# Use of Amendments in Reclamation of Alkali Soils in India

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About 2.5 million hectares of alkali soils occur in Northern India. These soils are characterized by high exchangeable sodium, varying degrees of calcareousness and excessively low permeability. The primary objective in reclamation of alkali soils is to reduce their exchangeable sodium content to levels safe for optimum plant growth. The exchangeable sodium is commonly replaced with calcium even though ions like hydrogen and magnesium may also be involved in the exchange reaction. Calcium in the exchange reaction is derived either from the added calcium amendment or Ca of the native calcium carbonate of the soil is mobilized with acids and acid formers. Earliest report on use of amendment in alkali soils came from LEATHER [34] who found that gypsum improved the permeability of these soils. Later work by NASIR [37], TAMHANE and KRISHNA [49], SINGH and NIJHAWAN [42], TALATI [50], AGARWAL and MEHROTRA [6], KANWAR and BHUMBLA [29], YADAV and AGARWAL [56], and the work of Central Soil Salinity Research Institute, Karnal [11] has demonstrated the usefulness of gypsum in ameliorating alkali soils. SINGH and NIJHAWAN [42] compared the effectiveness of gypsum and $CaCl_2$ at the same rate of application. Pressmud as sugar factory waste was used alone (NIJHAWAN [38], KANWAR and CHAWLA [30]), in combination with farm yard manure (FYM) (KANWAR and BHUMBLA [29]) and molasses (DHAR and MUKHERJEE [18], KANWAR and BHUMBLA [29]). In calcareous alkali soils varying degrees of success have been reported with the application of sulphur (BASU and TAGARE [8], KANWAR and BHUMBLA [29], sulphuric acid (KANWAR and BHUMBLA [29], MILAP CHAND et al. [36]) and pyrites (SINGH et al. [46], VERMA and ABROL [54]). Use of farm yard manure (YADAV and AGARWAL [57], KANWAR et al. [31], DARGAN et al. [15]), green manures (UPPAL [51], KANWAR et al. [31]) molasses (DHAR [17], BASU and TAGARE [8]), and spent wash (SINGH et al. [47]) has also been made for the reclamation of alkali soils. Of all the amendments gypsum and pyrites are popular owing to their easy availability, greater efficiency and low cost as compared with other amendments. Whereas gypsum is a direct source of calcium, the acid produced upon oxidation of pyrites reacts with calcium carbonate of the soil to release calcium for the exchange reaction. This paper reports some basic studies on the solubility of these amendments, their rate and method of application and effect on soil properties and crop yields. The salient characteristics of the soils referred in the text are given in Table 1.

*Table 1*

**Salient characteristics of soils used in different studies**

| Description and soil properties | Ghabdan loam | Kaheru sandy loam | Haibowal silt loam | Domeli loam |
|---|---|---|---|---|
| Order | Alfisol | Alfisol | Entisol | Inceptisol |
| Subgroup | Salic Natraqualfs | Aquic Natraqualfs | Aeric Fluvaquents | Natraquic Ustochrept |
| Family | Fine loamy, mixed, calcareous, hyperthermic | Fine loamy, mixed, calcareous, hyperthermic | Fine loamy, mixed, calcareous, hyperthermic | Fine loamy, mixed, hyperthermic |
| Sand, % | 43.5 | 45.2 | 45.2 | 50.4 |
| Silt, % | 16.5 | 24.5 | 30.0 | 38.4 |
| Clay, % | 39.6 | 30.5 | 25.0 | 11.6 |
| pH (1 : 2 soil/water) | 10.6 | 10.6 | 10.6 | 10.2 |
| EC (1 : 2 soil/water) mmhos/cm | 4.3 | 2.5 | 1.6 | 2.2 |
| CEC, me/100 g soil | 16.0 | 10.9 | 7.6 | 7.0 |
| ESP | 87.4 | 83.2 | 94.1 | 84.2 |
| Gypsum requirement t/ha | 74.3 | 42.5 | 24.7 | 30.0 |

## Calcium amendments

*Gypsum* ($CaSO_4 \times 2H_2O$). — One reason for gypsum being a popular amendment in India is its availability. The resources of gypsum in the country are estimated to be about 1004 million tons (ROHATGI et al. [41]). It is mined by removing the over burden which is usually 0.3 to 2.4 m thick. The gypsum exists in layers of varying thickness and is mined in different grades depending upon the purity which ranges from low grades to as high as 90 %. The mined product used as amendment is crushed and ground near the mine site and packed in high density polyethylene bags for transport to different destinations. In addition about 1.7 million tons of by-product gypsum are available from chemical industry producing tartaric acid, formic acid, oxalic acid, citric acid, common salt and phosphoric acid. The major source of by-product gypsum is phosphoric acid industry which accounts for almost 90 per cent of the available production. The by-product gypsum contains about 25 per cent moisture, 0.5 to 1.5 per cent fluorine, 0.2 to 0.3 per cent $P_2O_5$ and other impurities depending upon the composition of rock phosphate used for the manufacture of triple superphosphate. The annual availability of mined and by-product gypsum in India is roughly 2.5 million tons which is sufficient to meet demand for agricultural use. Owing to the importance of gypsum as an amendment for alkali soils, considerable work has been done in the country to work out optimum dose of its application and resultant response by different crops (KANWAR and CHAWLA [30], SINGH et al. [45], ABROL et al. [3], BHUMBLA and ABROL [9]). The Central Soil Salinity Research Institute has carried out detailed investigations on fineness of the amendment, its method of application and accompanying management practices in reclamation of alkali soils (ABROL et al. [3], YADAV [55], BHUMBLA and ABROL [10], CHAWLA and ABROL [12]).

This paper elaborates those aspects of this amendment which needed further investigation.

