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Use of Langbeinite to Reclaim Sodic and Saline Sodic Soils

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ABSTRACT

Langbeinite is a soluble potassium-magnesium sulfate mineral ($K_2SO_4 \cdot 2MgSO_4$) found as an evaporite in many regions of the world. Langbeinite was used as a reclaiming material in a fine textured (clay loam) saline sodic soil (Grabe Series). This amendment can be dissolved and directly into the irrigation water, displacing sodium (Na) quickly with minimal water use. This amendment was superior over gypsum as a reclaiming material for a saline sodic soil in batch, column, and greenhouse studies. Langbeinite required 50% less irrigation water than gypsum to displace and leach exchangeable Na from soils. Langbeinite improved the infiltration rates of saline sodic soils, but not as effectively as gypsum. Significant increases in germination percent dry matter production mass of lima bean (*Phaseolus lunatus* L.) plants were observed when using langbeinite over the gypsum soil amendment.

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INTRODUCTION

An edaphological problem commonly encountered with developing arid and semiarid lands is the accumulation of either soluble salts, or exchangeable Na, or both in the soil in excessive concentrations. Geographically, salt affected soils are widely spread throughout the continents of the world which have a continental or arid and semi-arid climate and where, therefore evapotranspiration exceeds precipitation (Kovda, 1965). Gupta and Abrol (1990) estimated that salt affected soils occupy, on a global basis, 952.2 million ha of land. These, constitute nearly 7% of the total land area or nearly 33% of the potential agricultural land area of the world.

Growth inhibiting levels of salinity and sodicity based on tolerance reference points exhibited by traditional glycophytic (sweet-water) crops (e.g., corn, alfalfa, and cotton). Soils that affect the growth of traditional crops are collectively referred as salt affected soils. Saline soils contain excessive concentrations of soluble salts, as measured by saturated paste extract electrical conductivity (ECe), (ECe>4 dS m^{-1}) and have exchangeable Na percentage (ESP) values less than 15 and pH less than 8.5. Sodic soils are characterized by excessive contents of exchangeable Na (ESP>15), ECe less than 4 dS m^{-1} and a pH value often greater than 8.5. Saline sodic soils contain excessive concentrations of soluble salts (ECe>4 dS m^{-1}) and high levels of exchangeable Na (ESP>15) and a pH value seldom greater than 8.5 (U.S. Salinity Laboratory Staff, 1954). It is generally accepted that reclaiming sodic and saline sodic soils involves the displacement of exchangeable Na and its subsequent leaching from the root zone.

Reclamation of sodic and saline sodic soils can be accomplished in many ways, best dictated by local conditions, available resources and time, and the kinds of crops to be grown on the reclaimed soils (Gupta and Abrol, 1990). High crop yields per unit area can still be obtained on these lands with the use of appropriate technologies. For example, about 70,000 metric tons of gypsum were used to reclaim saline sodic soils in the State of Arizona during the 1989 season (ACAH-OSC, 1990). With a general tendency of increasing total area of salt affected soils, the use of chemical amendments is expected to grow in Arizona as it is around the world.

Among the various chemicals, Ca applied as gypsum is very good in effecting the displacement of exchangeable Na and improving soil physical and chemical properties (Oster and Frenkel, 1980). Traditionally, gypsum ($CaSO_4 \cdot 2H_2O$) is applied broadcast on the soil surface after the soil has been rough tilled and leveled. However, the water solubility of gypsum is very low, only 2.1 to 2.6 g L^{-1}. Consequently, multiple applications of water are needed to dissolve all the gypsum, for the Ca ion to react with the exchange site, and to leach the displaced Na from the root zone. The U.S. Salinity Laboratory Staff (1954) recommends the use of 1.7 metric tons of gypsum per acre-foot (~0.4 ha-30 cm) of soil to displace one milliequivalent (meq) of exchangeable Na per 100 g of soil. Considering the low

solubility of gypsum, 0.5 acre-foot (616 m^3) of water will be required to dissolve 1.7 metric tons of gypsum. In practice, however, once the gypsum is spread (dry application), 30 cm of applied water may dissolve as little as 0.15 metric tons of gypsum (FCH, 1988). This is due to varying grain and particle size and varying purities of gypsum materials used for reclamation purposes, and unsaturated flow conditions found in the field. The solubility of the gypsum mineral increases with salinity. For example at an EC of 15 dS m^{-1} gypsum is twice as soluble than at 3.5 dS m^{-1} (API 1997). Nevertheless, this solubility increase is of limited benefit in the reclamation of salt-affected soils, using poor quality water, because Na concentrations also increase in brackish waters.

