Reclamation of calcareous saline-sodic soils in southcentral Montana with by-product sulfuric acid
by Richard Lyman Cates

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Soils
Montana State University

Abstract:
Copper smelters produce sulfuric acid in the sulfur scrubbing process. Oil refineries use commercial grade sulfuric acid in alkala-tion units, and the resultant "spent" acid is a waste product.

Field and laboratory experiments were conducted to evaluate the effectiveness of these sources of sulfuric acid for reclaiming calcareous, saline-sodic soils. Three experimental sites were located on montmorillonitic loam to clay loam soils in irrigated agricultural valleys of southcentral Montana. The soils had high pH, ECe, SAR, and ESP values. Subsurface drainage varied substantially with site.

Treatments used in the studies included rates of scrubber acid and comparisons with gypsum, ammonium polysulfide, spent acid, and scrubber acid used in combination with feedlot cattle manure.

Reclamation effectiveness in the field study was evaluated by saturated paste pH, extract conductivity, and SAR values. Available P, Cu, Zn, Mn, and Fe levels were determined. Barley (Hordeum distichum) dry matter yields were harvested the second year.

"Undisturbed" cores from one of the sites were used in a 131-day saturated flow leaching study. Hydraulic conductivity and leachate EC and pH were measured with time. Soil cores were analyzed for changes in EC and SAR of the extract from 1:5 soil-water ratios after completing the leaching study.

Field data indicate that reclamation occurred in the surface 5 to 20 cm of sulfuric acid treated plots. Progress in reclamation was indicated by all soil criteria measured. Barley dry matter yields increased by significant amounts the second cropping year. Yields due to the highest rate of acid were more than four times that of the check.

Acid effectiveness increased with rate. Spent acid generally reacted similar to scrubber acid. Sulfuric acid affected soil properties and barley production similar to gypsum and ammonium polysulfide. Feedlot cattle manure plus scrubber acid increased barley dry matter yield nearly 40% over acid alone.

Laboratory data indicate that hydraulic conductivity values tend to increase, then decrease under continuous saturation. Low soil SAR and EC5 values were generally associated with high hydraulic conductivity and low leaching EC values. Leachate pH may decline if the total volume of leachate that passed through cores is high. Sulfuric acid was superior to gypsum and ammonium polysulfide in all criteria measured.

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RECLAMATION OF CALCAREOUS SALINE-SODIC SOILS IN SOUTHCENTRAL MONTANA WITH BY-PRODUCT SULFURIC ACID

by

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A thesis submitted in partial fulfillment
of the requirements for the degree

of

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in

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INTRODUCTION

The Yellowstone and Clark's Fork of the Yellowstone River Valleys in southcentral Montana are generally very productive, irrigated agricultural areas. The growing season is 125-130 days. Principal crops are corn for silage, sugar beets, alfalfa, and barley. The soils are calcareous, and typically silt loam to clay loam in texture. There are significant areas of soils where salts have concentrated to the extent that growth of most plants is severely limited. Sodium is often present in quantity, and in combination with montmorillonite, the dominant clay in these valleys, the soils are impermeable when dry and "puddled" when wet.

The original source of the salts is from weathering of underlying shale and leaching from the shale beds which protrude from higher land adjacent to the valleys. Hansen (1914) conducted soils research on the Huntley Irrigation Project in the Yellowstone River Valley. He reported that there were areas of salt existing in the surface soil even before irrigation began in 1907. Low lying soils were usually the affected areas. In 1910, Hansen measured the ground water level at various sites during the growing season. The water level was 180 to 240 cm below the surface and was found only in underlying gravel. The lower layers of the soil, between the upper 30 to 60 cm and the underlying gravel, contained little moisture. As irrigation became more extensive, the water table rose. During the growing season in 1913, Hansen found the water table to be within approximately 90 cm of the surface at the same sites he had observed in 1910.

Irrigation practices have intensified and extended the salt problem that originally existed in southcentral Montana. Unlined ditches have been used almost exclusively. Seepage from the ditches, as well as excessive application of irrigation water, have raised the water table. Where the water table is within 120 to 150 cm from the surface, water with its dissolved salts moves up the soil profile by capillarity in response to the evaporative demand (Doering and Willis, 1975). The salts are concentrated in the root zone when the water evaporates at the soil surface.

Sulfuric acid (H_2SO_4) has been known for many years to be an effective amendment on Na-affected calcareous soils in the Southwestern United States (Overstreet et al., 1951). Traditionally, it has been expensive, and combined with the handling problems associated with any acid, its use in reclamation has been limited.

Nonferrous smelting and coal fired industries produce sulfuric acid in the "scrubbing" process. The purpose of "scrubbing" is to prevent sulfur oxides from entering the atmosphere. The acid thus produced is 91-95% concentrated. Commercial sulfuric acid is 93-98% pure. Copper smelting activity in the Rocky Mountain states and strict Federal air pollution standards are producing a continuing supply of acid.

In addition, oil refining and natural gas purification processes are providing a waste product sulfuric acid. Commercial grade 98% sulfuric acid is used by refineries in alkalation units until its concentration is reduced to 93%. The resultant acid is called "spent" acid. It appears black and has a strong, organic odor.

Scientists in the Southwest have done extensive work with scrubber produced sulfuric acid (Stroehlein et al., 1978). They have experimented with calcareous and Na-affected calcareous soils, and have researched application of acid in irrigation water as well as directly to the soil. The literature search indicates that research with "spent" acid has not been reported.

The purpose of this 2-year study was to determine the effectiveness of scrubber produced and oil refinery "spent" sulfuric acid for initiating reclamation of several calcareous, saline-sodic soils in southcentral Montana.

LITERATURE REVIEW

Definitions and Properties of Salt-Affected Soils

The original source of the Earth's salts is the crust. Weathering releases minerals (salts) from rock, and water becomes the agent for their transport. Soils with poor drainage and a high evaporation to precipitation ratio, may concentrate salts within the soil profile.

Predominant cations and anions present in salt-affected soils are typically Ca, Mg, Na, K, SO_4, Cl, CO_3, HCO_3, OH, and occasionally NO_3 and Si (U. S. Salinity Laboratory Staff, 1954). Relative cation and anion concentrations, and their combinations into ion pairs, are significant and will be discussed below.

