

# USING GYPSUM AND OTHER CALCIUM AMENDMENTS IN SOUTHWESTERN SOILS

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Soil aggregate formation and stability, the primary features of soil structure, are two of the most important manageable soil physical properties. Water, air, and roots primarily move between soil aggregates, which are clumps of soil particles cemented together. The pores between aggregates are fairly large, whereas the pores between particles within aggregates are often too small for effective water movement or root penetration, and sometimes even too small for bacteria to enter. In all but the sandiest soils, good aggregate structure is required for adequate root penetration, water infiltration, air exchange, and soil drainage.

Calcium (Ca) can help stabilize aggregate structure of some soils; using Ca in other soils will not improve soil physical or chemical properties. Therefore, it is helpful to understand how Ca interacts with soil particles.

The most commonly used Ca sources include gypsum, agricultural lime, and a few other Ca salts. In some soils, existing Ca minerals can be dissolved, releasing the Ca they contain. It is important to be familiar with the properties of these various Ca materials, and to understand the chemical processes that occur when amendments are applied to soil.

## Why is calcium important?

Negatively charged soil clay particles can be bound together into clumps or aggregates by positively charged molecules (cations). The formation of stable soil aggregates, a process called

flocculation, encourages water infiltration and drainage and prevents surface soil crusting. Flocculation is promoted by high levels of salinity (which may not be conducive to plant growth) and by the presence of cations that are strong flocculators. The dominant soil cations in medium to high pH soils are the monovalent cations (one positive charge per molecule) sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ), and the divalent cations (two charges per molecule) magnesium ( $\text{Mg}^{2+}$ ) and calcium ( $\text{Ca}^{2+}$ ). In highly acidic soils the trivalent aluminum cation ( $\text{Al}^{3+}$ ) may be present.

The ability of the dominant soil cations to flocculate soil clays, a function of their charge and size, is shown in Table 1. In this table the flocculating power of  $\text{Na}^+$  is assigned a value of 1, and the other cations assigned values relative to  $\text{Na}^+$ . We can see that  $\text{K}^+$  is a stronger flocculator than  $\text{Na}^+$ , but that  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are much more powerful flocculators than either of the monovalent cations. Calcium is clearly the cation of choice for flocculating soil clays.

We generally consider  $\text{Na}^+$  to be the major 'weak' flocculator, and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to be the most common 'strong' flocculators. We can get a rough idea of how stable a soil's structure is by looking at the relative amounts of these weak and strong flocculators. This can be done by calculating the Sodium Adsorption Ratio (SAR), where cation concentrations are in millimoles per liter (mmol/L) or millimoles per kilogram (mmol/kg).

Table 1. Relative flocculating power of major soil cations (Rengasamy and Sumner, 1998).

Ion	Chemical Symbol	Relative Flocculating Power
Sodium	$\text{Na}^+$	1.0
Potassium	$\text{K}^+$	1.7
Magnesium	$\text{Mg}^{2+}$	27.0
Calcium	$\text{Ca}^{2+}$	43.0

$$SAR = \frac{[Na^+]}{\sqrt{[Ca^{2+}] + [Mg^{2+}]}}$$

An alternative equation for expressing the impact of  $Na^+$  on aggregate stability is Exchangeable Sodium Percentage (ESP) with units of centimoles of charge per kilogram (cmolc/kg):

$$ESP = \frac{[Na^+]}{\text{cation exchange capacity}}$$

In addition to the relative proportions of flocculating cations, it is also important to know the total concentration of soluble salts in the soil. Cations are always accompanied by negatively charged ions (anions), and together they are called salts. Salts dissolved in water conduct electricity, so we can measure the electrical conductivity or EC of a soil-water mixture to determine the amount of salt.

Together, SAR and EC largely control soil aggregate stability. Figure 1 illustrates the effect of irrigation water quality on aggregate stability. If a soil has a combination of high SAR and low EC, the aggregates will tend to disperse. If it has a high EC and/or low SAR, the soil particles will be aggregated.

