Assessment of Basic Slag on Reduction of Fe and Al Toxicity in Acid Sulfate Soils under Various Moisture Regimes

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Abstract: Acid sulfate soils (ASSs), which are one of the worst soils in the world, release huge amounts of acid and toxically high concentrations of metals, affecting biological activity in the soils as well as in the surrounding water environments, which requires sustainable measures for their reclamation. Accordingly, an incubation study was conducted with the topsoil of two different ASSs (Cheringa and Badarkhali) to assess the effects of basic slag (BS: size <1 mm; pH 9.6; Ca 20.8 %; Mg 9.8 %, etc.) on reduction of Fe and Al toxicity in ASSs. It is noted that BS is a byproduct of steel industry in Bangladesh and can be collected almost free of charge. These soils received BS at the rate of 0 (T_0), 11 (T_1), 22 (T_2) and 33 (T_3) t ha^{-1} under various moisture regimes (saturated condition $M_{1,}$ i.e. 100 % moisture content, wetting-drying cycles of 100 and 50 % moisture $M_{2,}$ and moisture at field condition $M_{3,}$ i.e. 50 %). The impacts of these treatments on selected parameters in these soils were studied within180 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 at the end of incubation. These increments were more striking with the highest doses of BS under saturated moisture conditions in both of the soils. The treatments exerted significant ($p \leq 0.05$) effects on the decrement of Fe and Al ions in different period of incubation. The striking changes were recorded for the rate of decrements of Fe and Al ions, under saturated condition compared with the control after 180 days of incubation. These results suggest that the application of BS not only reduction of soil acidity but also to improve these soils at desirable pH (pH>5) levels in the same moisture conditions. [Journal of American Science 2009;5(4):33-42]. (ISSN: 1545-1003).

Keywords: acid sulfate soils, Fe and Al ions, basic slag, incubation time, moisture regimes.

1. Introduction

Acid sulfate soils (ASSs), which are one of the worst soils in the world, release huge amounts of acid and toxically high concentrations of metals, affecting biological activity in the soils as well as in the surrounding water environments (Gosavi et al., 2004; Mathew et al., 2001; Minh et al., 1997; Thawornwong and van Diest 1974). Acidification from ASSs cause a number of chemical, biological and physical problems arise such as aluminum and iron toxicities, decrease availability of phosphate, nutrient deficiencies, arrested soil ripening, hampered root growth, blockage of drains by ochre and corrosion of metal and concrete structures (AARD and LAWOO, 1992). The initial heavy rain on acid sulfate soils cause a 'first-flush' runoff and drainage of toxic water with properties including low pH, low concentration of dissolved oxygen and high concentration of dissolved aluminum which caused massive fish kill (Anon, 1990; Lin and Melville, 1994). The ASSs cause on- and off- site problems (Ritsema et al., 2000). On-site problems, which have been extensively reviewed (Dent 1986), include Al toxicity in drained soils, Fe and H_2S toxicity in flooded soils, salinity and nutrient deficiencies, especially decrease availability of phosphate. Engineering problems include (i) corrosion of steel and concrete and (ii) uneven subsidence, low bearing strength and fissuring leading to excessive permeability of unripe soils; blockage of drains and filters by ochre; and the difficulties of establishing vegetation cover on earthworks and restored land. Off-site problems stem from drainage effluents, earthworks, excavations, and mines. The acid drainage water carries Al released by acid weathering of soil minerals. Drainage waters may also be enriched in heavy metals and arsenic, a toxic cocktail endangering aquatic life and public health. Acid drainage and floodwaters may travel for many kilometers before they are neutralized. Acid drainage can have disastrous effects on freshwater and estuarine fishes, especially on invertebrates that are unable to escape. These soils could display a high agricultural potential if they were to be reclaimed by appropriate methods (Khan, 2000). Moreover, the reclamation of these soils may be difficult but very essential due to the formation of acidity during dry periods of the year and hampering not only crop growth but also destroying aquatic lives.The conventional reclamation by the application of lime and flash leaching in the proposed soils are not effective and sustainable (Khan, 1994). Because, soil acidity produced by 1% oxidizable sulfur requires about 30 ton of $CaCO_3$ per ha (van Breemen, 1993). Usually ASSs contain 1-5% oxidizable sulfur and showed antagonistic effect on micronutrient levels as well as on the balance of basic cations in plants (Khan et al., 1996). Tri et al., (1993) revealed that construction of raised bed is the most important land management practices for acid sulfate soils. However, this practice has not enough success. Its success depends on several factors of the soils, their position and environmental conditions (AARD and LAWOO, 1992). Acidity and salinity problems relating to rice production in the studied acid sulfate soils were alleviated by the application of leaching. Khan and Adachi (1999) reported that reclamation of the soils through leaching enhanced the losses of basic cations from top soils, whereas increased acidic cations in the top soils by exchange reactions. After seven years of leaching practices on acid sulfate soils in Vietnam, Sterk (1993) reported that the acid content of the topsoils is not decreasing, which might be attributed to enrichment of acidic cations like aluminum in the top soils. Khan (1994) reported that leaching is an effective method for reclaiming both salinity and acidity of the soils but losses of basic cations through leaching should be considered for the greater success of reclamation. Takai et al., (1992) claimed that nutrient deficiency is an important factor for the improvement of acid sulfate soils. Khan (1994) revealed that for the reclamation and improvement of ASSs, BS would be effective to reduce acidity of the soils because BS was found to increase soil solution pH and optimized the concentration of some elements like Ca, Mg, P and Si, which are very essential/beneficial for crop production as well as alleviates the toxicity of Fe and Al. Moreover, there is evidence that high Ca and Si concentrations in drainage/waste waters protect fish against Al toxicity (Birchall et al., 1989). Potential ASSs may have high pH like 6 to 7 does not mean that the soils are safe because at that situation it may create H_2S, Fe and some organic acids problems (Kabir, 2005).