Salt-affected soils are classified under the headings saline, saline-sodic, and sodic (U. S. Salinity Laboratory Staff, 1954). Saline soils are those with a saturation extract electrical conductivity (EC_e) greater than 4 mmhos/cm, and an exchangeable sodium percentage (ESP) less than 15. This concentration of neutral soluble salts is sufficient to interfere with the growth of most plants, but creates no adverse soil physical conditions. The pH of these soils is usually below 8.5. The salt ions present in greatest quantities are generally Cl and SO_4 of Ca, Mg, and Na. Soluble salts in a saline soil cause reverse osmosis in the plant cell. Less salt concentrated water within the plant cells moves toward the more salt concentrated soil solution. In addition to water stress plants growing in saline soils often show nutrient deficicencies due to competition from non-nutrient ions (U. S. Salinity Laboratory Staff, 1954).

Reclamation of a saline soil may be accomplished by creating adequate drainage, then leaching the salts through the soil profile with low sodium adsorption ratio (SAR) and salt content water.

Sodic soils have an EC_e less than 4 mmhos/cm and an ESP greater than 15. The pH is usually greater than 8.5. High ESP creates adverse physical conditions such as a hard impermeable crust when the soil is dry, and "puddling" when wet. The crust decreases aeration, and makes seedling emergence and root and water penetration difficult. When these soils are wet the deflocculated or "puddled" condition slows water movement through the profile with the result that anaerobic conditions may be dominant for extended periods of time. Thus, root respiration and aerobic microbiological activity are decreased (Mahmoud et al., 1969). A high concentration of Na also has adverse effects on plant metabolism and nutrition (Satyanarayana and Rao, 1963; Bhumbla, 1972; Chander and Abrol, 1972; Laura and Idnani, 1973; Poonia and Bhumbla, 1973). Excessive pH is a result of the hydrolysis of sodium bicarbonate and sodium carbonate in the soil solution, or of Na on the exchange complex. Hydrolysis occurs because of the low relative concentration of neutral soluble salts (Brady, 1974). The processes are shown in equations 1, 2, and 3.

$$NaHCO_3 + H_2O \rightleftharpoons Na^+ + OH^- + H_2CO_3 \quad [1]$$

$$Na_2CO_3 + 2H_2O \rightleftharpoons 2Na^+ + 2OH^- + H_2CO_3 \quad [2]$$

$$NaX + H_2O \rightleftharpoons HX + Na^+ + OH^- \quad [3]$$

(X denotes the negative charged clay micelle)

The resultant concentration of OH in the soil solution is expressed by high pH. The high concentration of OH may impair root development and water uptake of plants (Thorup, 1969), and is detrimental to microorganisms (Miyamoto et al., 1973). Some plant nutrients are rendered unavailable (Bhumbla, 1972; Chander and Abrol, 1972). Another effect of high OH concentration is that soil organic matter is dissolved (Mitra and Singh, 1959; Bhumbla, 1972). The organic matter may be left on the soil surface as a black crust when evaporation occurs.

Saline-sodic soils have an EC_e greater than 4 mmhos/cm and an ESP greater than 15 with a pH value usually less than 8.5. The high neutral salt concentration lowers pH and may facilitate flocculation. The degree to which flocculation is affected depends on the relative amount of exchangeable Na to neutral soluble salts. Therefore, saline-sodic soils may or may not exhibit adverse physical properties, but high osmotic potential and the effects of high Na concentration are problems.

Theory of Reclamation of Saline-Sodic and Sodic Soils

An overview of the literature indicates that reclamation procedures should accomplish the following:

1. Decrease soil ESP and pH. This should result in improved physical conditions, reduction of the problems associated with high Na concentration, and improved soil nutrient status. The approach is to add a flocculating cation such as Ca to the soil, or an amendment that solubilizes precipitated soil Ca or Mg. In either case, cations must exchange with the Na on the exchange complex and effect reduced hydrolysis.

2. Remove soluble salts from the soil solution. This can be accomplished in part through uptake by extremely salt tolerant plants, or by leaching through the soil profile if adequate drainage is established.

Procedures which effect 1 or 2, but not both, are of little value alone. Removal of soluble salts from a saline-sodic soil creates a sodic soil. Only decreasing ESP results in a soil solution of greater salt concentration.

3. Improve physical conditions. This is attempted by deep tillage, the incorporation of organic material, or by the application of irrigation water with a high Ca + Mg:Na ratio. Improving physical conditions allows for better aeration and water penetration which

facilitate crop growth and further reclamation (lowering of ESP, pH, or removal of soluble salts).

Reclamation Techniques for Saline-Sodic and Sodic Soils

Deep Tillage

Deep tillage has been used in conjunction with other reclamation procedures. Bhumbla (1972) found that deep plowing resulted in lower yields of crops in a highly deteriorated saline-sodic soil. Branson and Fireman (1960) found subsoiling to 120 cm in a fine-textured poorly drained saline-sodic soil to be of no benefit. They attributed this to the slaking of the dispersed subsoil into the vertical channels upon irrigation. O'Connor (1974) advises that management techniques such as chiseling along with the incorporation of organic matter, should accompany leaching in order to maintain favorable infiltration rates in a fine-textured, saline-sodic soil. In contrast to O'Connor, Loveday (1976) found that deep tillage alone, to 45 cm, in a sodic clay soil enhanced leaching of soluble Ca and Na salts in the upper 80 cm. Effectiveness approached that of a combined gypsum-deep tillage treatment. Plowing to depths of 40 to 60 cm, and the subsequent mixing of surface soil, hardpan layer, and limesalt layer in equal proportions, has been used with lasting effectiveness on the solonetz soils (Natriborolls) of Canada's central provinces (Cairns and Beaton, 1976).

Organic Matter Utilization

Organic material has been used for reclamation in primarily three ways: 1) as a salt tolerant crop which is harvested; 2) as a green manure crop; or 3) as an amendment.

Growing plants improve soil conditions in several ways. Of primary importance is the physical action of their roots (Bower, 1959; Sharma, 1971; Puttaswamygowda, 1973; Yadav, 1975). Roots improve water movement and gas exchange as they break up the impermeable crust of a saline-sodic or sodic soil.

