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A SUPER-SULPHATED FORMULATION FOR AMELIORATION OF ALKALINE/SALINE SOILS

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Salinity and also sodic alkalinity of the soil is corrected by the use of various soil amendments of which gypsum is considered to be very effective. It is applied to sodium affected soil, which has only a limited amount of pores to allow calcium ions to replace the adsorbed sodium. Soil particles are thus facilitated to attain aggregation. The aggregation process is further influenced by alternate wetting and drying.

INTRODUCTION

A chemical formulation has been evolved such that sulphuric acid is adsorbed on various materials including gypsum. Sulphuric acid, upon application to soils containing lime, forms gypsum and provides soluble calcium indirectly while gypsum alone provides soluble calcium directly [1]. In this way the process of aggregation and replacement of adsorbed sodium is facilitated and pores are duly introduced in soils.

The present study describes the effect of the use of this developed soil amendment [2] and compares it with gypsum and sulphuric acid if used alone. The results suggest that it is possible to introduce a double effect, viz. availability of calcium ions from gypsum and hydrogen ions from the adsorbed sulphuric acid. The soil is thus cured in the shortest possible time.

Productivity of soil is lowered when the root zone has a comparatively high concentration of salts and alkalis. Saline and alkali soils are damaged primarily by the salts of sodium, calcium, magnesium, chloride, sulphate, and secondarily by bicarbonates, carbonates, nitrates and boron. Alkaline soils on the other hand contain excessive quantities of adsorbed sodium [3].

Soil particles bear negative electrical charges at their surface. They adsorb and retain cations like Ca^{++}, Mg^{++} and Na^{+}. The adsorbed cations are combined chemically with the soil particles but may be exchanged by other cations added to the soil solution, though slowly. There is a limit to the exchange capacity of each soil and when the exchangeable sodium percentage is 15 or more soil usually deteriorates considerably [4].

Calcium and magnesium are the principal cations in the normal and productive soil [1] solutions. When in contact with irrigation or drainage water containing higher sodium [4] percentage the latter shifts the equilibria and replaces the calcium and magnesium ions, thus turning the soil more and more alkaline.

Alkali soils are flocculated [5]. Their properties are similar to saline soils. Saline-alkali soils become non-saline alkali soils on leaching or ponding with excess water. Excess salts may be removed by leaching but the resulting alkaline soil remains deteriorated because of high pH which promotes a high dispersion of particles. The latter property is unfavourable for the entry and movement of water and air for plants to grow. Besides, adsorbed sodium is also toxic from the point of view of the nutrition of the plant [6].

Excess soluble salts can be removed by leaching. It is estimated that by leaching with 6 inches of water per foot of root zone, 50% of the salts can be removed from the said zone [4,7], one foot water would remove 80% salts and 2 feet would remove 90% salts from there. However, the removal of soluble salts does not restore productivity of the soil because most of the sodium ions continue to remain adsorbed. It is therefore imperative that the sodium ions be replaced by calcium and magnesium ions.

Removal of adsorbed sodium is possible through the application of chemical amendments which are of three types: (1) calcium salts of reasonable solubility, e.g. calcium chloride; (2) calcium salts of low solubility, e.g. gypsum; and (3) acids or acid formers e.g. sulphuric acid, sulphur, iron and aluminium sulphate [1].

The mechanism of reaction of the three types of amendments [1,8,9] is in general terms the same in that they all form gypsum as the end product, i.e. sulphur is slowly oxidized by micro-organisms in the presence of air and water to sulphuric acid which on reacting with lime present in the soil form gypsum [1]. Iron sulphate (copperas) and aluminium sulphate (alum) when applied to soil, dissolve in soil water and decompose to form sulphuric acid. Calcium polysulphide (lime sulphur) oxidises to sulphuric acid which on reacting with lime present in the soil forms gypsum. The latter reacts slowly with adsorbed sodium ions of the soil forming sodium sulphate and the highly soluble calcium chloride. When available at the root zone gypsum acts as a source of calcium to displace sodium and also of sulphur as nutrient. The reaction is, however, slow. There is therefore need to enhance the soil correction rate and provide soluble as well as slow releasing calcium and sulphate ions.