ASSs are of major environmental concern in many wetlands. Van Mensvoort and Dent (1998) claimed for about 24 M ha of ASSs of which about 0.7 M ha are located in different pockets of inundated coastal areas in Bangladesh where crop production is very low; some where the lands are unproductive though the soils have high agricultural potential (Khan, 2000). The nature and characteristics of these pockets of ASSs varied from place to place and even within pockets owing to the difference in mangrove vegetations and accumulation of sediments (Khan, et al., 2007). Since the ASSs can exert severe effects on surrounding ecosystems, immediate steps should be taken to improve these soils further (Khan, et al., 2002). Delayed effects of potential chemicals stored in the ASSs resulted in harmful effects, like a "chemical time bomb" on the associated environments (Khan and Adachi, 1999). It has recently been estimated that these affect some 100 million hectares (M ha) of land world-wide (Sheeran, 2003). For sustainable use ASSs, acceptable cost effective chemical reduction of the acidity is very essential. Soil acidity produced by one percent oxidizable sulfur after neutralization (3 to 30 t of $CaCO_3$ per ha, depending on clay content and mineralogy) by exchangeable cations requires about 30 t of $CaCO_3$ per ha (Van Breemen, 1993). Usually ASSs contains 1 to 5 % oxidizable sulfur which indicates a huge amount of lime would be needed. Generally calcite ($CaCO_3$) is used as agricultural lime but it is to some extent expensive. As a result farmers often become reluctant to ameliorate ASSs. With this objective BS, a low cost liming material was undertaken to use as an ameliorant of ASSs. From its suitability BS as a byproduct from the steel industry in Bangladesh can be collected almost free of charge. However, application of BS as agricultural lime is not well documented. Moreover, the reducing capacity and potentiality of the BS for the exchangeable cations in different ASSs 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 ASSs under different moisture regimes.

Jintaridth, 2006 reported that deficiency in plant base minerals is an important factor when the reclamation and management practices are performed in ASSs. Takai, et al., (1992) also claimed that nutrient deficiency is an important factor for the improvement of ASSs. 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 BS in ASSs 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 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 effects. The reclamation of these soils may be difficult but essential. Successful reclamation of the ASSs 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 ASSs, the real problem is resulted 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 ASSs 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). In ASSs, water management is the key to soil management and proper water management can limit acidification (Khan, et al.. 2006b). However, the potentiality of BS for the reduction of ASSs and associated ion dynamics under variable soil moisture regimes and wetting-drying cycles should have much influence regarding sustainable reclamation and improvement of ASSs. Considering the above background, the present study was done in order to assess the remedying capacity of BS under various moisture regimes and its effects on the reduction of Fe and Al ions in the soils.