Of secondary importance is the uptake of salts. Haq and Khan (1971) reported that kallar grass (*Diplachna fusca*) was effective in absorbing salts and exchangeable Na from the soil solution. A variety of salt tolerant plants are listed by the United States Salinity Laboratory Staff (1954). Plants that are tolerant to salty conditions concentrate the majority of salts in their roots, but there is generally an increase in salt uptake into the harvestable portion of the plant (Satyanarayana and Rao, 1963; Poonia and Bhumbla, 1973).

Of tertiary importance is the carbon dioxide produced by plant roots during respiration. Carbonic acid formed helps to dissolve calcium carbonate in the soil (Overstreet et al., 1951). Calcium is free to exchange with Na on the exchange complex. The sodium bicarbonate produced is soluble and may be leached. Equations 4 and 5 illustrate these chemical reactions:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad [4]$$

$$2NaX + H_2CO_3 + CaCO_3 \rightleftharpoons CaX + 2NaHCO_3 \qquad [5]$$

Carbonic acid will also lower soil pH (Boumans and Hulsbos, 1960; De et al., 1974). Root respiration is not of significant influence in soil reclamation and alone cannot be relied on to reduce ESP and lower pH (Goertzen and Bower, 1958).

Organic material added to a salt-affected soil provides all of the benefits that accompany its addition to any other soil. It improves permeability and aeration, supplies plant nutrients, increases microbial activity, and increases cation exchange capacity (Brady, 1974). Decomposition of organic matter by microorganisms produces carbon dioxide with resulting influences as just mentioned for carbon dioxide produced in root respiration.

A green manure plant commonly used with success in ameliorating physical problems is the legume jantar or dhaincha (Sesbania aculeata) (Zaidi et al., 1968; Bhumbla, 1972; Saraswat et al., 1972; Dargan et al., 1975; Yadav, 1975). Rye (Hansen, 1914) and salar mar grass (Dalpachine fusca) (Zaidi et al., 1968) have also been used with success.

Some organic amendments are the following. Argemone mexicana, a noxious weed, is ground to a powder and incorporated into the soil (Ramamoorthy and Agrawal, 1966; Krishnamurthy and Soundararajan, 1967;

Saraswat et al., 1972). Manure (Branson and Fireman, 1960; Krishnamurthy and Soundararajan, 1967; Saraswat et al., 1972; Puttaswamygowda et al., 1973; Yadav, 1975) and compost (Pothiraj and Srinivasan, 1968; Laura and Idnani, 1973) have been used successfully for reclamation. Polysaccharides such as molasses (Krishnamurthy and Soundararajan, 1967; Saraswat et al., 1972; Yadav, 1975) and sugar or starch (Padhi et al., 1965; Saraswat et al., 1972; Puttaswamygowda et al., 1973) have been used to improve soil aggregation. Padhi et al. (1965) reported, though, that starch by itself was ineffective. Charcoal dust and sawdust (Laura and Idnani, 1973), straw (Puttaswamygowda et al., 1973; Singh, 1974), and rice husks (Mitra and Shanker, 1957) have shown varying degrees of success as amendments.

Organic materials are frequently used with gypsum and leaching for reclamation. Gypsum with livestock manure (Zaidi et al., 1968; Bhumbla, 1972; Puntamkar et al., 1972; Poonia and Bhumbla, 1974), with green manure (Mitra and Shanker, 1957; Taha et al., 1966; Krishnamurthy and Soundararajan, 1967), with crop residues (Mitra and Singh, 1959), and with compost (Taha et al., 1966; Bajpai et al., 1976) has been used with success in many instances. Sulfur combined with weed growth was less effective in reclamation than gypsum and weeds (Mitra and Shanker, 1957).

Pressmud, a product of the carbonation process in sugar refineries (60-70% calcium carbonate, 10% organic matter, and small amounts of N, P, and K), is an organic-inorganic amendment used with some success (Kanwar and Chawla, 1963; Bhumbla, 1972; Saraswat et al., 1972). Another form of pressmud which has been used with success results from a sulfitation process (Yadav, 1975; Chand et al., 1977). Bhumbla (1972) reports that pressmud from the sulfitation process is more effective than that from the carbonation process at pH values above 9.5. Algae, particularly blue green algae (*Anabaena naviculoides*), have been useful alone (Sims and Dregne, 1962), and in combination with a Ca amendment (Dhar and Srivastava, 1968) for supplying N as well as improving physical conditions of the soil.

Water in Reclamation

High Salt Water Dilution Method for Reclaiming Sodic Soils

The high salt water dilution method for reclaiming sodic soils involves the application of water with a high divalent cation concentration. The method gives best results on highly impermeable, sodic soils. The flocculating effect of the high-salt concentration facilitates infiltration, allowing reclamation to begin. As water with a high divalent cation concentration percolates through a sodic profile, Na is displaced from the exchange complex and ESP decreases according to the "valence dilution" principle observed by Reeve and Bower (1960). The "valence dilution" principle is that the adsorbed cation of lower valence tends, upon dilution, to be displaced by solution cations of higher valence. Successive dilutions of the water can then be used as reclamation proceeds. Badiger et al. (1969) report that reclaiming sodic soils through the use of high-salt water without amendments leads to a reduction in the cost.

Doering and Reeve (1965) found that the quantity of high-salt water needed for reclamation increased rapidly as the water's Ca + Mg content decreased. According to these scientists it is impractical to use a water if its Ca + Mg concentration is less than 30% of the total cation concentration. Reeve and Bower (1960) and Reeve and Doering (1966) used sea water with much success. Reeve and Bower drastically reduced ESP and increased hydraulic conductivity in 12 days using a total of 195 cm of water (three successive dilutions of sea water followed by Colorado River water). Equivalent reclamation with river water alone took 120 days.

High-salt water can be artificially prepared with soluble Ca amendments such as calcium chloride (Reeve and Bower, 1960; Badiger et al., 1969; Doering and Willis, 1975) or calcium nitrate (Doering and Willis, 1975). The solution is prepared and then applied to the land. Gypsum has generally been ineffective for this procedure due to its low solubility (Doering and Reeve, 1965; Muhammed and Amin, 1965; Badiger et al., 1969; Doering and Willis, 1975).