*Dissolution of gypsum in sodic soils.* — The solubility of gypsum in water is 0.26% at 25°C. An application of 92 to 122 cm of irrigation water was recommended to dissolve 9 to 11.2 metric tons/ha of applied agricultural grade gypsum of such fineness that 85% of the material will pass through a 100-mesh sieve (RICHARDS [52]). DUTT [21] and DUTT et al. [22], using a simulation model, developed a computer programme based on the solubility of gypsum and sodium exchange equation. They predicted that 52 to 72 cm of water was

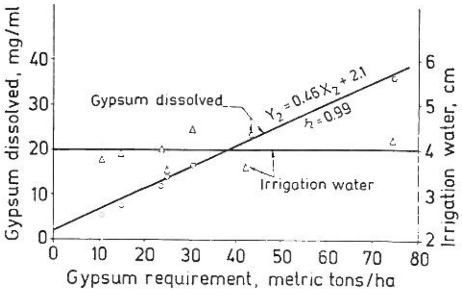


*Fig. 1*
Effect of gypsum requirement of the soil on gypsum solubility and on irrigation water needs for gypsum dissolution

required to dissolve 16.5 to 24.0 tons/ha of applied gypsum. OSTER and HALVORSON [39], however, showed that the solubility of gypsum increased more than 10-folds when mixed in an alkali soil. Therefore along with composition of soil solution, temperature and water flow velocity during leaching, the solubility of gypsum must also be affected by the degree of sodium saturation of the soil and the fineness of the amendment which increases the contact area. Effect of exchangeable sodium: Upon mixing, gypsum participates in following reactions in an alkali soil:

$$CaSO_4 \times 2H_2O \text{ (Solid)} - Ca^{2+} + SO_4^{2-} + 2H_2O \quad (1)$$

$$2Na(Ex) + Ca^{2+} \rightleftarrows Ca(Ex) + 2Na^+ \quad (2)$$

where (Ex) represents soil exchange complex. Soil exchange complex acts as a sink for $Ca^{2+}$ released from the solid phase. The solid phase gypsum will thus continue to dissolve until the solution phase is saturated or the ion activity product of $Ca^{2+}$ times $SO_4^{2-}$ equals the solubility product of gypsum. As $Ca^{2+}$ released by gypsum dissolution is used up in replacing exchangeable $Na^+$, more of it will be released from the solid to the solution phase. Thus the amount of gypsum dissolved per unit of water applied is increased. HIRA and SINGH [26] observed that the amount of water required to dissolve the added gypsum and to reclaim a sodic soil did not increase with the amount of gypsum added, provided it equalled the gypsum requirement of the soil (Fig. 1.). They found that 4 cm of water was sufficient to dissolve all agricultural grade gypsum of particle size <0.26 mm when added to an alkali soil. The relationships described in Fig. 1 show that gypsum dissolution per unit water increased as the gypsum requirement of the soil, which is a measure of total exchangeable $Na^+$ present in the soil, increased. ABROL et al. [4] and HIRA et al. [26] reported that the solubility of gypsum increased linearly with increase in the ESP of the soil (Table 2.). A relationship $Y = 0.0186X + 0.18$ ($r = 0.98$), between Y — the mean per cent gypsum solubility — and X — the ESP of the soil — was observed. The value of the intercept was quite close to the mean solubility of gypsum in the river sand.

*Effect of fineness of gypsum.* — An increase in the fineness of gypsum should increase its solubility owing to increase in the surface area of gypsum

*Table 2*

**Effect of ESP and of fineness of gypsum on the dissolution of gypsum**

| ESP | Gypsum dissolved, g/100 ml | Depth of water involved, cm | Fineness of gypsum, mm | Amount of gypsum dissolved, g/100 ml | Depth of water involved, cm |
|---|---|---|---|---|---|
| 0 (Sand) | 0.19 | 26.50 | <0.10 | 2.00 | 2.50 |
| 5 | 0.25 | 20.00 | <0.26 | 1.43 | 3.50 |
| 25 | 0.55 | 9.00 | <0.50 | 1.05 | 4.75 |
| 45 | 0.95 | 5.25 | 0.26—0.50 | 0.59 | 8.50 |
| 70 | 1.34 | 3.75 | 0.50—2.00 | 0.42 | 12.00 |
| 94 | 1.43 | 3.50 | | | |

particles that comes into contact with the soil—water system. HIRA et al. [26] found that the depth of water required for the dissolution of applied gypsum decreased from 12 cm to 2.5 cm as the particle size of the amendment decreased from 0.5—2.0 mm to less than 0.1 mm (Table 2.). They observed that decreasing the particle size sharply increased gypsum dissolution as shown by high initial sulphate concentration of the leachate of a gypsum treated alkali soil. Using these data they examined the validity of Equal-reduction Hypothesis (SWARTZENDRUBER and BARBER [48]) for gypsum dissolution and found it a reasonable first approach for estimating irrigation water requirement for gypsum dissolution in alkali soils.

The Equal-reduction Hypothesis postulates that the rate of particle diameter reduction during dissolution is independent of particle size. The basic assumption in the development of this hypothesis is that the rate of gypsum mass dissolution is directly proportional to the instantaneous surface area of gypsum spheres and the total instantaneous exchangeable sodium. The mathematical formulation (HIRA et al. [25]) was stated as below:

$$\frac{dm}{dI} = K\sqrt{s}\, E_{\mathrm{Na}} \tag{3}$$

where $m$ is the amount of gypsum (g equivalent) that has disappeared from the spherical gypsum surfaces in $I$ depth of irrigation water (cm) after gypsum has been mixed uniformly with the soil, s is total area of the spherical surface ($cm^2$), $E_{\mathrm{Na}}$ is exchangeable $Na^+$ (g equivalent) and $K$ is dissolution rate constant ($cm^{-2}$). Assuming that the range in initial particle size is not too great and the initial amount of gypsum added in the soil is equivalent to the initial amount of exchangeable Na per unit surface area of the soil ($E_{Na_0}$), HIRA et al. [25] reduced Eq. (3) to the following expression:

$$\left(\frac{m_0 - m}{m_0}\right)^{-1/3} = 1 + K\, E_{Na_0} \sqrt{\frac{2}{3\varrho D_0 m_0} I} \qquad (4)$$

where $m$ is the amount of gypsum (g equivalent) that has disappeared in $I$ depth of irrigation water (cm), $m_0$ is the initial amount of gypsum applied per unit surface area of the soil, $D_0$ is the initial particle diameter (cm), $\varrho$ is the density of gypsum (g/cm$^3$) and $K$ is dissolution rate constant. The experimental results verified the above relation.