2. Methods and Materials

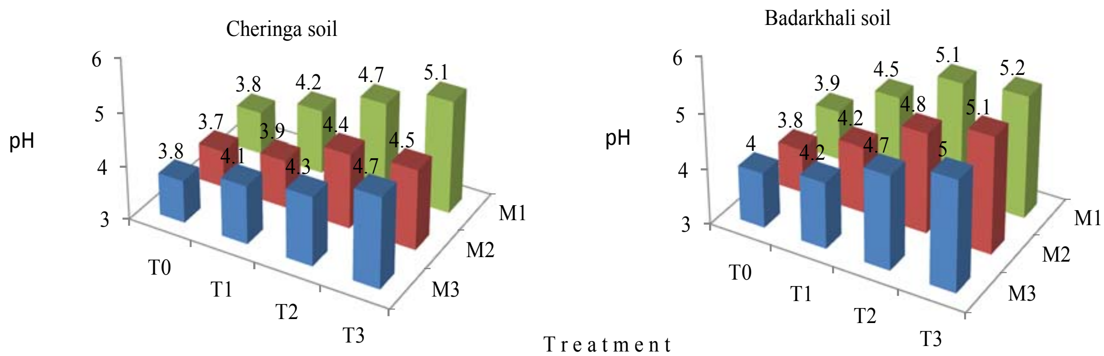
2.1 Incubation experiment

For assessing of BS on reduction of Fe and Al toxicity in ASSs under various moisture regimes, an incubation study was carried out in the laboratory of the Department of Soil, Water and Environment, University of Dhaka, Bangladesh during 2000 to 2001. Accordingly, an experiment was conducted for 180 days (six months) under saturated moisture condition (water content = 100 % by weight), moisture at field capacity (50 % by weight) and wetting-drying cycles of these treatments. It is mentioned that during the incubation experiment, the moisture contents was monitored and kept it at a fixed value by watering when it is required. The effects of these treatments with time were also considered for this experiment.

Table1: Some selected physical and chemical properties of the acid sulfate soils (depth 0-20 cm) before the incubation study.

Soil properties	Cheringa soil	Badarkhali soil
Texture	Silty clay loam	Silty clay loam
Moisture at field condition (vol. %)	48	49
Soil pH (Field)	3.8	4
Soil pH (Soil:Water=1: 2.5)	3.6	3.9
Soil pH (Soil:0.02 M $CaCl_2$=1.2.5)	3.3	3.4
Pyrite content (%)	7.3	6.6
Electrical Conductivity (1: 5 dS m^{-1})	18.5	19
Organic matter (Wet oxidation, g kg^{-1})	39.1	30.7
Available nitrogen (1.3 M KCl, mM kg^{-1})	3.6	3.3
Available phosphorus (0.02N H_2SO_4, mM kg^{-1})	0.1	0.11
CEC (1 M NH_4Cl: cmol kg-1, at pH 7.0)	17.2	18.5
Aluminium-saturation (1M NH_4Cl: %)	40.3	41.2
Iron-saturation (1M NH_4Cl: %)	8.3	7.1
Sodium-saturation (1M NH_4Cl: %)	12.4	13
Potassium-saturation (1M NH_4Cl: %)	1.4	1.6
Calcium-saturation (1M NH_4Cl: %)	1.8	1.9
Magnesium-saturation (1M NH_4Cl: %)	5.5	6.2
Water-soluble ions		
Sodium (Flame photometry: cmol kg^{-1})	3.01	3.2
Potassium (Flame photometry: cmol kg^{-1})	0.3	0.25
Calcium (*AAS: cmol kg^{-1})	0.3	0.37
Magnesium (AAS: cmol kg^{-1})	3.34	3.43
Iron (AAS: cmol kg^{-1})	0.35	0.31
Aluminium (ASS: cmol kg^{-1})	2.1	1.9
Sulfate ($BaCl_2$, : cmol kg^{-1})	4.86	4.2

*Atomic Absorption Spectrophotometer



T0=Control; T1=Basic slag (BS)@11; T2=BS@22; T3=BS@33 t ha^{-1}; M1=Saturated condition; M2=Wetting-Drying cycle; and M3=Moisture at field condition

Figure 1 Effcets of basic slag and moisture regimes at the end of incubation times on pH in the soils.