Doering and Reeve (1965) indicate that a leaching water is capable of reclaiming a particular sodic soil if its SAR is less than that of the equilibrium soil solution at the existing ESP. By successively lowering the SAR of the salt water solution added to the soil, rapid reclamation occurs. Vander Pluym et al. (1973) concluded that leaching water with a given total salt concentration produced hydraulic conductivity values inversely related to its SAR. Rawat and Singh (1974) and Massoumi (1975) have also found that leaching with water high in salt concentration, but with low SAR values, is an effective method for reclaiming sodic soils.

Reeve and Bower (1960) and Reeve and Doering (1966) leached by successive dilution until the soil was fully equilibrated. However, Muhammed et al. (1969) found that the efficiency of reclamation is highest at the beginning of any equilibration step. The soil and water were assumed to be in equilibrium when the SAR of the leachate was essentially equal to that of the applied water. At each dilution step application of only two-thirds the amount of gypsum-saturated sea water required for full equilibration was as effective at reducing ESP as greater amounts of water in both a coarse- and fine-textured soil.

Reclamation of Saline-Sodic Soils by Leaching with Pure Water Only

Authors have reported that pure water has been effective in reclaiming a saline-sodic soil (Antipov-Karataev, 1960; Boumans and

Hulsbos, 1960; Flannery, 1960; Reuss and Campbell, 1963). Effectiveness has been attributed to solubilizing Ca (or Mg) salts already present in the soil profile. For example, dissolved gypsum reacts with adsorbed Na by the process in equation 6. Sodium sulfate that is produced can be leached from the soil profile.

$$2NaX + CaSO_4 \rightleftharpoons CaX + 2Na_2SO_4 \qquad [6]$$

Calcium ions are also solubilized through hydrolysis of calcium carbonate as desdribed by Goertzen and Bower (1958) in equation 7. The resultant soluble Na can be leached from the soil profile. These scientists were not able to effect complete reclamation by this process due to the low solubility of calcium carbonate.

$$2NaX + CaCO_3 + H_2O \rightleftharpoons CaX + NaHCO_3 + NaOH \qquad [7]$$

Water Management

Leaching of soluble salts from saline-sodic and sodic soils requires application of water in excess of what is required for crop growth. The majority of the leaching should be accomplished after application of the amendment, and before planting. This allows the seed the most favorable environment for germination and growth.

Successful reclamation depends on movement of water into and through the soil profile. Land to be reclaimed should be perfectly level (Amemiya and Robinson, 1958; Bhumbla, 1972) and dikes can be built in and around a field to insure uniform and thorough wetting.

The quantity of leaching water required to achieve a desired soil solution EC depends on the salt content of that water. Leaching requirement (LR) is expressed as a fraction of the water applied per season that must pass through the determined depth to be reclaimed in order to maintain a steady state (U. S. Salinity Laboratory Staff, 1954). Equation 8 illustrates the concept

$$LR = \frac{ECiw}{ECdw} = \frac{Ddw}{Diw} \qquad [8]$$

where: EC = electrical conductivity,

D = depth,

iw = irrigation water, and

dw = drainage water.

Rhoades (1968) describes LR for controlling SAR of the soil solution as well. Rhoades et al. (1974) suggest that the lowest possible volume of leaching water be used, commensurate with satisfactory crop growth, to minimize salt load in the drainage water. There is an increase in the total dissolved salts (TDS) of the soil solution when amendments that decrease soil ESP are used (Miyamoto et al., 1975a). Therefore, the amount of water that must pass through the zone to be reclaimed increases. The additional depth of water that must be applied to achieve the original TDS level can be approximated as being equal to the depth of soil to be reclaimed (Miyamoto et al., 1975a). This extra water is required in addition to that determined by the LR. Stromberg (1972) reports that a depth of water equal to the depth of soil to be reclaimed will remove about 80% of the salts, but to remove 90% of the salts twice as much water is required. Stromberg believes that soil texture has little to do with the amount of water required to remove a given salt load, but it will affect the speed of reclamation. That is, soils with lower permeability will require a greater length of time to be reclaimed because leaching is slower.

Leaching removes soluble plant nutrients such as NO_3. Fertilizer recommendations must take this into account. Mahmoud et al. (1969) observed that leaching removed organic matter from highly sodic soils.

When leaching is used in conjunction with amendments, water with a low EC is most desirable. Low SAR waters are always desirable. Water high in Na and CO_3 or HCO_3 is especially poor. Upon application to the land these ions cause precipitation of soil solution Ca creating "residual Na_2CO_3" as observed by a number of authors (Schoonover et al., 1957; Fine et al., 1959; Tisdale, 1970; Gumaa et al., 1976). "Residual Na_2CO_3" means that sodium carbonate and sodium bicarbonate dominate the soil solution. Hence, SAR is effectively increased along with a corresponding rise in soil ESP. Cairns and Szabolcs (1973) found that leaching with water high in sodium sulfate caused a downward displacement of Ca, subsequent soil dispersion, and reduced hydraulic conductivity.

Leaching can be performed by continuous or intermittent ponding. According to Bower (1959) intermittent ponding, due to the alternate wetting and drying, has generally been the most successful method for improving soil structure and thereby increasing hydraulic conductivity values. Reuss and Campbell (1963) found that alternate flooding and drying at 2-week intervals was most effective at reducing EC in a saline-sodic soil. Abed (1975) reported that leaching efficiency is increased with intermittent ponding, but continuous ponding effected lower ESP values with or without gypsum amendments. Sahota and Bhumbla (1970) found intermittent ponding to be more effective at increasing leaching efficiency in the 0 to 30 cm depth, but that continuous ponding was more effective below 30 cm. Abrol and Bhumbla (1973) found that continuous and intermittent ponding were similar and not very effective for assisting reclamation of a highly impermeable sodic soil.