This paper describes a formulation which can react slowly with adsorbed ions in the solid state and rapidly when ponded with water. It makes available calcium ions in solution to replace adsorbed sodium and simultaneously corrects the alkalinity of the soil.

EXPERIMENTAL

Material preparation. Gypsum having an analysis listed in Table 1 was dehydrated by heating at 260° for 16 hrs. The anhydrite so obtained had the analysis also listed in Table 1. Sulphuric acid Analar with a density of 1.84 was added gradually to the freshly prepared anhydrite in the ratio of 55 parts of anhydrite to 45 parts of sulphuric acid. A semi-solid agglomerate was obtained, which on reaction with water released sulphuric acid as noted in Table 2. A master batch of this material, hereafter called Soilcure-45, was prepared and added to anhydrite in various proportions as described in Table 2. The total quantity of Soilcure-45 and Anhydrite mix, listed in Table 2, was hydrolysed by adding 100 ml water in 25 ml portions with stirring until the reaction subsided. The amount of acid and calcium and magnesium ions released were determined by standard methods [10,11].

Table 1. Analysis of gypsum and anhydrite used for the preparation of Soilcure-45

Composition	Gypsum (%)	Anhydrite (%)
1. Free water	0.35	Nil
2. Combined water	10.58	Nil
3. Silica and Insolubles	0.49	0.51
4. Lime (CaO)	35.12	39.32
5. Magnesia (MgO)	3.76	4.18
6. Sulphur trioxide (SO_3)	49.73	55.84
7. Sodium chloride (NaCl)	0.08	0.09
8. Combined oxides (R_2O_3)	0.04	0.04

Samples of soil were collected from four different places belonging to salinity stricken areas of Mirpur Sakro, 100 km east of Karachi. Sample No.1 is from a farmland on which water was ponded. The analysis of ponded water collected on farmland as well as that supplied to the area through canals and found in the well are listed in Table 3. Sample No.2 is from an abandoned dry land. Sample No.3 belongs to an area where the water table is high. Sample No.4 represents soil which was wet but ponded by saline water. The physical properties of these soils and the chemical analysis of their water solubles appear in Table 4. The soils were treated with soilcure-45 as described: 100 g soil sample was taken as received in each case. Soil No.1 was treated with 0.3862 g Soilcure-45, No.2 with 0.4603 g, No.3 with 0.8941 g and No.4 with 0.4814 g. The water solubles obtained after treatment were analysed [12] and are listed in Table 5. Soil sample No.2 was separately treated with gypsum and sulphuric acid in quantities equivalent to that provided by Soilcure-45 in the earlier experiment and also with excess sulphuric acid viz. 1.84 g. The results of these treatments appear in Table 6.

RESULTS AND DISCUSSION

It would appear from Table 2 that the amount of sulphuric acid released does not correspond to that calculated with respect to Soilcure-45. The entire quantity of sulphuric acid is not released in any case and particularly beyond 25%. Even Soilcure-45 does not release more than 37.7% acids. This is apparent from Table 2 which suggests that almost 20% of the acid is retained by anhydrite, indicating the possibility that Soilcure-45 contains acid which is chemically combined as well as adsorbed on the surface of the anhydrite.

The amount of calcium and magnesium ions released on hydrolysis with water was found to increase with concentration of Soilcure-45 in the anhydrite mix, indicating that the super-sulphated form has a profound influence on their release since otherwise the solubility of these ions should decrease with increasing concentration of sulphuric acid. The release of the ions is shown in Fig. 1 from which it can be noted that even with the addition of super-sulphated gypsum/anhydrite the amount of calcium ions released did not increase appreciably and levels off after 30%. This indi-

Table 2. Release of sulphuric acid, calcium and magnesium from Soilcure-45-anhydrite mix

S. No.	Soilcure-45-anhydrite mix proportions		H_2SO_4		Calcium ion	Magnesium ion
	Soilcure-45 (g)	Anhydrite (g)	Calculated (%)	Released (%)	(g)	(g)
1.	0.5	12.5	1.73	0.4	0.068	0.022
2.	2.5	12.5	7.46	5.4	0.056	0.113
3.	5.0	12.5	12.85	6.23	0.066	0.138
4.	7.5	12.5	16.85	10.7	0.074	0.148
5.	10.0	12.5	20.0	19.2	0.084	0.170
6.	12.5	12.5	22.4	19.5	0.088	0.175
7.	16.5	12.5	25.60	24.8	0.093	0.202
8.	19.5	12.5	27.18	24.04	0.092	0.217
9.	24.8	12.5	31.01	24.6	0.095	0.209
10.	42.4	12.5	34.8	25.02	0.0985	0.303
11.	10	Nil	45.0	37.7	0.075	0.050