Surface layer (Topsoils: depth 0 to 20 cm) of two different ASSs (Cheringa and Badarkhali) 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 meshes) 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 application rates were selected from feasible stand point of view). The BS was collected from a steel industry and then grounded to less than 1 mm sizes. The 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). It was mixed thoroughly as per treatments. The distilled water was added at saturation condition of soil (by 50 ml), moist at field condition (by 20 ml) and at wetting-drying cycles (by 20 ml on drying and 50 ml on wetting). 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° C) for natural air drying towards field capacity during the following 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 analyses the soil pH, ECe (EC of saturation extract of soil) and exchangeable cations at 1, 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.

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), ECe (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), exchangeable cations (Jackson, 1973) such as Na^+, K^+ (Flame photometry), Ca^{2+}, Mg^{2+}, Fe^{2+} and Al^{3+} (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

The studied soils, namely Cheringa and Badarkhali (depth: 0-20 cm) showed a silty clay loam texture, initially low pH of 3.6 for the Cheringa and 3.9 for the Badarkhali soils, high ECe (18.5 for Cheringa and 19.0 dS m^{-1} for Badarkhali soils) and high amount of organic matter . Some selected physical and chemical properties of the studied ASSs (depth 0 to 20 cm) before the incubation study are given in Table 1.

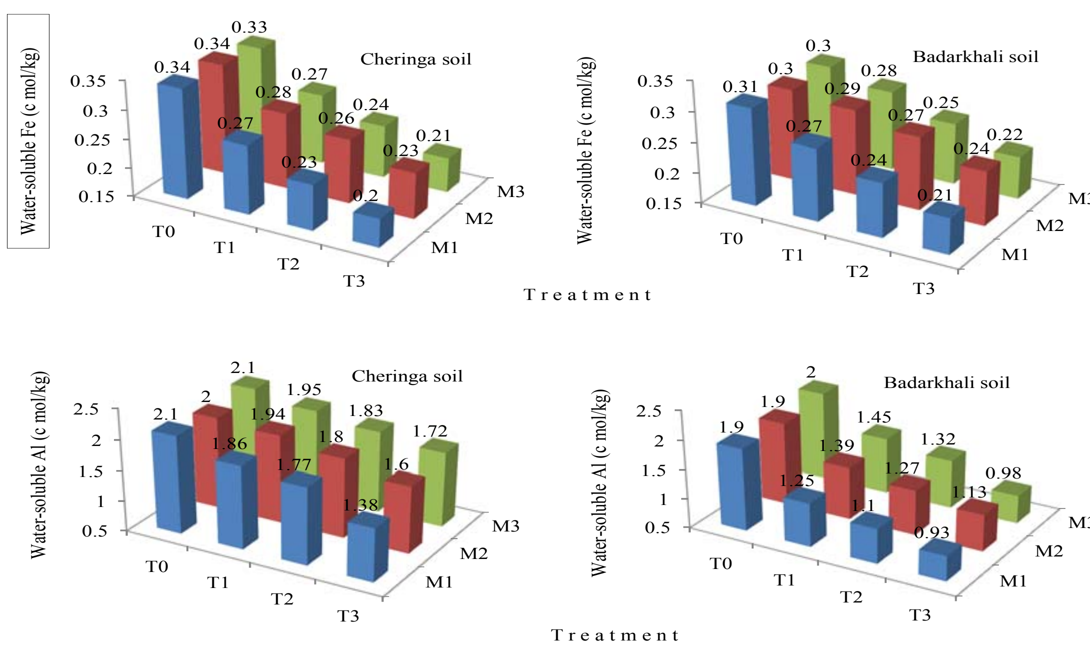
3.1 Changes in soil pH