Proper drainage is paramount if leaching is to be effective (Tobia and Pollard, 1958; Branson and Fireman, 1960; Lewis, 1966; Puttaswamygowda et al., 1973; Sharma et al., 1974; Pandey et al., 1975). There will simply be a dilution of the salts in the soil solution and a rise in the water table unless soluble salts and leaching water are drained from the affected area. Since most salt-affected soils have a drainage problem, installed drainage is usually required. The water table should remain at least 130 cm deep, in a loam soil in the northern Great Plains, to keep the upward flow rate near zero (Doering and Willis, 1975). Lewis (1966) reports that 180 cm is the minimum depth in lower latitudes.

Flushing as used by Yadav and Agarwal (1959) is defined as running excess water across the surface of the soil. The authors found that flushing was effective in removing surface salts from poorly drained soils not treated with gypsum, if a proper gradient existed.

Irrigation of salt-affected soils requires special management. Plant root growth is slow and shallow in soils with poor structure (Padhi et al., 1965; Chhonkar et al., 1971; Abrol et al., 1975; Doering and Willis, 1975). In addition, available water is limited to the depth that has been reclaimed. These conditions necessitate frequent, yet lighter irrigations (Overstreet et al., 1951; Bhumbla, 1972; Abrol et al., 1975; Doering and Willis, 1975; Fletcher and Schurtz, 1975). Flood irrigation is more desirable than furrow irrigation. The latter causes a concentration of salts in the ridges as water rises by capillary action to wet them (Stromberg, 1972).

Amendments Supplying Calcium

General

There are many soil amendments supplying Ca. Most of them are in the form of a soluble Ca salt. The primary purpose for their application is to effect a lower ESP as Ca exchanges with Na on the exchange complex.

The application of a Ca amendment, accompanied by sufficient water to solubilize it, increases the concentration of Ca in the soil solution. The SAR of the soil solution is thereby decreased and is no longer in equilibrium with the soil ESP. As Na leaves the exchange complex to re-establish equilibrium, Ca ions are available to take its place. The process is indicated in equation 9.

$$2NaX + CaSO_4 \rightleftharpoons CaX + Na_2SO_4 \qquad [9]$$

Leaching must be accomplished to remove the Na salts produced. Calcium amendments may be applied whether or not insoluble Ca (or Mg) is native in the soil. These amendments do not have to be repeated each year unless leaching and irrigation water have a high SAR, or drainage is poor and Na salts are not removed. Besides reducing ESP, Ca amendments also react with sodium carbonate and bicarbonate that exist in soil solution. Equations 10 and 11 indicate reactions that occur when gypsum is applied as an amendment.

$$Na_2CO_3 + CaSO_4 \rightleftharpoons CaCO_3 + Na_2SO_4 \qquad [10]$$

$$2NaHCO_3 + CaSO_4 \rightleftharpoons Na_2SO_4 + Ca(HCO_3)_2 \qquad [11]$$

The resulting sodium sulfate is a neutral salt and is more desirable than sodium carbonate or sodium bicarbonate which are caustic to plants (Bower, 1959; Ábrahám, 1970).

Authors describe other mechanisms by which Ca amendments aid reclamation besides direct reaction with Na. Ábrahám and Szabolcs (1964) determined that Ca amendments added to the soil exert a beneficial influence on processes in plant physiology. Loveday (1976) found that hydraulic conductivity of a sodic, clay soil improved initially with the addition of gypsum due to an electrolytic effect (the increased concentration of divalent cations in the soil solution facilitated flocculation) rather than from cation exchange with Na. Many authors have employed the electrolytic effect in reclamation of sodic soils with high-salt water (Reeve and Bower, 1960; Doering and Reeve, 1965; Rhoades, 1968; Badiger et al., 1969; Muhammed et al., 1969; Rawat and Singh, 1974; Doering and Willis, 1975; Massoumi, 1975). Boumans and Hulsbos (1960) indicated that Ca amendments cause a decrease in pH by exchanging with H ions on the exchange complex.

Gypsum

Gypsum has been by far the most utilized Ca amendment due to its accessibility, low cost, easy handling, and effectiveness. The literature abounds with research that has showed gypsum to be an effective reclaimant on Na-affected soils. Gypsum has been used successfully in combination with various forms of organic amendments and leaching (Mitra and Shanker, 1957; Mitra and Singh, 1959; Taha et al., 1966; Krishnamurthy and Soundararajan, 1967; Zaidi et al., 1968; Bhumbla, 1972; Puntamkar et al., 1972; Poonia and Bhumbla, 1974; Bajpai et al., 1976). Gypsum as a single amendment, in conjunction with leaching, has reclaimed sodic soils (Overstreet et al., 1951; McGeorge et al., 1956; Bower, 1959; Yadav and Agarwal, 1959; Balba, 1960; Branson and Fireman, 1960; Gibaly, 1960; Srivastava et al., 1962; Kanwar and Chawla, 1963; Ábrahám and Szabolcs, 1964; Padhi et al., 1965; Verhoeven, 1965; Chaudhry and Warkentin, 1968; Kobbia et al., 1969; Mahmoud et al., 1969; Ábrahám, 1970; Sahota and Bhumbla, 1970; Tisdale, 1970; Mehrotra, 1971; Sharma, 1971; Bhumbla, 1972; Khosla and Abrol, 1972; Abrol and Bhumbla, 1973; Maskina et al., 1974; O'Connor, 1974; Sharma et al., 1974; Abed, 1975).

Chhonkar et al. (1971) found that pelleting *Phaseolus aureus* seed with gypsum and calcium carbonate significantly increased growth, nodulation, and N-fixation in a sodic soil. Complete soil reclamation could not be effected, but the environment around the germinating seed was improved.

The gypsum requirement (GR) for reclamation of a Na-affected soil is determined by a laboratory test described by the United States Salinity Laboratory Staff (1954). The GR measures the amount of gypsum needed to replace almost all of the Na from the exchange complex, to a determined depth. Complete replacement is usually not possible due to the high bonding energy for part of the exchangeable Na (Chaudhry and Warkentin, 1968), or because leaching water may contain Na (Boumans and Hulsbos, 1960). The quantity of CO_3 and HCO_3 ions in the soil solution will affect the GR. Khosla and Abrol (1972) pointed out that the minimum amount of amendment necessary to initiate reclamation has to be more than the amount needed to combine with the free CO_3 and a major fraction of the soluble HCO_3.