Table 3. Analysis of water collected from salinity stricken areas

Parameters		Canal water	Well water	Ponded water
pH		6.8	7.25	7.7
Chloride	(mg/lit)	113	56	4,538
Sulphate	(")	45	55	2,543
Carbonate	(")	Nil	Nil	Nil
Bicarbonate	(")	293	244	85
Calcium	(")	42	58	625
Magnesium	(")	16	13	345
Sodium	(")	90	41	2,400
Potassium	(")	3	2	12
Total alkalinity (as $CaCO_3$)	(")	240	200	70
Total hardness (as $CaCO_3$)	(")	172	196	596
Total dissolved solids	(")	430	320	12,300

cates that maximum sulphuric acid which could be adsorbed on the surface of anhydrite with a particle size of 100-125 micron lies between 25 and 30%. It may be noted from Table 2, that with each addition of water there is a release of sulphuric acid as well as soluble calcium and magnesium ions which are the main ingredients for the cure of slinity stricken soil.

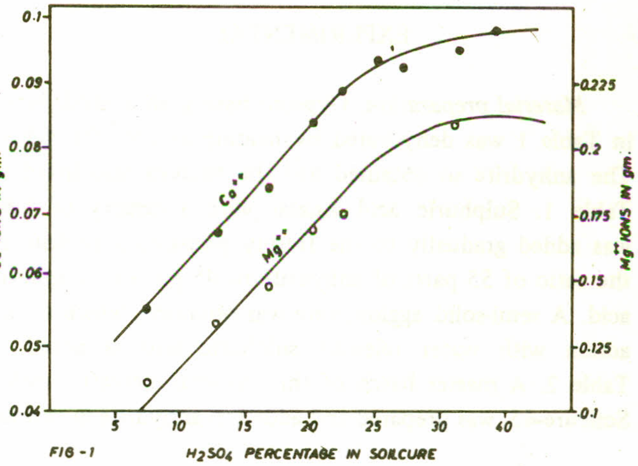

Fig. 1.

When Soilcure-45 was added to the soil there was an additional quantity of salts released from the treatment. It may be seen from Table 4 and 5 that the soluble salts present in soil sample No.1 are in least quantities. Its conductivity is low but its pore space is also low, perhaps due to the effect of ponding which might have brought down the soluble salts content within the acceptable range for salt tolerant crops and it was found that the concerned farmers had prepared it for growing rice. Analysis of canal and well water as shown in Table 3 indicates the uptake of salts on ponding.

Sample No.2 has high salinity and is more alkaline. The moisture content is the lowest among the 4 samples and it appears that pores are increased, while conductivity was found to be high. In the case of soil sample 3 also, the salinity and conductivity are high and so is the pore space. The soil was wet and the alkalinity due to salt's was high in the case of soil sample 4 which was also from wet soil, the salinity due to sodium chloride is very high and so is the alkalinity. The pore space was determined after drying the soil and was also found high.

The results of treatment with Soilcure-45 (Table 5) suggest that the alkalinity is reduced particularly in the case of sample 3. The salinity due to sodium chloride is not much affected in the case of sample 4 but in the other samples it has gone up slightly. In each case the calcium and magnesium levels are higher than in the untreated soil showing the release of these ions from the super-sulphated form and the efficacy of the treatment. This is borne out by the conductivity of soil samples which is considerably high ranging from 11 to 77 mmhos per cm and on treatment it is reduced to 0.8 to 9.0 mmhos. Soil density and premeability data elsewhere [2] further support the efficacy of treatment and suggest that there is an increase in pore space.