Because of its low solubility, gypsum moves slowly into the soil. Therefore, it should be mixed to the depth of the soil where replacement of exchangeable Na is to be effected. For gypsum to displace Na the soil profile should be near saturation. These factors make the reclamation of Na affected soils very much water intensive and time and energy consuming. Applications of 10-15 metric tons of gypsum per acre (0.4 ha) of land on moderately saline sodic and sodic soils are common. Very high amounts (as high as 20 metric tons) of gypsum (FAO, 1989) or even as high as 30 metric tons (Abrol and Bhumbla, 1979) per acre of land are required for highly sodic soils and if rapid reclamation is needed.

Langbeinite Sources

Langbeinite is often included in the group of "potash" minerals. Goldsmith (1969) stated that the name "potash" is derived from "pot-ashes" an impure mixture of potassium carbonate and other salts. However, potash minerals include sylvite ($KCl \cdot MgCl_2$), carmallite ($KCI \cdot MgCl_2 \cdot 6H_20$), langbeinite, and polyhalite ($2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$) that usually contain K, Cl, SO_4, Ca, Mg as major ions. Langbeinites are double sulfates with the general chemical formula: $(M^+)_2$ $(N^{++})_2$ $(SO_4)_3$ with M=K, Rb, Co, Ti, NH_4, and N=Mg, Ca, Mn, Co, Ni, Zn, Cd, Fe (Oelkrug et al., 1988).

Langbeinite is a co-crystallized form of two water soluble salts of sulfate: potassium sulfate and magnesium sulfate mined and processed in New Mexico. This evaporite mineral unlike gypsum, it is one of the water soluble salts found in the ocean. Its average chemical composition is; 22% K_2O (18.2% K^+), 18.5% MgO (11.1% Mg^{2+}), and 67% SO_4^{2-} (22% S) (Hagstrom, 1986; IMC, 1990).

Langbeinite mining has also been reported in other parts of the world. In the former USSR langbeinite and kainite are the chief potassium minerals in the Stebink ore deposit (Apollonov et al., 1981). Potassium sulfate salts including langbeinite were also reported in the Ural-Caspian Basin (Azizov and Tikhvinskii, 1978; Borisenkov et al., 1980). In the Caspian area, the most widely developed potassium salt is polyhalite, while in Ural areas the rock-forming minerals are usually kainite and langbeinite (Azizov and Tikhvinskii, 1978). Other langbeinite deposits were reported in the Hannover region, Germany (Bauer and Kuhn, 1966) and five series

of deposits were recently identified in the Zechstain halogenous formation in Western Europe (Korenevskii, 1989).

In the Shandong Province, China, large amounts of anhydrite, gypsum, halite, polyhalite, and langbeinite were also reported in the Dawenkou depression at the west end of Wenmeng-faulted basin in the middle of Luxi uplift (Zhu, 1988).

Some evaporites that contain potassium and magnesium salts are developed in Africa where the most important potash resources are in the Congo Basin (30,000 mt) (Notholt, 1983) ($KCl{\cdot}MgCl_2{\cdot}6H_20$) and more bischofite (Garrett, 1996). Also in Africa, numerous mixed potash and magnesium sulfates have been discovered in Mali, Ethiopia (Dankil Depression), and Morocco Doukkala deposit (unmined) (Garrett, 1996; Notholt, 1983).

Argentina, Poland, and Australia also have potash mineral deposits. In the Rio Colorado region, Argentina, more than 300 Km^2 (not mined) area was reported to be a potash deposit (Garrett, 1996). On the other hand, Potash beds as thin layers of mixed polyhalites occur north of Gdansk on the Leba upland of Poland (Garrett, 1996). In Australia, sylvinite was reported to occur in the Etonvale Formation's salt member in the Adavale basin (Queensland) and the salt area covers 8,000 Km^2 and 900 m thick (Garrett, 1996).