Several factors determine the efficiency with which a given Ca amendment operates. One factor is solubility. If limited water is available, Ca salts with low solubility such as gypsum or calcium carbonate are not very effective reclaimants (USDA, Agricultural Research Service, 1963; Doering and Reeve, 1965; Muhammed and Amin, 1965; Badiger et al., 1969; Doering and Willis, 1975). Another factor that affects efficiency is texture of the amendment material. Finer grained particles solubilize more rapidly. Gypsum has been found to be most effective when ground so that 100% passes through a 100 mesh United States Standard Sieve (Gibaly, 1960; Khosla and Abrol, 1972).

Gypsum is almost always applied dry, and directly to the soil. Bhumbla (1972) reports that gypsum is most effective for reclamation when incorporated to shallow depths (10-20 cm). Reclamation below the depth of incorporation can occur slowly as the gypsum moves downward in solution. In solonetz soils, where Na is primarily concentrated below the plow layer, deep incorporation is often useful (Sharma et al., 1974; Cairns and Beaton, 1976).

Other Amendments

Calcium amendments other than gypsum have been used with success. Calcium nitrate (Ábrahám and Szabolcs, 1964; De et al., 1974; Doering and Willis, 1975) and calcium chloride (Bower et al., 1959; Branson and Fireman, 1960; Reeve and Bower, 1960; USDA, Agricultural Research Service, 1963; Puttaswamygowda et al., 1973; Doering and Willis, 1975; Prather et al., 1978) are soluble and effective on soils with low hydraulic conductivity. Calcium carbonate has been used effectively in the seed pelleting experiment mentioned previously (Chhonkar et al., 1971), and in solonetz soils due to their slightly acidic A horizon which greatly increases calcium carbonate solubility (Ábrahám and Szabolcs, 1964; Cairns and Beaton, 1976). Ábrahám (1970) reports that "digo earth," which is a mixture of gypsum, calcium carbonate, and subsoil, is also effective on solonetz soils. Pressmud, a waste product of sugar refineries, produced by a carbonation process, contains 60-70% calcium carbonate (and about 10% organic matter with small amounts of N, P, and K). Several scientists have reported using it successfully (Kanwar and Chawla, 1963; Bhumbla, 1972; Saraswat et al., 1972) except at soil pH values over 9.5 (Bhumbla, 1972). Lime-sulfur (calcium polysulfide) owes its success partly to the Ca it supplies to the soil (Bower, 1959; Tisdale, 1970; Stromberg, 1972). Dhar and Srivastava (1968) reported that calcium phosphates in conjunction with organic matter and blue green algae were successful in reclaiming a saline-sodic soil. Sims and Dregne (1962) reported that calcium nitrate plus single superphosphate (50% gypsum) produced positive growth responses due, in part, to the Ca they supplied. Branson and Fireman (1960) report the use of a soil conditioner, Krilium. They describe the product to be a "calcium carboxylate polymer of a hydrolyzed polyacrylonitrile." Calcium supplied by the product was in a slightly soluble form. The authors concluded that Krilium's moderate success in reclamation was probably not due to Ca. Mahalingam (1973) contributes the effectiveness of lignite fly ash to its high percentage of Ca, as well as Mg and SO_4.

De et al. (1974) reported the use of a variety of Ca salts. They observed the order of amendment effectiveness for decreasing soil pH and increasing P availability to be: Calcium nitrate > calcium sulfite > calcium citrate > calcium acetate > calcium sulfate > calcium sulfide > calcium oxide > calcium carbonate.

Amendments Supplying Ammonium

Van Schaik and Cairns (1974) found that the addition of high concentrations of NH_4 salts to a solonetz soil increased hydraulic conductivity. They believe that improvement is due to an increase in salt concentration in the soil solution and to the NH_4 adsorbed on the clay particles. It was concluded that the beneficial effect of NH_4 is less than that of added Ca, but nevertheless significant. Cairns and Beaton (1976) found NH_4 to be more effective when added as ammonium nitrate than as urea or ammonium sulfate. In a field study on a solodized solonetz soil, Carter et al. (1977) concluded that a high rate of ammonium nitrate (449 kg/ha) added annually was effective at lowering the soil's ESP. They found that ammonium nitrate plus gypsum was the superior treatment, and that ammonium nitrate alone was more effective than gypsum alone.

Amendments Solubilizing Native Calcium

General

Almost all amendments which solubilize native Ca contain S and are considered acidifying amendments. Acidifying amendments are not effective until the S is oxidized to sulfuric acid. Oxidation is accelerated by the bacteria strain Thiobacillus novellus (Rupela and Tauro, 1973a,b).

When S is in the form of sulfuric acid, reclamation is effected by the solubilization of native calcium carbonate. This process is illustrated in equations 12 and 13 (Overstreet et al., 1951).

$$H_2SO_4 + CaCO_3 + 2NaX \rightleftharpoons CaX + Na_2SO_4 + CO_2\uparrow + H_2O \qquad [12]$$

$$H_2SO_4 + 2CaCO_3 + 4NaX \rightleftharpoons 2CaX + Na_2SO_4 + 2NaHCO_3 \qquad [13]$$

Solubilized Ca replaces Na on the exchange complex. The exchanged Na forms soluble sodium sulfate and sodium bicarbonate. Leaching must accompany the application of these amendments because their effect is to create excess salts in the soil solution. The reaction in equation 12 occurs under the least efficient conditions. When there is an abundance of calcium carbonate, adequate moisture, and good soil-solution contact, the efficient exchange shown in equation 13 occurs. For each atom of S, four atoms of Na are exchanged with two atoms of Ca.