It is clear from Eq. (4) that rate of dissolution of gypsum will increase with decrease in particle size. On this account CHAWLA & ABROL [12] observed a sharp initial increase followed by a sudden decline in hydraulic conductivity of alkali soils amended with finer grades of gypsum. With coarser grades the hydraulic conductivity was lower but it maintained a more steady rate. According to them more calcium from the amendment precipitated as $CaCO_3$ after reaction with soluble carbonates where particles were finer. Possibly inactivation of finer particles by $CaCO_3$ coating could also be responsible for the observed decline in hydraulic conductivity. KHOSLA and ABROL [32] reported that in the presence of soluble carbonates the precipitation of calcium carbonate which coats finer particles of gypsum prevents their further dissolution. Probably, for these reasons, KHOSLA et al. [33] found that in soils containing soluble carbonates gypsum mixed in shallow depth of soil was more beneficial to barley, rice and wheat than when it was mixed in greater depths.

*Method of application.* — Experiments conducted at C.S.S.R.I., Karnal with an alkali soil (pH 10.3 and EC 9.45 mmhos/cm) showed that mixing of gypsum equivalent to 25% of the gypsum requirement of the soil in 10 cm soil depth gave higher yields of barley, rice and wheat compared with mixing of the same quantity of gypsum in 20 cm or 30 cm depths (KHOSLA et al. [33]). At higher rates of gypsum application (50% of gypsum requirement) the differences in crop yields with 10 cm and 20 cm depths of mixing disappeared. HOUSTON and MCCORMICK [27] found that surface application of 20–45 t/ha of gypsum was effective for reclamation of alkali soils. The dose used was rather high. As discussed earlier, mixing of gypsum with the soil reduces its efficiency owing to the precipitation of Ca as $CaCO_3$. It has been shown that soluble carbonates move with the wetting front (ABROL et al. [2], HIRA et al. [26]). Since application of gypsum is usually followed by leaching, surface application of gypsum should be preferred in soils containing soluble carbonates. An experiment was therefore conducted with Ghabdan loam in which surface application of gypsum was compared with its mixing in 10 cm soil (the best treatment of KHOSLA et al. [33]) when the amendment was applied at different rates on the day of rice planting. Rice yields did not vary with the method of application (Table 3.) even though higher rates of amendment application significantly increased yields.

*Post-application leaching.* — Leaching after gypsum application is aimed to dissolve added gypsum and to leach down soluble salts already present in the soil and the reaction products of amendment with the soil. A post-application flooding of soil with water for 15 days has been recommended (ABROL and FIREMAN [1]). This is presumably based on the assumption that gypsum

*Table 3*

**Effect of rate and method of gypsum application and of gypsum dose and post-application flooding on rice yield (kg/ha)**

| Gypsum applied t/ha | Mixed in 10 cm soil | Surface applied, | Mean | Gypsum applied, t/ha | 15 days flooding | No flooding | Mean |
|---|---|---|---|---|---|---|---|
| 10 | 2531 | 2582 | 2567 | 9.9 | 2070 | 2550 | 2310 |
| 20 | 4108 | 3900 | 4004 | 19.8 | 3420 | 3730 | 3575 |
| 30 | 4339 | 4308 | 4354 | | | | |
| Mean | 3659 | 3620 | | | 2745 | 3140 | |
| Control | 460 | — | | | — | 230 | |

C. D. at 0.05%:

| | | | |
|---|---|---|---|
| Method of application | 558 | Flooding | 830 |
| Gypsum dose | 671 | Gypsum dose | 920 |

solubility is low in water. Recent studies show that solubility of gypsum when mixed with alkali soils increased as the exchangeable sodium increased (OSTER and HALVORSON [39], ABROL et al. [4], HIRA and SINGH [24]). The depth of irrigation water required to dissolve gypsum in the soil was much less (HIRA et al. [26]) as compared with the earlier figures reported by DUTT [21] and DUTT et al. [22]. Keeping this in view a field experiment was conducted on Ghabdan loam to verify if 15-day post-application flooding was necessary with rice as the first crop during reclamation of alkali soils. It was observed that flooding the soil for 15 days following application of gypsum was in no way better than transplanting rice on the same day after applying the amendment (Table 3.).

Reclamation of alkali soils is normally recommended with rice as the first crop. There are situations where reclamation needs to be initiated with wheat/barley. There is no information on post-gypsum application leaching requirements of soil when a crop like wheat is the first crop. Whereas in the case of rice sowing time and later irrigations would leach away the reaction products, pre-sowing leaching following the application of gypsum should be necessary in case of wheat. This aspect was studied in an experiment with Ghabdan loam. Gypsum was applied in doses equivalent to 1/8 and 1/4 gypsum requirement of the soil. This was followed by continuous leaching with 14, 21 and 28 cm of water. The leaching was so initiated that the sowing of wheat fell on the same day. Application of 28 cm leaching water recorded significantly higher wheat yields as compared with the application of 14 and 21 cm leaching water (Table 4.). The optimum amount of leaching water was ascertained in another experiment on the same soil where post-application of 28 cm and 42 cm water was made. It did not significantly affect wheat yield (Table 4.). These studies indicate that when reclamation is to start with wheat as the first crop, approximately 4 irrigations (equivalent to 28 cm water) given after gypsum application should be sufficient for a soil like Ghabdan loam.

*Dose.* — During reclamation of alkali soils the aim is to get a reasonably good return from the first crop of rice. It has been observed that application of gypsum in amounts equal to 1/4 to 1/2 gypsum requirement of soil, as determined by SCHOONOVER's method, is sufficient for this purpose (SINGH er al.

*Table 4*

**Effect of gypsum dose and post-application leaching on wheat yield (kg/ha)**

| Gypsum levels, t/ha | Post-application water, cm | | | | Gypsum levels, t/ha | Post-application water, cm | | |
|---|---|---|---|---|---|---|---|---|
| | 28 | 21 | 14 | Mean | | 28 | 42 | Mean |
| 8.75 | 1918 | 905 | 754 | 1192 | 17.5 | 1870 | 1860 | 1865 |
| 17.50 | 2177 | 1380 | 851 | 1502 | 26.3 | 2250 | 2150 | 2200 |
| | | | | | 35.0 | 2350 | 2450 | 2400 |
| Mean | 2048 | 1143 | 851 | | | 2157 | 2153 | |
| Control | | | | | | 160 | | |

| | | |
|---|---|---|
| C. D. at 0.05%: | | |
| Water applied | 243 | 244 |
| Gypsum dose | 199 | 332 |

[45], ABROL et al. [3]). Presumably this is due to the reason that normal crop of rice can be obtained even in soils with ESP up to 55 (VERMA and ABROL [54]). In the SCHOONOVER's method gypsum requirement is worked on the basis of 30 cm depth of soil. Experiments do not show the necessity of mixing gypsum upto 30 cm depth. Surface application or mixing gypsum in surface 10 cm soil are equally effective (Table 3). It is also known that soluble carbonates which inflate actual gypsum requirement, as determined by the above method, move with the wetting front without reacting with the amendment (ABROL et al. [2], HIRA et al. [16]). In addition to these factors economic considerations also influence the dose of amendment.