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 (Figure 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 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 both the soils (Figure 1). The lower pHs were observed 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. 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 reduce more acidity in both the soils. The facts that these soils contain pyrite were reported by many researchers (Khan et al., 2006). 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 of 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 reducing capacity of BS by releasing exchangeable cations 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 reduction of produced acids with the released basic ions with the passes of time and the slow releasing of basic ions from the BS might hold the steady increase in pHs of the soils. Throughout the incubation period, it was noticed that the potentiality of BS as a liming material will be effective for reducing 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 BS 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).

3.2 Changes in water-soluble iron and aluminium

Iron is mostly a pH dependent element. The amount of water-soluble Fe was low throughout the incubation time and the quantity was found to be decreased with the increment of pH in both the soils as compared with the control (Figure 2). The leased amount of Fe were determined in the soils of high pH as a result of BS at 33 t ha^{-1} under saturated condition in both the soils followed by the condition of field capacity and wetting-drying cycle. The steepest fall in the concentration of the Fe were observed with the application of lime (Khan et al., 1996). They also reported that the concentration of K, Ca and Mg were increased while the concentration of Fe and Mn decreased in the ASSs.



T0=Control; T1=Basic slag (BS)@11; T2=BS@22; T3=BS@33 t ha^{-1}; M1=Saturated condition; M2=Wetting-Drying cycle; and M3=Moisture at field condition

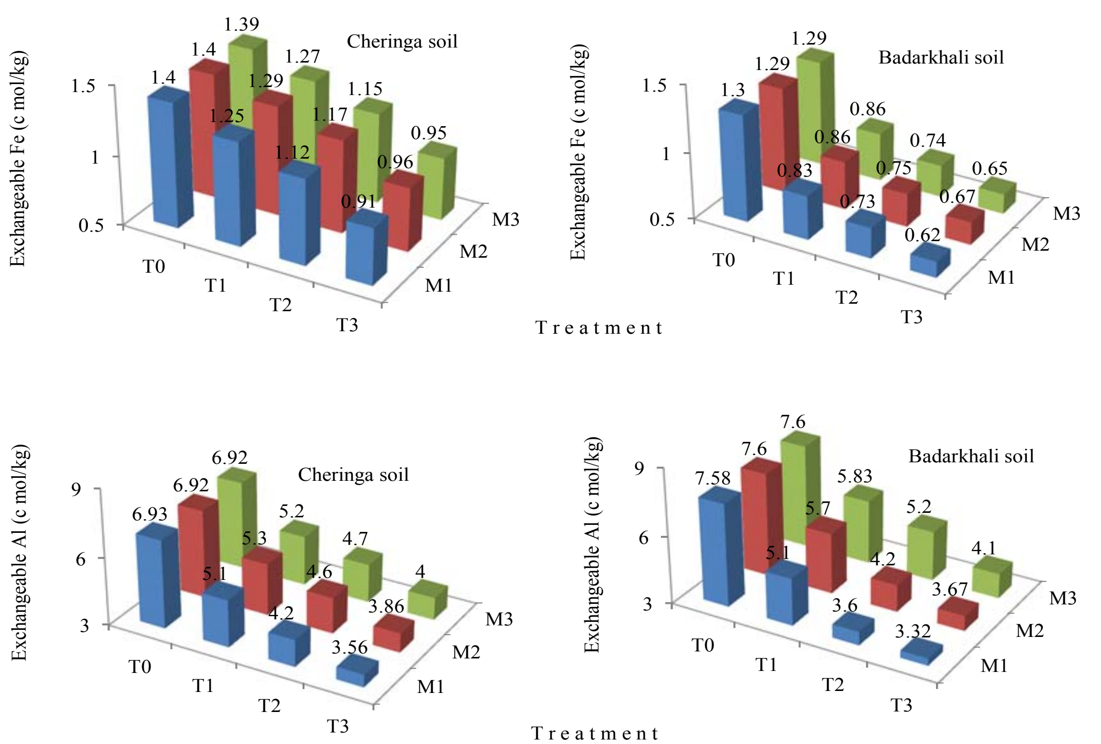
Figure 2 Effcets of basic slag and moisture regimes at the end of incubation times on water-soluble Fe and Al ions in the soils.