Langbeinite and Gypsum Properties

The water solubilities of gypsum and langbeinite are ~2.4 g L^{-1} and 280 g L^{-1} (Hagstrom, 1986), respectively. Therefore, langbeinite is more than 130 times more water soluble than gypsum. Hence, langbeinite could easily be applied along with the irrigation water either at low or very high rates for reclaiming Na affected soils. In theory, this would result in a more efficient exchangeable Na displacement and leaching with significant water savings as compared with gypsum. Moreover, although conflicting results exist. There is general acceptance that the behavior of Mg in the soil exchange complex is more like Ca than the monovalent cations such as Na and K (Smith et al., 1949; U.S. Salinity Laboratory Staff, 1954; Ahmed et al., 1969; Thellier and Sposito, 1989).

The selectivity coefficient of Mg over Na is usually close, but not as high (favorable) as that of Ca over the Na ion. The symmetry values (% saturation or selectivity) of K, Mg, and Ca ions over Na in montmorillonite clay are 64, 82, and 88%, respectively (Dixon and Weed, 1989). Thus, both Mg and Ca ions can readily displace exchangeable Na (Dixon and Weed, 1989; Sposito, 1989). Potassium, which constitutes about 33% of the cation equivalent capacity of langbeinite, will also help to displace exchangeable Na because its selectivity coefficient is higher than that of Na for most soils. This is particularly true in soils with high levels of swelling and expanding smectite clays (Dixon and Weed, 1989). Therefore, increased levels of K ions in the soil solution should displace Na from the exchange sites by preferred K over Na ions and by mass action. Moreover, K saturated soils usually swell less than Na saturated soils (U.S. Salinity Laboratory Staff, 1954).

TABLE 1. Soil characteristics.

Soil class	pH*	ECe* dS m^{-1}	SAR*	CEC meq 100 g^{-1}	ESP (%)
Grabe clay loam	8.2	5.3	21.6	20.9	24.9

*Measured in a saturated paste extract.

Langbeinite has a total of 14.3 cation equivalents per kg, of which 9.5 (66%) are due to the divalent cation (Mg), whereas gypsum has a total of about 11.6 cation equivalents that come from Ca ion. Langbeinite crystals are 18% more dense than gypsum crystals, and commercially available langbeinite has a purity of ~95%, whereas the purity of commercial gypsum is often less than 70%. However, the cost of gypsum ranges between $30 and $40 per ton, while langbeinite sells for about $90 per ton in the United States.

This study had several objectives. Determine the optimum levels of langbeinite and gypsum required to displace exchangeable Na and lower the ESP of a sodium affected soil to an agriculturally acceptable level. Measure how much water is required for the reclamation of a saline sodic soil using langbeinite and gypsum and compare the amendments regarding their water use efficiencies. Compare the infiltration rates of a saline sodic soil saturated with exchangeable Mg and K ions, and compare it with one saturated with exchangeable Ca ions. Evaluate and compare seed germination, growth and dry matter yield responses of a lima bean crop grown in the greenhouse on a saline sodic soil reclaimed with langbeinite and gypsum.

MATERIALS AND METHODS

Fertilizer grade langbeinite (95% pure) from New Mexico was used in these experiments. To facilitate the process of dissolution, langbeinite crystals were ground to ~100 micron size. Commercial grade (70% purity medium grain) gypsum was used as the reference soil amendment. A clay loam (Grabe series) soil with saline sodic properties, from Safford, AZ, was used in this study (Table 1). Two types of local irritation waters where used, graded as poor and good quality waters with ECs of 2.0 and 0.3 dS m^{-1} and SAR_{adj}s of 13 and 5, respectively (Table 2).

Batch studies were conducted using 1:1 soil:irrigation water suspensions using eleven applications rates ranging from 0 to 20 metric tons ha^{-1}. The suspensions were mixed and stirred and allowed to stand overnight. After a 24-hour contact time, the suspensions were shaken for 30 minutes and centrifuged at 1500 rpms for 15 minutes. The extracts were filtered through a fine filter (Whatman #42) and

TABLE 2. Sources of irrigation and water quality. Note: cation and anion concentrations are in mg L^{-1}.