*Particle size.* — The optimum size of gypsum particles is determined by its efficiency in reclaiming alkali soils and the cost involved in sieving, grinding and application of the amendment. Finer fractions are very reactive in the beginning but their efficiency is lowered by relatively greater precipitation of dissolved Ca in the presence of soluble carbonates often present in alkali soils (ABROL et al. [2], HIRA et al. [26]). In Haibowal soil application of 8—30 mesh size gypsum lowered ESP of the surface 15 cm soil to greater extent as compared with gypsum having particle size less than 60 mesh (Table 5.). In a field experiment in the same soil rice yields were, however, unaffected by applying gypsum of different mesh sizes (Table 5.). This is probably due to the fact that

*Table 5*

**Effect of the fineness of gypsum on ESP and on rice yield**

| Soil depth, cm | Mesh size of the applied gypsum | | | Fineness of gypsum mesh | Dose of gypsum, t/ha | | | |
|---|---|---|---|---|---|---|---|---|
| | <60 | 30–60 | 8–30 | | 4.0 | 8.0 | 12.0 | Mean |
| | ESP | | | | Yield, kg/ha | | | |
| 0— 3 | 5.9 | 2.2 | 3.3 | 8—16 | 6120 | 6880 | 6770 | 6590 |
| 3— 6 | 11.4 | 2.9 | 2.9 | <16 | 6200 | 6960 | 6520 | 6560 |
| 6— 9 | 11.4 | 3.7 | 3.7 | <30 | 5920 | 6800 | 7000 | 6573 |
| 9—12 | 16.2 | 13.3 | 7.6 | <60 | 5880 | 6680 | 6770 | 6443 |
| 12—15 | 43.9 | 39.9 | 26.1 | <100 | 6240 | 6480 | 7000 | 6573 |
| | | | | Mean | 6070 | 6760 | 6810 | |

ESP of soil in each treatment was lowered to levels safe for rice crop. These results show that it is not necessary to grind gypsum to very fine fractions.

*Calcium chloride ($CaCl_2 \times 6H_2O$).* — This is a highly soluble salt and gives a concentration of $27.5 \times 10^3$ milliequivalents per liter in water. In a field experiment on an alkali soil SINGH and NIJHAWAN [42] compared the efficiency of calcium chloride and gypsum both applied at the rate of 5 tons/ha. Calcium chloride proved superior to gypsum. But high cost of calcium chloride prohibits its use on a large scale.

*Pressmud (carbonation process).* — Pressmud, a sugar factory waste contains about 70 per cent calcium carbonate. The solubility of calcium carbonate is only 1—1.2 milliequivalents per liter and depends upon $CO_2$ partial pressure and pH of the soil. KANWAR and CHAWLA [30] compared the effect of pressmud containing 24.4 % Ca with gypsum both added to supply 50 per cent of gypsum requirement of the soil. Gypsum brought greater improvement in the physical condition of the soil and lowered its exchangeable sodium content more than pressmud. A comparative study on the use of pressmud and other amendments was made on an alkali soil at C.S.S.R.I., Karnal (MILAP CHAND et al. [36]). Barley yields were lowest where pressmud was used as an amendment at all rates of application. However, this amendment when applied along with FYM or molasses gave as good yields as the application of gypsum (KANWAR and BHUMBLA [29]).

*Spent wash.* — It is a waste from alcohol distillaries. Analysis of a typical sample shows that its pH is about 5.0 and it contains 160 milliequivalents per liter of Ca plus Mg. Use of this material to ameliorate alkali soils, if such soils are in the neighbourhood of a factory, is an attractive proposition and a good way of preventing pollution of ground waters. Alkali soils near Khasa distillary in Punjab have been reclaimed with spent wash. SINGH et al. [47] used spent wash to reclaim an alkali soil of Domeli series. The exchangeable sodium percentage decreased from 100 in the original soil to 2 in the top 15 cm soil. Application of spent wash followed by irrigation, rather than the dilution of spent wash at the time of its application, was very effective in the reclamation of alkali soils of Domeli series.

## Acids

Commercial grade nitric acid, hydrochloric acid and sulphuric acid have been used to reclaim alkali soils (KANWAR and BHUMBLA [29]). Of these use of sulphuric acid ($H_2SO_4$) is more common. Acids directly react with soil $CaCO_3$ to produce $CaSO_4$. The reaction is very fast. Consequently application of sul-

*Table 6*

**Effect of gypsum, sulphuric acid and aluminium sulphate on barley yield, kg/ha**

| Soil | Gypsum | Sulphuric acid | Aluminium sulphate |
|---|---|---|---|
| Kamma | 2170 | 2560 | 2440 |
| Karnal | 2390 | 2620 | 2380 |

phuric acid to calcareous alkali soil has given promising results. In an experiment conducted on an alkali soil (ESP 40—60) at Kanpur, sulphuric acid proved superior to gypsum when both were applied at 80 per cent of gypsum requirement (YADAV [55]). Experiments conducted on Kamma soil (KANWAR and BHUMBLA [29]) and at C.S.S.R.I. (MILAP CHAND et al. [36]) show that sulphuric acid was as effective as gypsum (Table 6.). Considerations like cost and difficulty in handling strong acids restrict their use for reclamation on a large scale.

## Acid formers

Unlike acids, acid formers must first oxidize/hydrolyse in the soil to produce acid. Of this group the commonly used amendments are pyrites, sulphur and aluminium sulphate.

*Pyrites.* — The mining of sedimentary pyrites in Bihar and Rajasthan in the past few years has accelerated their use as an amendment for alkali soils. In fact iron pyrite is now competing with gypsum in parts of Uttar Pradesh and Bihar. Research on use of pyrites as an amendment has not kept pace with their use. One reason has been the easy availability of gypsum in the country. The results of the first systematic study on comparative efficiency of pyrites and gypsum in reclamation of alkali soils came from VERMA and ABROL [53]. On the whole in comparison with gypsum much less is known about the chemistry of oxidation and reaction of pyrites in alkali soils. Special attention is paid to these aspects in the following paragraphs.