Table 4. Analysis of saline/alkaline soils

Sample No. Parameters	I	II	III	IV
pH	7.75	7.45	7.7	7.7
Moisture %	22.28	12.29	16.56	19.5
Sp. gravity	2.334	2.614	2.317	2.273
Pore space %	36.33	47.85	55.8	44.52
Conductivity (mhos/cm)	1.12×10^{-2}	5.2×10^{-2}	6×10^{-2}	7.7×10^{-2}
Organic matter %	0.04	0.21	0.64	0.43
Water solubles (%)				
Alkalinity as $CaCO_3$	0.073	0.087	0.169	0.091
Sodium (Na^+)	0.243	2.511	4.485	4.772
Calcium (Ca^{++})	0.132	0.932	0.640	1.24
Magnesium (Mg^{++})	0.026	0.854	0.415	0.735
Bicarbonate (HCO_3^-)	0.089	0.106	0.206	0.111
Chloride (Cl^-)	0.293	7.773	8.36	11.065
Sulphate (SO_4^{--})	0.584	0.455	1.75	1.032
Total solids (T.S.)	1.433	15.53	17.32	20.81

Table 5. Analysis of soil samples after treatment with Soilcure-45

Sample No. Parameters	I	II	III	IV
pH	7.6	7.7	7.5	7.7
Sp. gravity	1.174	1.232	2.29	1.824
Conductivity (mhos/cm)	0.8×10^{-3}	4.28×10^{-3}	6.96×10^{-3}	9.3×10^{-3}
Water solubles (%)				
Alkalinity (as $CaCO_3$)	0.05	0.05	0.075	0.075
Sodium (Na^+)	0.3	2.75	4.1	4.85
Calcium (Ca^{++})	0.18	1.42	0.88	1.35
Magnesium (Mg^{++})	0.026	0.955	0.43	0.745
Bicarbonate (HCO_3^-)	0.061	0.061	0.091	0.091
Chloride (Cl^-)	0.425	8.528	7.216	11.12
Sulphate (SO_4^{--})	0.721	0.753	2.436	1.483
Total solids (T.S.)	1.83	18.53	17.26	23.61

Table 6. Comparative statement of treatment with different amendments

Parameters	Treatment with			
	Soilcure-45	Anhydrite	Sulphuric acid	Excess sulphuric acid
Water solubles (%)				
Alkalinity (as $CaCO_3$)	0.05	0.057	0.047	0.046
Sodium (Na^+)	2.750	3.078	3.135	2.612
Calcium (Ca^{++})	1.420	1.073	1.271	1.444
Magnesium (Mg^{++})	0.955	0.918	0.974	0.923
Bicarbonate (HCO_3^-)	0.061	0.045	0.127	0 087
Chloride (Cl^-)	8.528	8.926	8.827	7.545
Sulphate (SO_4^{--})	0.753	0.684	1.283	2.054

Sulphuric acid has been known for a long time as a cure of sodic alkalinity but it has proved hazardous in handling [8]. Soilcure 45 is a formulation in which sulphuric acid is adsorbed on clays, soils, agricultural residues and minerals, for which a patent has been filed [2]. For the cure of alkalinity, Soilcure-45 containing 45% sulphuric acid adsorbed on anhydrite has been found to have an advantage over gypsum or sulphuric acid alone, since a larger content of the sulphate ions perhaps helps in providing a better cure than just the sulphates either from a mineral or from the acid former.

The trend of only slight increase in Na^+ and Cl^- ions concentration but a relatively large increase for Ca^{++}, Mg^{++} and SO_4^{++} ions indicates that the presence of anhydrite helps in reducing the amount of sodium chloride in the saline/alkaline soil. Furthermore Mg^{++} ions in the anhydrite also help in increasing its concentration in the cured soil.

Data presented in Table 6 for soil No.2 shows that treatment with gypsum and acid in equivalent quantities and also with excess sulphuric acid does not make much improvement in Na/Ca+Mg ratio. There is only a slight decrease in the said ratio by using excess sulphuric acid but such a treatment would be rather expensive.

It may be concluded from the data presented here that the super-sulphated formulation, *viz.* Soilcure-45 prepared from anhydrite and sulphuric acid is able to provide a better cure for the treatment of salinity/alkalinity through the double effect of calcium and magnesium ions availability and acidity. In addition Soilcure-45 has advantages over the use of (1) sulphuric acid alone whose handling is hazardous, (2) acid formers which are expensive and (3) sulphur and low solubility compounds which react very slowly.

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