Ca and Mg. The highest contents of water soluble Ca were recorded after 180 days of incubation and the values were 3.2 and 3.4 in Cheringa and Badarkhali soils, respectively under saturated conditions by the highest (33 t ha $^{-1}$) dose of BS (**Fig 4**). These increments of water soluble Ca in the soils was due to the processing of the BS to fine dust and the decomposed organic matter in the soils were the result of their initial processing. In a few cases, the Ca was found to be decreased under the similar conditions having similar BS treatments. The low values of Ca in the soils after several months might be due to formation of insoluble calcium compounds like gypsum, akaganeite (Bigham, et al. 1990) upon reacting with the acidic materials in both the soils. The application of BS was found to be the best among the individual treatments in order to the increment in Ca content, agreeing with the results of Abou-Seeda, et al. (2002) and Barbosa-Filho (2004). The highest water soluble Mg contents were obtained after 180 days by the BS treatments and the values were 4.6, 3.8, 4.1 cmol kg^{-1} at Cheringa soil and 5.2, 3.8, 4.8 c mol kg $^{-1}$ at Badarkhali soil under saturated, wetting- drying cycle and moisture at field conditions, respectively. The application of BS was also found to be the best among the individual treatments in order to the increments in Mg contents, agreeing with the results of Abou-Seeda, et al. (2002) and Barbosa-Filho (2004).

4 CONCLUSIONS

Acidity problems of the studied acid sulfate soils can be neutralized by the application of basic slag (BS). Moisture at saturated condition was found to be best for the maintenance of availability basic cations in both the soils, which will be helpful for planning of crop production on these soils. The highest dose (33 t ha^{-1}) of BS in Cheringa and Badarkhali acid sulfate soils were found to be neutralized these soils at desirable pH levels (pH >5) under saturated soil conditions. The BS not only increased the soil pH but also optimized the concentration especially of Ca and Mg of these soils, suggesting that these acid sulfate soils could be improved under saturated moisture condition following the application of BS before 60 days (two months) of crop cultivation. However, further researches are needed to work out the optimum doses of BS to neutralize the different acidity levels of acid sulfate soils and the release of basic cations for a long time.

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