*Oxidation of pyrites:* Sulphur in iron pyrites is present in a highly reduced state. It readily accepts oxygen and auto-oxidizes to form sulphur compounds of higher oxidation state. The rate of reaction depends upon factors like moisture content, oxygen availability, temperature, particle size and accumulation of poisoning materials around the amendment particles. Biological oxidation of sulphur in pyrites is chiefly carried out by *Thiobacillus ferrooxidans* but only when soil pH is favourable (pH less than 4) which is not the case in alkali soils.

The oxidation of pyrites starts as soon as the material is mined and exposed to air. The reaction, even though slow, is wasteful as some of the sulphur may escape to atmosphere as follows:

$$FeS_2 + 3O_2 = FeSO_4 + SO_2 \qquad (5)$$

The dominant reaction occurs in the presence of water and both the products formed as below directly or indirectly react with the soil.

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4 \qquad (6)$$

According to the above reaction immediate effectiveness of amendment would vary with the date of mining of the material and storage conditions. SINGH et al. [46] placed a sample of pyrites on a filter paper and extracted it with water for few days. About 1/3 of sulphur could be extracted in the first 2 hours but oxidation rate considerably decreased thereafter. This aspect must be recognized while comparing the effectiveness of pyrite in alkali soils treated with different samples of the amendment.

*Effect of soil moisture content on oxidation:* SINGH et al. [46] mixed gypsum and pyrites in Haibowal silt loam at 100 per cent gypsum requirement of the

*Table 7*

**Effect of water content on soil pH following application of gypsum and pyrites at different saturation levels**

| Time, h | Control | | | Gypsum | | | Pyrites | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1/1 | 1/2 | 1/4 | 1/1 | 1/2 | 1/4 | 1/1 | 1/2 | 1/4 |
| | moisture saturation levels | | | | | | | | |
| 2 | 10.4 | 10.4 | 10.4 | 9.7 | 9.8 | 10.1 | 9.2 | 9.5 | 9.6 |
| 10 | 10.3 | 10.3 | 10.3 | 9.4 | 9.5 | 9.8 | 9.3 | 9.6 | 9.8 |
| 24 | 10.3 | 10.2 | 10.3 | 9.4 | 9.5 | 9.8 | 9.4 | 9.8 | 9.9 |
| 48 | 10.1 | 10.1 | 10.2 | 9.2 | 9.5 | 9.9 | 9.4 | 9.8 | 10.0 |
| 72 | 10.0 | 10.0 | 10.2 | 9.2 | 9.5 | 9.9 | 9.4 | 9.8 | 10.0 |

soil and incubated the soil for 72 hours at moisture contents varying from complete soil saturation to 1/4 saturation. Soil pH was measured in a 1 : 2 soil—water suspension at different time intervals. Pyrites lowered soil pH by almost one unit immediately followed by a rise in pH after a lapse of 2 hours (Table 7.). The decline in soil pH continued upto 72 hours in gypsum treated saturated soil. Apparently the acid in pyrites immediately reacts with soluble carbonates and bicarbonates in the soil. Later on the soil attains an equilibrium pH depending upon the composition of ions in the exchange complex and in the solution phase. A part of the calcium mobilized by the amendment may reprecipitate. The presence of soluble Ca in the case of gypsum probably acts as a buffer against abrupt rise in pH at later stages. Even the simultaneous leaching may be important when amendments are added in alkali soils.

*Effect of particle size on oxidation* — Oxidation of pyrites depends upon the particle size because auto-oxidation should be favoured by increase in surface area. A fresh sample of pyrites was ground and fractionated into sizes ranging from 8 mesh to less than 300 mesh. Twenty g soil samples were poured into conical flasks and enough distilled water was added daily to keep pyrites moist. In another set same quantities of pyrites were incubated for a similar period without adding any water. Water soluble sulphur was determined at weekly intervals for 5 weeks. Increasing the fineness of pyrites increased their water soluble S content (Fig. 2.). After 35-day incubation, the water soluble S content in pyrites increased by 0.26, 0.27, 0.27, 0.31 and 0.50 per cent in 8—30 mesh, 30—60 mesh, 60—150 mesh, 150—300 mesh and less than 300 mesh fractions, respectively. Singh et al. [46] studied the effect of 4 size grades of pyrites on pH of an alkali soil. They found that very fine samples of pyrites were more effective in lowering soil pH initially but differences in soil pH amongst different size grades were very small after a lapse of 4 days.

*Method of application.* — Owing to the presence of soluble carbonates in alkali soils, the method of application significantly influences the effectiveness of amendment. The soluble contents of pyrite react with the soil much faster than gypsum. Mixing of both amendments in alkali soils should, therefore, produce different effects. This was investigated in an experiment with Haibowal silt loam where gypsum and pyrites (10.8% water soluble S) were applied on chemically equivalent basis to meet 50 per cent gypsum requirement of the soil packed in a 50 cm long column. The amendments were either

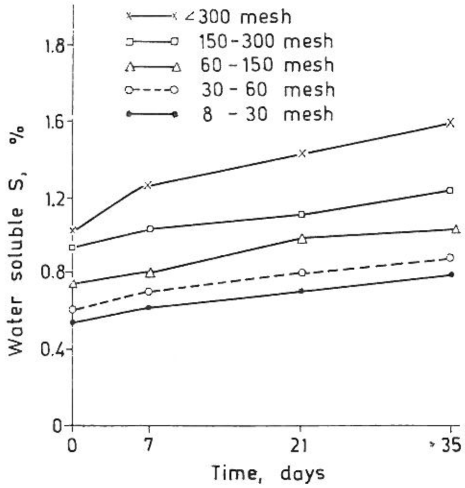


*Fig. 2*
Effect of particle size on the oxidation of pyrites

applied to the surface or mixed in 10 cm surface soil. The columns were leached with 14 cm water at a constant water head of 2 cm. The water intake rate was faster with surface applied pyrites where it took only 200 hours to leach 14 cm water as compared with 1296 hours when pyrites were mixed in the surface 10 cm soil (Fig. 3.). The poor performance in the latter case was probably due

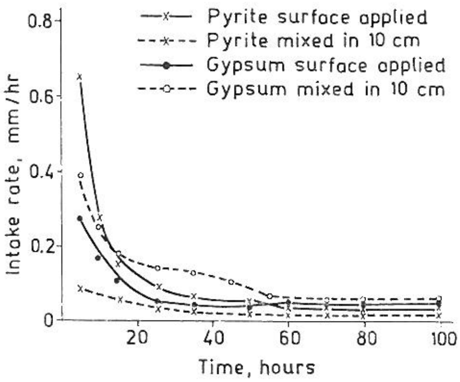


*Fig. 3*
Effect of method of application of pyrite and gypsum on water intake rate.

to neutralization of free acid in pyrites by soluble carbonates of the soil. Most of the soluble carbonates move with the wetting front (Khosla et al. [33], Hira et al. [26]) and therefore do not find a chance to react with the surface applied pyrites.