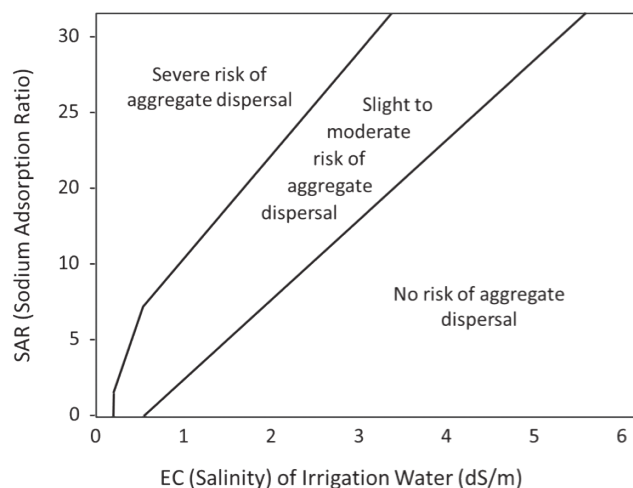


Figure 1. Soil and irrigation water electrical conductivity (EC) and Sodium Adsorption Ratio (SAR) determine aggregate stability (Ayers and Westcott, 1985)

In soils without adequate soluble  $Ca^{2+}$ , increasing the  $Ca^{2+}$  in solution will help to flocculate clay particles. Calcium acts as 'glue' that holds soil particles together into aggregates and stabilizes soil structure. There are two methods that can be used to increase soluble Ca. One is to solubilize Ca already present in the soil; the other is to add a supplemental Ca source.

## How can you solubilize Ca already present in the soil?

Let's look at the first option, solubilizing existing soil Ca. This strategy works only if there is an excess of calcium carbonate ( $CaCO_3$ ) minerals in the soil. Soils with excess or solid-phase

$CaCO_3$  are referred to as calcareous soils. They can be identified through a soil analysis. Look for 'free lime' on the soil test. It will usually be reported in general categories such as 'high', 'medium' or 'low'. You can test for the presence of carbonates yourself by putting a drop of dilute acid on them and observing whether or not they effervesce (Figure 2) as the  $CaCO_3$  reacts with the acid (sulfuric acid in the equation below) to produce carbon dioxide ( $CO_2$ ) bubbles:



In calcareous soils, acid can be applied to dissolve soil  $CaCO_3$ . The products of the reaction of  $CaCO_3$  and sulfuric acid are  $CO_2$ , water ( $H_2O$ ), sulfate ( $SO_4^{2-}$ ), and  $Ca^{2+}$ . The  $Ca^{2+}$  released from the soil  $CaCO_3$  can now act as a flocculant.

Any acid can dissolve soil  $CaCO_3$  and release the bound Ca. Sulfuric acid is most common because it is relatively inexpensive and adds less salt to the soil than hydrochloric acid (HCl). Sulfurous acid ( $H_2SO_3$ ) can be produced by combustion of elemental sulfur in a 'sulfur burner', which is a popular alternative to sulfuric acid. Additionally, acid-forming materials such as elemental sulfur can be used. Elemental sulfur is converted to sulfuric acid by sulfur oxidizing bacteria, producing the same effect as sulfuric acid. Sulfur conversion is a biological process, however, and requires several weeks to months to take place (depending on soil conditions), unlike acids, which react instantly.



Figure 2. Calcareous soil effervescing when acid is applied.

Acids and acid-forming materials will only be effective in calcareous soils! The soil should effervesce when acid is applied, or have 'medium' to 'high' or 'very high' free lime soil test levels.

## Calcium additives

Now let's look at Ca additives. There exist several Ca bearing salts that can be used to add  $Ca^{2+}$  to soil but in order to be effective they must be soluble. A salt is a compound made up of a cation and an anion. Calcium salts, of course, contain  $Ca^{2+}$  as their cation.

The anion is sulfate ( $\text{SO}_4^{2-}$ ) for calcium sulfates, carbonate ( $\text{CO}_3^{2-}$ ) for calcium carbonate, chloride ( $\text{Cl}^-$ ) for calcium chloride, and nitrate ( $\text{NO}_3^-$ ) for calcium nitrate.

## Gypsum and calcium sulfate anhydrite

The most widely used Ca soil additive is gypsum. Gypsum is one of the family of calcium sulfates. The chemical formula for gypsum is  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . This means that each gypsum molecule contains one  $\text{Ca}^{2+}$  cation, one  $\text{SO}_4^{2-}$  anion, and two waters. There are other calcium sulfates, such as calcium sulfate anhydrite ( $\text{CaSO}_4$ ). Chemically, these two salts are closely related, the difference being that calcium sulfate anhydrite does not contain water. Consequently, calcium sulfate anhydrite contains more Ca on a weight basis than gypsum. Calcium sulfate anhydrite contains 29.4% Ca, whereas gypsum contains 23.2% Ca.

Both of these Ca salts are mined, and then ground into a powder for use as soil additives. Additionally, by-product gypsum materials, waste products of phosphate fertilizer production (phosphogypsum) or from power plant stack scrubbers (flue gas desulfurization gypsum), are also used.