Water source	pH	EC ($dS\ m^{-1}$)	SAR	SAR_{adj}	Ca	Mg	Na	K	Br	Cl	NO_3	SO_4	HCO_3
Safford	7.8	2.0	8.7	13	125	18.4	433	3.0	2.3	406	48	217	361
Tucson	7.8	0.29	1.3	1.5	32	2.4	29	1.5	<.4	9.2	4.7	21.2	150

analyzed for cations using atomic absorption and emission spectroscopy techniques. All extractions where carried out in duplicate sets.

Column experiments were conducted using 15 cm (H) by 5 cm (D) columns packed with known amounts of soil under saturated conditions at a flow rate of two pore volumes per day. All soil columns were packed with the same amounts of soil (435 g) to bulk density 1.5 g cm^{-3}. This value is within the range (1.2 to 1.6 g cm^{-3}) of bulk densities commonly found in agricultural soils. The flow rate was controlled using a high pressure pump, and samples were collected using a programmable auto sampler into scintillation vials. Water infiltration rate measurements were made with a constant head manifold and a digital scale with automated data acquisition. All Column experiments were replicated. Predetermined amounts of gypsum where mixed in with the soil before packing. Langbeinite treatments were applied dissolved into the first pore volume of water.

Seed germination and yield responses were obtained using sodium sensitive lima beans (*Phaseolus lunatus* L.) using the Grabe soil and the two irrigations waters in a climate-controlled greenhouse. Based on the results from the laboratory column leaching experiments two sets of greenhouse crop response studies were conducted. These included the four gypsum, four langbeinite and eight control treatments with three leaching volumes, in a factorial arrangement of 4x3x3 for both treatments. Therefore, all greenhouse treatments were run in triplicate. Additionally, these experiments were performed once with Safford water and again with Tucson water (Table 2).

RESULTS AND DISCUSSION

Batch Studies

The ease of displacement of Na was tested using with batch experiments using 1:1 soil:water extracts and varying amounts of gypsum or langbeinite. The "applied" gypsum or langbeinite rates ranged from zero metric tons/ha (control) to 20 metric tons ha^{-1} in increments of two. Thus, 11 treatments were tested; the data are shown in Table 3 and Figure 1. Langbeinite was significantly more efficient than gypsum in replacing exchangeable Na especially at applications rates above 4 metric tons/ha (Table 3). Gypsum did not significantly displace more Na at

TABLE 3. Exchangeable Na (meq 100 g^{-1}) displaced by gypsum and langbeinite treatments using laboratory batch

Applied treatment (metric tons ha^{-1})	Gypsum means*	Langbeinite means*
0	0.00c	0.00h
2	1.14b	1.40g
4	1.99a	1.99f
6	2.01a	2.05f
8	2.04a	2.34ef
10	2.00a	2.57de
12	2.06a	2.68de
14	2.13a	2.95cd
16	2.11a	3.25bc
18	2.18a	3.43b
20	2.12a	4.27a

*Means followed by the same letter are not significantly different at the 0.05 probability level as tested by Duncan's Multiple Range Test.

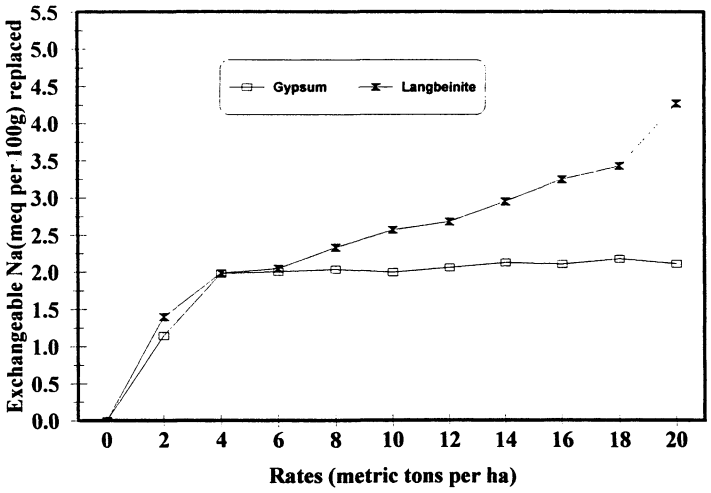

FIGURE 1. Exchangeable Na (meg per 100 g soil) displaced due to gypsum and langbeinite using laboratory batch extractions (1:1).