To verify the above results a field experiment was conducted on Ghabdan loam, a highly deteriorated alkali soil. Gypsum was mixed in surface 10 cm soil,

*Table 8*

**Effect of method of pyrites and gypsum application on rice yield in Ghabdan loam**

| Amendment | Amount applied (t/ha) | Water soluble S (t/ha) | Method of application | pH | Rice yield kg/ha |
|---|---|---|---|---|---|
| Pyrites | 4.5 | 1.4 | Surface | 8.65 | 770 |
| Pyrites | 9.0 | 1.4 | Surface | 8.45 | 1370 |
| Pyrites | 4.5 | 4.1 | Surface | 8.50 | 780 |
| Pyrites | 9.0 | 4.1 | Surface | 8.10 | 2480 |
| Pyrites | 4.5 | 6.9 | Surface | 8.35 | 2760 |
| Pyrites | 9.0 | 6.9 | Surface | 8.05 | 3280 |
| Pyrites | 4.5 | 6.9 | Mixed in 10 cm | 8.45 | 2180 |
| Pyrites | 9.0 | 6.9 | Mixed in 10 cm | 8.40 | 2410 |
| Gypsum | 9.0 | — | Mixed in 10 cm | 8.50 | 3350 |
| Gypsum | 18.0 | — | Mixed in 10 cm | 8.10 | 4220 |
| Control | — | — | — | 9.00 | 190 |
| C. D. at 0.05%: Yield | | | | | 1121 |

and pyrite was applied either to the surface or mixed in the surface 10 cm soil. Pyrite mixed in the surface soil in comparison with its surface application brought less improvement in 0–15 cm soil and thereby gave lower rice yields (Table 8.). This corroborates the laboratory results obtained with Haibowal soil where surface application of pyrites reduced soil ESP to greater extent as compared with pyrites mixed in the top 10 cm soil (Table 9.).

*Table 9*

**Effect of method of applying amendments on some soil properties**

| Amendment | Method of application | Weighed ESP (0–16 cm) | pH | Cumulative time taken to leach 14 cm water, h |
|---|---|---|---|---|
| Gypsum | Surface | 18.9 | 8.65 | 360 |
| Gypsum | Mixed in 10 cm | 15.2 | 8.60 | 180 |
| Pyrites | Surface | 19.0 | 8.60 | 200 |
| Pyrites | Mixed in 10 cm | 30.6 | 9.10 | 1296 |

*Dose.* — Laboratory and field experiments show that pyrites as an amendment for alkali soils compare poorly with gypsum (SINGH et al. [46], PATHAK et al. [40], VERMA and ABROL [54]). In the above experiments the dose of pyrites was calculated on the total sulphur content basis, regardless of their water soluble S content. It is now known that oxidation of pyrites in alkali soils is very slow. The importance of soluble S content in pyrites is well brought out in Table 8. where rice yields are shown to be related to the soluble S content of the amendment. Rice yields were very low in the freshly mined sample con-

*Table 10*

**Effect of soluble S content of pyrites on rice yield in Ghabdan loam**

| Soil treatment | doses, t/ha | Rice yield, kg/ha | Soil analysis after rice EC | pH (1 : 2) | ESP |
|---|---|---|---|---|---|
| Pyrites | 15 | 4365 | 2.5 | 9.8 | 36 |
| Pyrites | 30 | 4825 | 3.2 | 9.3 | 30 |
| Pyrites | 45 | 6133 | 4.3 | 8.8 | 17 |
| Gypsum | 20 | 4368 | 4.5 | 9.2 | 15 |
| Control | | 455 | 1.6 | 10.2 | 50 |

taining 1.4% soluble S as compared with the aged sample with 6.9% soluble S. Mixing in the soil decreased the efficiency of soluble S. Rice yields obtained with surface application of 4.5 t/ha pyrites (6.9% soluble S) were more than those with 9 t/ha of the same material when mixed in the soil. These results indicate that the dose of pyrites should be based on its soluble S content rather than its total S content.

Studies reported previously show that even in the finest fraction of pyrites, maximum increase in water soluble S was 0.5% in 25 days. Oxidation in alkali soils would be even less because of unfavourable pH for ***Thiobacilli***. The effeciency of pyrites would therefore be governed by their soluble S content at the time of application. This is also evident from a field experiment on Ghabdan loam where pyrites were added on total S basis (15 t/ha) and on water soluble S basis (45 t/ha). Rice yields with gypsum (20 t/ha) were similar to pyrites when the dose of pyrites (containing 6% water soluble S and 22% total S) was calculated on total S content basis (Table 10.) even though im-

*Table 11*

**Effect of different doses of pyrites on rice and wheat yields in Domeli loam**

| Soil treatment | doses, t/ha | Rice yield, kg/ha | Wheat yield, kg/ha | pH after rice (1 : 2) |
|---|---|---|---|---|
| Pyrites | 10 | 6649 | 3718 | 9.6 |
| Pyrites | 20 | 7590 | 4837 | 9.2 |
| Pyrites | 30 | 7658 | 4999 | 8.3 |
| Gypsum | 15 | 6871 | 4801 | 8.3 |
| Control | | 2614 | 2047 | 9.8 |

provement in the soil was not to the same extent. Application of pyrites on water soluble S basis reduced pH and ESP of the soil to the same level as with gypsum. In another field experiment on Domeli loam pyrites showed similar behaviour with respect to rice yield and pH of the soil when they were applied either on total S equivalent basis (10 t/ha) or on water soluble S basis (30 t/ha). Wheat yields were lower with pyrites applied on total S basis as compared with gypsum (Table 11.). Since rice is relatively more tolerant to alkalinity than wheat, its yields were almost comparable to those obtained with gypsum when both amendments were applied on chemically equivalent basis. It may, however, be recognized that in both experiments pyrites contained 6% soluble S. In conclusion it may be stated that the efficiency of pyrites as an amendment for alkali soils is mainly determined by the water soluble S. Thus sufficient oxidation of pyrites is essential after the material is mined and before used for reclamation of alkali soils. This could be achieved by storing finely ground pyrites under moist conditions for a reasonably long period