The availability of Al is also highly pH dependent, i.e. available at the lower pH value of <4.5 and the higher pH of > 10 (Donahue et al., 1987). With the amendments through BS, the pHs of both the soils were found to be increased strikingly as compared with the initial pHs, which resulted the low availability of Al. The amount of water-soluble Al in both the soils was found to be decreased under saturated condition. Cheringa soil was found to be content more, Al, which might be due to their initial high potential acidity as compared with Badarkhali soils. Application of BS of 33 and 22 t ha^{-1} were found to be effective in decreasing Al contents in both the soils regardless of moisture regimes. The BS at 33 t ha^{-1} exerted more detrimental effect regarding the availability of Al, which reduced to almost half of the amounts of its initial contents in these soils (Figure 2).

3.3 Changes in exchangeable iron and aluminium

The results showed that the contents of exchangeable iron remarkably decreased with time. The lowest content of Fe^{2+} was determined by the highest dose of BS (33 t ha^{-1}) under saturated conditions in both the soils where the corresponding pH rises at highest levels of 5.1 at Cheringa and 5.2 at Badarkhali soils (Figure 1). So, the exchangeable Fe^{2+} was found to have negative relationship with their corresponding pH.

The initial very high contents of exchangeable Al^{3+} in both the ASSs were found to be decreased strikingly with the higher dose of BS regardless of moisture regimes (Figure 3). The maintenance of saturated moisture condition of soil was found to be more suitable practice in order of decrement in contents of exchangeable Al^{3+} in both the soils followed by moisture at field capacity and wetting-drying cycle. The amounts of exchangeable Al^{3+} was very high in Badarkhali soil as compared with Cheringa soil, which might be due to the variation in their corresponding pH level. The lowest value of exchangeable Al^{3+} was recorded by the higher rates of BS (33 t ha^{-1}) as 3.56 c mol kg^{-1} in Cheringa soil and 3.32 c mol kg^{-1} in Badarkhali soil under the moisture at saturation condition. The second lowest contents were found for the condition of moisture at wetting-drying cycle (3.86 c mol kg^{-1} for Cheringa and 3.67 c mol kg^{-1} for Badarkhali soils) followed by the condition of field capacity (4.0 c mol kg^{-1} for Cheringa and 4.1 c mol kg^{-1} for Badarkhali soils) having the treatment of BS 33 t ha^{-1}. The lower doses of BS (11 and 22 t ha^{-1}) exerted comparatively the higher contents of exchangeable Al^{3+} in both the incubated ASSs. It was noticed that the exchangeable Al^{3+} in ASSs fell steeply as soon as pH rose above 4.0 (Gotoh and Patric, 1974; Hart, 1959). Moreover van Breemen (1973 and 1976) has shown that Al activity was inversely related to pH, increasing roughly 10 folds per unit pH decrease.



T0=Control; T1=Basic slag (BS)@11; T2=BS@22; T3=BS@33 t ha^{-1}; M1=Saturated condition; M2=Wetting-Drying cycle; and M3=Moisture at field condition

Figure 3 Effcets of basic slag and moisture regimes at the end of incubation times on Exchangeable Fe and Al ions in the soils.

4. Conclusions

From the results, it was revealed that the Fe and Al toxicity of the studied acid sulfate soils (ASSs) were remarkably decreased by the application of basic slag (BS). Moisture at saturated condition was found to be best for the reduction of these ions in both the soils, which will be supportive for planning of crop production on these soils. The highest dose (33 t ha^{-1}) of BS in Cheringa and Badarkhali ASSs were found to be reduced the acidity of these soils at desirable pH (pH>5) levels under same moisture conditions. The present findings suggest that by the use of BS or material rich in basic cations in these soils is a pre-requisite to be brought into productive land in order of quick reduction of acidity problems.

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