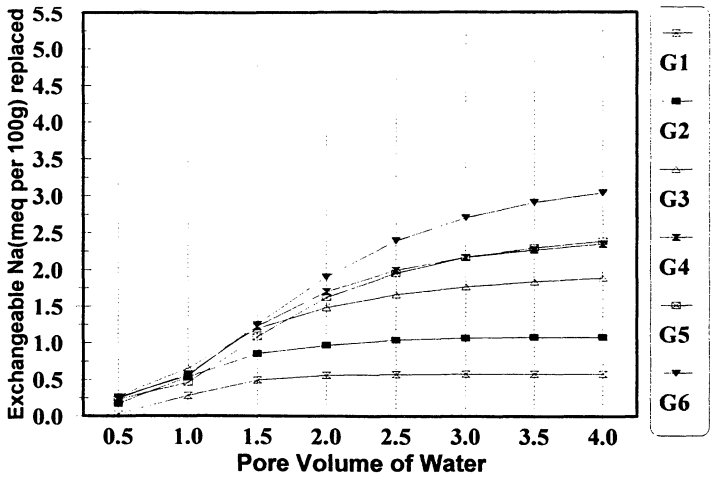

FIGURE 2. Effects of gypsum rates and volumes of leaching water on the removal of exchangeable Na.

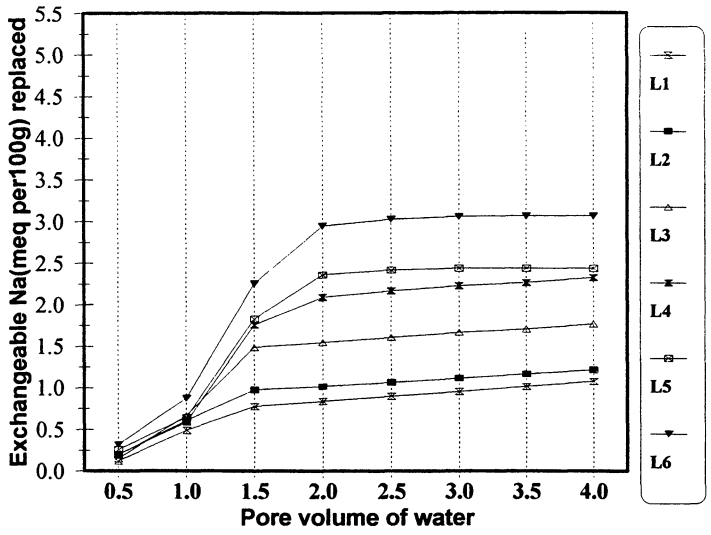

FIGURE 3. Effects of langbeinite rates and volumes of leaching water on the removal of exchangeable Na.

application rates between 4 and 20 metric tons ha^{-1} (Table 3). The data suggest a rate of exchangeable Na displacement limited by the low solubility of gypsum. On the other hand, Langbeinite more than doubled Na displacement at similar applications rates. Langbeinite, not being constrained by solubility limitations, continued to increase the displacement of exchangeable Na up to 80% at the 20-metric ton ha^{-1} rate (Figure 1).

Column Studies

These studies considered the results of the batch experiments by setting the treatment rates from zero the 12 metric tons ha^{-1}. The maximum treatment was set to 12 metric tons because at this rate langbeinite removed about 50% of the exchangeable Na; enough to change the soil class from sodic (ESP:24.9 to non-sodic (ESP:12). Also, if applied at a similar rate and dissolved in more water, gypsum could theoretically lower the ESP to acceptable levels. Therefore, the leaching rate was set up to four pore volumes of Safford water, applied to each column continuously over a 48-hour period. The data are presented in Figures 2 and 3. These cumulative Na displacement plots show that the amount of exchangeable Na removed by gypsum and langbeinite was similar when up to four pore volumes of water were used for leaching. However, langbeinite removed 30-50% more Na than gypsum with just two pore volumes of leaching water. The langbeinite removal rate leveled off after two pore volumes. Accordingly, savings of more than 20 cm of irrigation water could be realized by using langbeinite over gypsum to lower the ESP of the soil to about 10% when both amendments are applied at a rate of 12 metric tons ha^{-1}.