## Sulphur

Sulphur is biologically oxidized in the soil to form sulphuric acid, which reacts with calcium carbonate of the soil.

$$2S + 3O_2 = 2SO_3 \quad (7)$$

$$SO_3 + H_2O = H_2SO_4 \quad (8)$$

As with pyrites, oxidation of S in alkali soils is likely to be very slow owing to inhospitable conditions. BASU and TAGARE [8] obtained highest yield of sugarcane on a black clay soil having alkali problem by treating it with a combination of sulphur and farm yard manure. KANWAR and BHUMBLA [29] observed good yields of paddy and barley on alkali soil (gypsum requirement 16 me/100 g soil) with 1 t/ha sulphur applied. GIDNAWAR et al. [23] observed that during a period of 8 years annual application of sulphur at 300 kg/ha together with 5

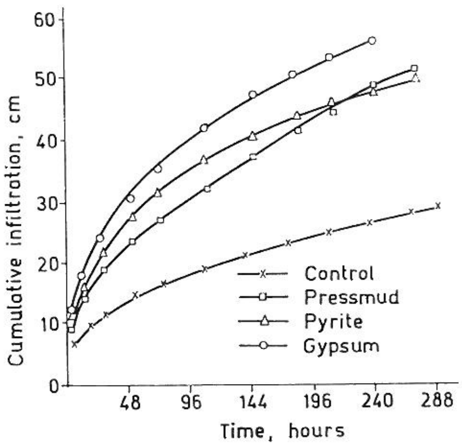


*Fig. 4*
Cumulative infiltration as affected by pyrite, pressmud and gypsum application

cartloads of farm manure reduced pH and salt content, and increased infiltration rate in saline-alkali soil where rainfed cotton and wheat were grown in alternate years. Sulphur is costly and is imported for the manufacture of sulphuric acid. These factors combined with low efficiency of S preclude its use as an amendment for alkali soils.

Pressmud available from sulphitation process sugar factories contains about 2—3% sulphur and 35.8 per cent organic matter. MILAP CHAND et al. [36] observed that higher dose (30 t/ha) of this material had a beneficial effect on crop growth and properties of alkali soils. Barley yields were low in the first year of application but improved significantly in the second year. In an experiment on alkali soil different amendments applied at 50 per cent of gypsum requirement of the soil on total sulphur equivalent basis showed that pressmud increased cumulative infiltration though it was always less than gypsum (Fig. 4.).

## Organic materials

During decomposition of organic matter under partially aerobic or anaerobic conditions the organic acids produced react with calcium carbonate of the soil and release calcium into soil solution (SINGH [44]). The rate of decomposition depends largely on carbon : nitrogen ratio of organic matter. Organic materials rich in nitrogen, such as *Sesbania aculeata*, decompose easily and improve alkali soil rapidly as compared with organic materials of wide C : N ratio as rice or wheat straw. Plant growth also helps in the reclamation of alkali soils through addition of organic matter and root respiration.

*Table 12*

**Effect of gypsum, green manure and crop rotation on pH, ESP, aeration porosity and cumulative water infiltration**

| Treatment | Crop rotation | pH (0—15 cm soil) | | ESP (0—15 cm soil) | | Aeration porosity, % | | Water infiltration (6 h, cm) | |
|---|---|---|---|---|---|---|---|---|---|
| | | Kaheru | Ghabdan | Kaheru | Ghabdan | Kaheru | Ghabdan | Kaheru | Ghabdan |
| Control | Rice-wheat | 10.00 | 10.10 | 38.1 | 63.7 | 6.98 | 6.60 | 1.57 | 0.85 |
| Gypsum | Rice-wheat | 9.75 | 9.85 | 21.2 | 52.4 | 7.45 | 9.53 | 1.75 | 1.00 |
| Gypsum + *Sesbania* | Rice-wheat | 9.50 | 9.70 | 17.4 | 45.7 | 11.70 | 12.17 | 3.65 | 1.90 |
| Control | Rice-clover | 10.00 | 10.05 | 47.7 | 67.5 | 7.08 | 6.79 | 1.30 | 1.70 |
| Gypsum | Rice-clover | 9.75 | 9.60 | 32.7 | 46.2 | 9.62 | 10.38 | 2.96 | 1.60 |
| Gypsum + *Sesbania* | Rice-clover | 9.55 | 9.50 | 25.2 | 36.5 | 10.57 | 13.77 | 2.91 | 2.80 |

*Green manures.* — Green manuring alkali soils with *Sesbania aculeata* has proved more useful than any other green manure crop (TALATI [50]; AGARWAL et al. [7]; UPPAL [51]; DHAWAN et al. [20]; YADAV and AGARWAL [57]; KANWAR et al. [31]). DHAWAN et al. [20] reported that *Sesbania aculeata* contained sufficient calcium and acid juices to replace Na by Ca. KANWAR et al. [31] observed that green manuring with *Sesbania* along with fertilizer application produced good yields of paddy on saline-alkali soils. DARGAN and CHILLAR [14] found that green manuring with *Sesbania* benefited the paddy crop with nitrogen equivalent to 80 kg/ha. In experiments on Ghabdan and Kaheru soils green manuring with *Sesbania* along with gypsum application decreased pH and ESP of these soils to greater extent as compared with gypsum alone both under paddy-wheat and paddy-clover crop rotations (Table 12.).

Cumulative water infiltration and aeration porosity at 100 cm suction were also much higher with green manure plus gypsum treatment, than gypsum alone (Table 12.). CSAUDHARY and BAJWA [13] observed that gypsum and *Sesbania* green manure combination rather than gypsum alone, caused better aggregation and brought greater improvement in the water transmission characteristics of 3 alkali soils.