Sulfuric acid also reacts with CO_3 and HCO_3 of Na in the soil in a manner similar to gypsum described earlier. The reactions are shown in equations 14 and 15. Once again the neutral salt sodium sulfate is produced and it is readily leachable.

$$Na_2CO_3 + H_2SO_4 \rightleftharpoons CO_2\uparrow + H_2O + Na_2SO_4 \qquad [14]$$

$$2NaHCO_3 + H_2SO_4 \rightleftharpoons 2CO_2\uparrow + 2H_2O + Na_2SO_4 \qquad [15]$$

Occasionally an acidifying amendment is used when there is no native Ca (or Mg) salt in the soil. The exchange reaction that occurs is diagrammed in equation 16.

$$2NaX + H_2SO_4 \rightleftharpoons 2HX + Na_2SO_4 \qquad [16]$$

The caution in this situation is that a small amount of amendment may lower the pH drastically. Calcium carbonate acts as a buffer, and although pH is lowered with application of acidifying amendments, change occurs predictably. Acidifying amendments are applied to the soil as a fraction of the gypsum requirement based on equivalent S content.

Sulfuric Acid

Descriptions and Cautions

Sulfuric acid is a viscous, corrosive liquid. Precautions for handling sulfuric acid are described by Fasullo (1965) and Stroehlein and Openshaw (1975). Tissue burn can result from application too near established plants. When acid is water applied, concrete-lined ditches and other conventional irrigation equipment will corrode when the rate exceeds buffering capacity; i.e., the $HCO_3 + CO_3 + NH_3$ content of the water. Transport should be in iron tanks. Only certain plastics are satisfactory. Diluting acid increases corrosiveness, and releases large amounts of heat. Dilution should only be done in a running stream of water and then by adding acid to the water. Sulfuric acid should be handled only by personnel with proper information and equipment.

Soil Applied Sulfuric Acid

1. Effect on Soil Properties and Crop Yields. The theory of sulfuric acid reaction in soils has been presented in the earlier discussion on acidifying amendments. Sulfuric acid requires no S oxidation period; thus, reclamation can begin immediately (Bower, 1959; Tisdale, 1970).

All of the experiments reported herein involved soils containing native calcium carbonate. An early series of experiments with sulfuric acid in reclamation was carried out by Overstreet et al. (1951). They compared S equivalent rates of gypsum, elemental sulfur, and 93% sulfuric acid at establishment of an irrigated pasture on a highly sodic soil with initial ESP values close to 100. In one experiment, treatment rates equivalent to the gypsum requirement were applied and the plots were deep chiseled. Leaching and irrigation followed treatment incorporation. For a period of 20 months the yields of pasture mix on sulfuric acid treated plots were markedly higher than those of the plots treated with gypsum or sulfur. Yields on sulfur treated plots were scarcely above the checks. After 20 months there was no significant difference among yields on gypsum, sulfur, and check plots. In further experimentation on the same soil, Overstreet et al. used acid rates as low as .06 of the rate used in the first experiment. Pasture yields and soil permeability increased over the check at all acid rates. Among different applications of sulfuric acid the final permeability rate varied directly with the amount of acid applied.

Prather et al. (1978) found that sulfuric acid was more effective than calcium chloride at lowering ESP of a highly sodic soil. However the latter treatment, due to its high electrolyte concentration, was most effective at increasing soil permeability. The researchers found that gypsum was less effective than either sulfuric acid or calcium chloride by both criteria measured. Combining either calcium chloride or sulfuric acid with gypsum in proportions of one-fourth to three-fourths, respectively, appreciably reduced the time and leaching needed to achieve reclamation as compared to gypsum alone. As reclamation began, and ESP lessened, gypsum compared more favorably to the other amendments because permeability was no longer preventative.

In a field experiment on a highly sodic soil Chand et al. (1977) found sulfuric acid compared favorably to gypsum and aluminum sulfate at improving soil properties and first crop barley yield. Manure, and pressmud from carbonation factories effected little improvement. High rates of pressmud from a sulfitation process effected improvement in soil properties and yields, but was inferior to sulfuric acid and gypsum. The effectiveness of aluminum sulfate had severely decreased at second cropping. By fourth cropping the effects of sulfuric acid and gypsum were no longer significant.

Yahia et al. (1975) in a lab experiment studied the effects of gypsum and 93% sulfuric acid on water penetration in calcareous and sodic, range soils. Sulfuric acid was more effective at increasing penetration than gypsum at all equivalent rates. The result was explained by the limited solubility and plugging of soil pores by gypsum. For all soils tested (ESP ranged from 4 to 100), water penetration increased with increasing levels of acid application up to certain rates, then decreased with further application. At high rates, a distinct surface crust formed. The crust was unstable and slaked upon addition of water, thereby clogging soil pore space. The increase in penetration resulting from sulfuric acid was generally greater for soils with initially high ESP values. Stroehlein and Halderman (1975) also advocate sulfuric acid to increase water penetration into Na-affected soils.

Miyamoto et al. (1975a) conducted a lab test in which they found ESP and total dissolved salts (TDS) to be continuous functions of the acid application rate. That is, with increasing acid there is a decrease in ESP and an increase in TDS until a condition is reached at which no change takes place as a result of Ca reprecipitation. Calcium from the soil solution, along with SO_4 from the acid, precipitate as gypsum. Increasing the application of water restricts reprecipitation.

2. Effect on Soil Nutrients. Ryan et al. (1974) tested sulfuric acid for its effect on the solubility of trace elements Mn, Zn, and Fe in a calcareous, non-sodic soil. They applied sulfuric acid at varying degrees of saturation of the acid titratable basicity (ATB). Miyamoto et al. (1973) define ATB to be a measure of all the base constituents with which acid may readily react, or a measure of the buffering capacity of the soil. Hence, acid rates less than 100% saturation of the ATB will effect continual but slight pH decreases, whereas rates greater than 100% saturation create drastic changes. At less than 100% saturation of the ATB there was a significant increase in water soluble

Mn, and in DTPA extractable Fe and Mn compared with the untreated soil (Ryan et al., 1974). A significant increase in water soluble forms of Fe and Zn occurred only when acid application was greater than 100% ATB. These increases occurred with acid rate and time of soil-acid contact. Ryan et al. (1974) recommend acid rates less than 100% ATB because plant growth can be severely affected if the pH was extremely lowered. Nevertheless, rates near 100% ATB are most advantageous. They conclude it would be impractical to neutralize the entire surface rooting zone because of the great amounts of acid that would be required and because of probable damage to plants due to increased concentration of soluble salts. Band application along the planted furrow is most reasonable. Ryan et al. (1975) determined that sulfuric acid was more effective for increasing available Fe in a calcareous soil than either iron sulfate or Fe-EDDHA.