One of the most deleterious effect of high levels of exchangeable sodium in clay soils is the reduction of water infiltration rates. Relative infiltration rate changes were measured in column experiments using a constant head water application device. The data are presented in Figures 4 and 5. Water Infiltration improved initially as a function of increasing treatment rates for gypsum and langbeinite. The control columns had initial rates of about 1.8 mm hr^{-1} and the addition of gypsum or langbeinite improved the rate more than 2.5 times. However, positive effects of langbeinite applications were limited to the first two pore volumes. This suggests that Mg and K ions saturation do not favor clay flocculation as well as Ca ions do. However, the gypsum amendment offered a longer lasting improvement in infiltration rate over langbeinite after four pore volumes of leaching. This was due to the slow release of Ca ions into solution. The infiltration rate of the gypsum treated soil (@12 metric tons ha^{-1}) went up from 0.5 to 2.5 mm hr^{-1}; whereas, the langbeinite treated soil rate increased from 0.5 to 1.2 mm hr^{-1} with the same volume of leaching water (Figures 4 and 5). It should be noted that steady state infiltration rates were not attained with the use of gypsum nor langbeinite in any of the treatments. This effect was due column experimental conditions that favor the displacement of fine particulates in saturated flow experiments.

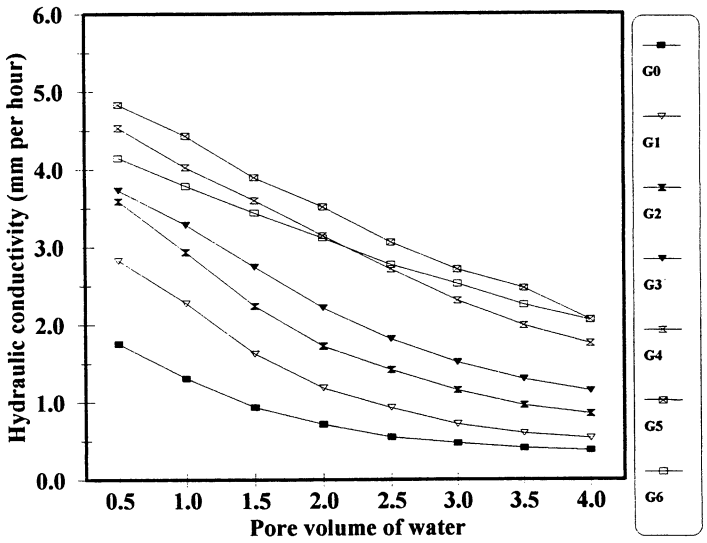

FIGURE 4. Effects of applied gypsum levels and volumes of leaching water on soil hydraulic conductivity of Grabe clay loam (saline sodic) soil.

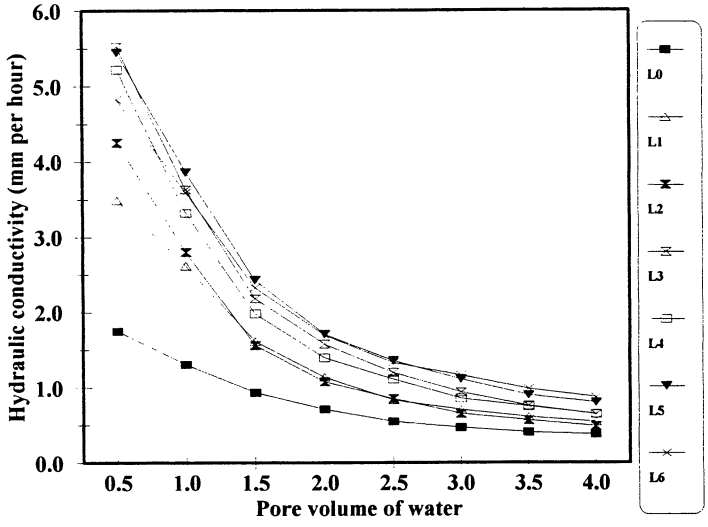

FIGURE 5. Effects of applied langbeinite levels and volumes of leaching water on soil hydraulic conductivity of Grabe clay loam (saline sodic) soil.