*FYM and crop residues.* — Farm yard manure, pressmud (sulphitation process), rice straw, rice husk and other crop residues have been used to reclaim mild alkali soils. UPPAL [51] found that FYM was beneficial in the reclamation of saline-alkali soils. KANWAR and BHUMBLA [28] reported that FYM was effective with Kamma soil but not at Nilokheri where the soil was highly deteriorated.

DARGAN et al. [16] obtained higher yields of berseem and paddy grown in succession in the treatment having application of both gypsum and FYM than in the treatments having either of the two. MENDIRATHA et al. [35] also observed that gypsum gave better results in combination with FYM in saline-alkali soils.

*Table 13*

**Balance sheet of Na in the Willoms silty clay (WSC) soil 8 weeks after incubation**

| Treatment | Na removed in leachate | Soluble Na in the soil | Exchangeable Na in the soil |
|---|---|---|---|
| | me | | |
| Barley straw (aerated) | 21.7 | 7.4 | 77.4 |
| *Sesbania* (aerated) | 32.7 | 8.0 | 68.0 |
| Barlay straw (saturated) | 46.3 | 5.5 | 54.3 |
| *Sesbania* (saturated) | 56.4 | 5.7 | 48.8 |

Role of crop residues in reclamation of salt affected soils has also been investigated. Application of paddy straw proved beneficial in the reclamation of an alkali soil (AGARWAL and GUPTA [5]). DHAWAN and MAHAJAN [19] suggested application of rice hulls at 3750 kg/ha to saline-alkali soils for reducing pH, degree of alkalization and soluble salts. ZENDE et al. [58] reported that waste products like groundnut hulls and safflower hulls reduced salinity status.

The role of organic materials in reclamation of alkali soils is mainly through the production of organic acids especially under partially or completely anaerobic conditions. SINGH [43] compared the effect of 2 narrow and wide C : N ratio organic materials incubated under aerated and saturated conditions on the reclamation of a sodic soil. He observed that removal of exchangeable

*Table 14*

**Effect of straw and *Sesbania* green manure on aggregation and ESP of 3 alkali soils**

| Treatment | <0.25 mm aggregate size | | | Exchangeable sodium percentage | | |
|---|---|---|---|---|---|---|
| | Ghabdan | Isri | Kaheru | Ghabdan | Isri | Kaheru |
| Control | — | — | — | 72.3 | 83.9 | 74.9 |
| Gypsum | 3.6 | 4.7 | 5.3 | 34.4 | 15.8 | 14.9 |
| Gypsum + *Sesbania* | 15.9 | 12.0 | 13.2 | 10.2 | 11.2 | 5.3 |
| Gypsum + Paddy straw | 9.8 | 10.2 | 10.1 | 18.2 | 11.6 | 4.9 |

Na from the soil increased under saturated conditions (Table 13.). Sodium removal in both calcareous and non-calcareous soils was greater where *Sesbania* was the source of organic matter as compared with barley straw which has a wider C : N ratio than the former. SINGH [44] reported that the role of decomposition products of added organic matter in sodium removal from alkali soils was more chemical than physical in nature. Anaerobic decomposition of easily decomposable organic matter produced large quantities of organic acids. Under such conditions H ions could also replace sodium from the exchange complex.

CHAUDHARY and BAJWA [13] observed better aggregation and greater decrease in exchangeable sodium percentage in treatments that received gypsum plus *Sesbania* green manure as compared with gypsum plus paddy straw or gypsum alone (Table 14.). A combination of crop residues and gypsum can therefore be more suitable for reclamation of alkali soils.

## Summary

The primary objective in the reclamation of alkali soils is to reduce exchangeable sodium in the soil to levels safe for optimum plant growth. Exchangeable sodium is usually replaced with calcium which is derived either from the added calcium amendment or calcium from the native calcium carbonate is mobilized by using acids and acid formers. Experiments show that gypsum ($CaSO_4 \cdot 2H_2O$) is a cheap and very effective amendment for alkali soils. Information has been obtained on the method of application, particle size and water requirement for dissolution of gypsum in different alkali soils. Mineral acids are effective but are costly and offer problems during bulk transport and application. Root respiration and decomposition of organic matter especially under partial anaerobiosis generate organic acids that increase dissolution of calcium carbonate in the soil and help in reclamation.

Of the acid formers sulphur and pyrites ($FeS_2$) are important amendments but their oxidation is slow in alkali soils. Pyrites offer greater promise even though field and laboratory experiments show that on chemically equivalent basis it is less effective than gypsum. Different aspects on the use of this amendment are discussed and comparative effects of amendments on crop yields and soil properties are reported.

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## Discussion

DARAB, K.
How was the quantity of dissolved gypsum determined at different levels of ESP?
What is the reason of the high solubility of finely dispersed gypsum?
SINGH, N. T.
The dissolved amount of gypsum was calculated from the gypsum requirement of the soil.
The high solubility is connected with the increased effectiveness of gypsum with fine particles as it exposes greater surfaces and thus becomes increasingly soluble to meet the demand of the sodium dominated exchange complex which acts as a sink for Ca ions in the soil solution.
MOLNÁR, E.
What is the source of $Al_3(SO_4)_2$ applied for the reclamation of alkali soils and what will happen to the Al after hydrolysis of chemical?
Have you long-term experiments concerning the application of pyrite? Is the iron soluble after oxidation of pyrite and does it cause any redox problem in soils?
SINGH, N. T.
Commercial grades of aluminium are available from industry. Oxides of aluminium precipitated upon hydrolysis of the chemical.
The soluble sulphur in pyrites immediately reacts with the soil. Unoxidized forms oxidize very slowly in alkali soils. Iron oxides are precipitated under such conditions.
BHATTACHARYYA, A. K.
How does the application of organic matter of different C : N ratios (viz. wide and narrow) influence the pH of the alkali soils? What are the different C : N ratios used and corresponding pH values of the soils obtained?
SINGH, N. T.
Organic matter with a narrow C : N ratio oxidizes very rapidly. Under partially aerobic or anaerobic conditions, the decomposition products are organic acids and alcohols. Organic acids lower the soil pH more rapidly when C : N ratio of the added material is narrow. The C : N ratios used were probably around 80 : 1 and 20 : 1. The pH values in the latter case were reduced by more than one unit in 48 hours when the material was well ground at the time of application under saturated soil conditions.