Ryan and Stroehlein (1979) ran a lab experiment on calcareous soils deficient in available P. The objective was to determine whether 93% sulfuric acid, mixed thoroughly with the soil, could increase that element's availability. They grew tomatoes (Lycopersicum esculentum) through three 8-week periods, and marked a significant P increase over check plots the entire time at acid rates of 20, 40, 60, 80, and 100% ATB. Sulfuric acid application effected a pH decline which made P more available. Plant uptake of P matched the dry matter yield response. Increasing acid rate affected the form in which P was found in the soil:

Ca-P decreased, soluble-P and Al-P forms increased, Fe-P and reductant soluble P forms remained unchanged. Sulfuric acid injected in bands at a rate equivalent to 1,344 kg/ha was found to be as effective as 336 kg actual P/ha as super-phosphate. Extractable Fe and Al increased with increasing acid rates. Miyamoto et al. (1975b) also suggest sulfuric acid for increasing P availability.

Ryan and Stroehlein (1976) experimented with "jarosite" (an iron bearing by-product of the copper smelting process)-sulfuric acid mixtures to increase Fe availability on calcareous soil while growing sorghum (Sorghum bicolor) in a greenhouse. Mixtures increased yields and chlorophyll significantly over either of these materials used alone and the results were comparable to those obtainable with conventional inorganic and chelated sources of Fe. Iron availability changed only slightly as mixtures were varied.

Tobia and Pollard (1958) used aluminum sulfate, ferrous sulfate, and sulfuric acid on neutral, calcareous, and sodic soils. They observed the effects of the three acidifiers on Mn, P, Fe, and Al availability under continuous and intermittent irrigation and found that acidity (pH values of 4.5-6.5) produced by sulfuric acid and ferrous sulfate was short lived, whereas, that produced by aluminum sulfate persisted for a year. Sulfuric acid brought more P, Fe, and Al into solution than did the other treatments. Aluminum sulfate was most effective in solubilizing Mn and at increasing permeability of all three soils. Continuous flooding of the neutral and calcareous soils resulted in P fixation, presumably by Fe activated by anaerobic conditions. This effect was not noticed with the sodic soil.

3. Effect on Soil Microorganisms. Leaching and the application of sulfuric acid to a sodic soil accounted for an increase in N-fixing microorganisms, microorganisms that mineralize organic compounds, and cellulose-decomposers (Shil'nikova and Babaeva, 1977). These scientists found gypsum and manure accomplished the same changes.

Soil vs. Water Applied Sulfuric Acid

Miyamoto and Stroehlein (1975) found that on calcareous soils water-applied acid is as effective as soil-applied acid when rates are less than 5 metric tons/ha. When acid rates are higher than this, excessive amounts of carbon dioxide bubble through the wet soil and destroy aggregation. Some of the carbon dioxide is trapped and restricts water penetration. When acid is applied directly to a dry soil surface carbon dioxide escapes instantaneously without any detrimental effects. Subsequent application of irrigation water is then beneficial to begin the leaching process. Miyamoto et al. (1975a) report that water-applied acid theoretically lowers ESP more than soil-applied acid at shallow depths, but is not as effective at lower depths. Gumaa et al. (1976) believe that acid application to water has its greatest advantage if the water is Na-affected. If the soil is already affected with Na they recommend application directly to the surface.

Ryan et al. (1977) conducted a greenhouse study, on calcareous soil, to evaluate the effects of comparable rates of soil- and water-applied sulfuric acid on dry matter yield, and P and Fe uptake by sorghum. The water to which the acid was applied was high in sodium bicarbonate. Acid was applied in excess of the water's buffering capacity. Significant increases in the three variables were produced only by soil treatments. The results are presumably due to the fact that dilute sulfuric acid, as added through irrigation water, is immediately neutralized by the soil whereas point application creates an acid zone sufficient to release Fe and P from relatively insoluble forms. In another greenhouse study with bermudagrass (Cynodon dactylon) on calcareous soil, Ryan et al. (1975) applied 93% sulfuric acid at equivalent rates of 1, 3, 5, and 10 metric tons/ha by various direct soil methods and as a 3% irrigation treatment. All treatments were leached after application. Crop growth increased through the first four of seven harvests in a 1-year period. The last three showed a decreasing trend. Growth, chlorophyll content, and Fe availability in the soil increased with rate, but there was no difference between methods of application. Long-lasting positive effects were not produced by any of the treatments.

Drainage Water Quality from Sulfuric Acid Reclamation

In a lab study using a calcareous sodic soil, Miyamoto (1977) evaluated the salt load in drainage waters generated by the application of sulfuric acid at a rate of 5 metric tons/ha. He concluded that the salt load generated by acid is only a minor portion of the total salt load created by the leaching process, and thus, the quality (SAR) of the drainage water from these soils is little affected by acid treatment at this rate.

Other Amendments

Sulfur has been used by many authors (Overstreet et al., 1951; McGeorge et al., 1956; Bower, 1959; Branson and Fireman, 1960; Misra and Sharma, 1967; Mahmoud et al., 1969; Tisdale, 1970). A major problem with sulfur as an amendment is the time it takes to oxidize to sulfuric acid. At temperatures below 15.5 C oxidation almost ceases. Tisdale (1970) reports that if the soil is warm, moist, and well aerated, and if the sulfur is finely divided (80 mesh or finer), oxidation will be virtually complete within 4 weeks. But conditions less than ideal will slow the process so that complete oxidation may take several years. Overstreet et al. (1951) report that after 20 months sulfur plots showed no improvement over check plots due to the extreme alkaline condition which inhibited the action of oxidizing bacteria.

Aluminum sulfate, or "alum" (Tobia and Pollard, 1958; Bower, 1959; Misra and Sharma, 1968; Tisdale, 1970), as well as ferric sulfate, or "copperas" (Tobia and Pollard, 1958; Bower, 1959; Branson and Fireman, 1960; Tisdale, 1970), and ferrous ammonium sulfate (Misra and Sharma, 1968) have been used successfully as reclaimants. Several authors