TABLE 4. Seed germination (%) of lima beans affected by langbeinite and gypsum applications and water leaching pore volumes (PV) using Tucson water.*

Langbeinite/ gypsum (metric tons ha^{-1})	Water PV=0	Water PV=1.5	Water PV=2.5	Water PV=3.5	Mean**
0	50.0/50.0	44.4/44.4	44.4/44.4	38.9/38.9	44.4b/44.4b
4	50.0/50.0	77.8/61.1	88.9/66.7	88.9/72.2	76.4a/62.5b
8	50.0/50.0	77.8/72.2	77.8/72.2	94.4/72.2	75.0a/66.7a
12	50.0/50.0	77.8/61.1	94.4/72.2	94.4/77.8	79.2a/65.3a
Mean**	50.0d/50.0b	69.4b/59.7a	76.4b/63.9a	79.2a/65.3a	

*The interaction between leaching water volumes and treatment (gypsum and langbeinite) were significant.

**Means within a row or column followed by the same letter are not significant at the 0.05 level.

Greenhouse Studies

Seed germination and dry matter yield of lima bean plants was studied using the same soil under green house conditions treated at rates of zero, 4, 8, and 12 metric tons ha^{-1} of gypsum or langbeinite. The first study also used Safford irrigation water (Table 2). A statistical analysis of the data (not presented) suggested that the high water sodicity masked the langbeinite and gypsum treatment effects because lima beans are very sensitive to Na in irrigation water. Nonetheless, the langbeinite treatment pots had about 10 and 20% higher than gypsum germination rates and dry matter yields, respectively. To reduce the Na effect from irrigation

TABLE 5. Dry matter yield (g pot^{-1}) of lima beans affected by langbeinite and gypsum applications and water leaching pore volumes (PV) using Tucson water.*

Langbeinite/ gypsum (metric tons ha^{-1})	Water PV=0	Water PV=1.5	Water PV=2.5	Water PV=3.5	Mean**
0	3.84/3.84	3.58/3.58	3.38/3.38	3.72/3.72	3.63c/3.63c
4	3.84/3.84	5.59/4.06	6.21/4.15	7.78/5.20	5.86b/4.31b
8	3.84/3.84	5.86/4.70	7.26/5.22	7.38/5.38	6.09b/4.79a
12	3.84/3.84	6.24/4.71	7.91/5/45	8.35/5.69	6.59a/4.72a
Mean**	3.84d/3.84d	5.32c/4.26c	6.19b/4.55b	6.81a/5.00a	

*The interaction between leaching water volumes and treatment (gypsum and langbeinite) were significant.

**Means within a row or column followed by the same letter are not significant at the 0.05 level.

water, a second set pots with similar treatments where done with Tucson water (Table 2), low in Na. The data are presented in Tables 4 and 5.

Statistical analysis showed that there was a significant difference ($P<0.05$) in the response of lima beans following 0 to 2.5 PVs of irrigation water, and between applications rates (between 0 and 8 metric tons ha^{-1}) in both treatments. Additionally, the langbeinite treatment showed significantly higher % germination and dry yields than gypsum. At the high treatment rate langbeinite had about 20% and 40% higher germination and dry yields than gypsum, respectively.

SUMMARY AND CONCLUSIONS

Langbeinite, is a soluble halide mineral, usually found as an evaporite in numerous regions of the world. To date its potential use as a soil reclamation agent has not been reported. The research presented here suggest that langbeinite can be used as reclaiming material, particularly in fine textured saline sodic soils when rapid remediation is valued. Because of its high solubility, langbeinite can be applied directly into the irrigation water, displacing Na quickly with minimal water use.

The langbeinite mineral used in this study proved to be superior over gypsum as a reclaiming material for a saline sodic soil in batch, column, and greenhouse studies. This mineral required 50% less irrigation water than gypsum to displace and leach exchangeable Na from soils.

Langbeinite improved the infiltration rates of saline sodic soils, but not as effectively as gypsum following several pore water applications.

Decreases in the Ca^{++}/Mg^{++} soil ratios, and increased concentrations of K^{+} did not adversely affect the fertility of the soil used in this study. In fact, significant increases in germination percent dry matter production mass of lima bean plants were observed when using langbeinite over the gypsum soil amendment.

This study did not examine the effects of multiple applications of lanbeinite to reclaim saline-sodic soils. Repeated applications of langbeinite may result in high Ca/Mg ion ratios, potentially unfavorable to plant fertility and to soil aggregate formation. Further research in the use of langbeinite and other highly soluble "potash" minerals containing K, Mg, and SO_4 ions as reclaiming materials under field conditions is needed.

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