Gypsum is a good choice for Ca addition because it is inexpensive, non-toxic, and safe to handle, and it is relatively soluble. We are interested both in solubility (how much of the salt will dissolve in the soil water) and the rate of dissolution (how fast the salt dissolves in water). Mined gypsum is well-crystallized, having formed over millions of years. Waste gypsum, on the other hand, is formed rapidly during industrial processes, and is less crystallized. Although they have the same chemical formula, the waste gypsum materials dissolve more rapidly than mined gypsum. Sometimes powdered gypsum is prilled in order to reduce dust and to improve handling properties, and this slows its rate of dissolution. A study that compared dissolution rates of gypsum sources found that flue gas gypsum dissolved 3.6 times faster than mined gypsum, whereas phosphogypsum dissolved 2.2 times faster than mined gypsum. The rate of dissolution is particularly important for treatment of soil crusting, which is caused by dispersion of clay particles at the soil surface. In this situation, rapid dissolution is critical to maintain a high level of dissolved  $\text{Ca}^{2+}$  in the surface soil as raindrops or irrigation water leach cations from the uppermost layer of soil. However, for general treatment of soil structure, the rate of dissolution is less important than the overall solubility.

Calcium sulfate anhydrite can also be used as a Ca supplement. The solubilities of gypsum and calcium sulfate anhydrite are similar, however the dissolution rates differ. Published reports indicate that the dissolution rate of calcium sulfate anhydrite is slower than that of gypsum – anywhere from 5% to 72% that of mined gypsum. In addition to the chemical composition, the dissolution rates of both gypsum and calcium sulfate anhydrite are dependent on type and degree of crystallization, particle size, presence of impurities, and method of manufacture for non-mined salts.

## Lime

Calcium carbonate or limestone is another mined Ca salt. It's often referred to as lime or agricultural lime, although agricultural lime may be a combination of calcium and magnesium carbonates if it is made from dolomitic rather than calcitic limestone deposits. The main use of lime is to raise soil pH (to reduce acidity). In the same manner that  $\text{CaCO}_3$  neutralizes sulfuric acid in the equation above, it also neutralizes acidity in low pH soils. Unlike gypsum and calcium sulfate anhydrite, lime solubility is dependent on soil pH. Its solubility increases in acid soils and decreases as soil pH increases. When soil pH is above approximately 8.2, lime becomes very insoluble. This is why most soils with a pH above this threshold are also calcareous, meaning that they contain solid mineral  $\text{CaCO}_3$ . In acidic soils, supplemental  $\text{CaCO}_3$  will dissolve, but in alkaline soils it will not; adding  $\text{CaCO}_3$  to calcareous soils accomplishes nothing in terms of increasing soluble Ca levels.

## Calcium chloride and calcium nitrate

Calcium salts that contain  $\text{Ca}^{2+}$  and a monovalent anion such as chloride ( $\text{CaCl}_2$ ) or nitrate ( $\text{Ca}[\text{NO}_3]_2$ ) are very highly soluble. They are not usually used as Ca amendments because of their expense and their high salt content. Applying enough of these salts to promote soil aggregation would generally increase soil salinity to unacceptable levels.

## Summary of calcium supplements

Table 2 provides a concise listing of the circumstances where each of the soil additives is likely to be effective or ineffective. Regardless of source, these soil amendments will only improve soil physical properties in soils with poor structure.

Table 2. Summary of conditions appropriate for various soil additives.

Material	Soil pH		Comments
	<7.0	>7.0	
Acids	NO	YES*	Only effective in calcareous soils (*calcareous soils usually have pH>8.0)
Gypsum	YES	YES	Will not change soil pH
Lime	YES	NO	Raises soil pH; not soluble in higher pH soils
$\text{CaSO}_4$	YES	YES	Dissolves more slowly than gypsum; will not prevent surface crusting
$\text{CaCl}_2$	YES	YES	Can raise soil salinity to unacceptable levels
$\text{Ca}(\text{NO}_3)_2$	YES	YES	Can raise soil salinity to unacceptable levels if used as a Ca source

## Do calcium additives such as gypsum supply calcium for plant use?

Calcium is a critical component of cell walls and is therefore an essential plant nutrient. It is needed for cell division and growth and for redistribution of carbohydrates within the plant. Calcium deficiency related to lack of available soil Ca is rarely encountered in moderate to high pH soils, and is usually limited to very acidic or sandy soils. Calcium supply and translocation within plants is dependent on an adequate and continuous supply of water and Ca deficiencies are usually the result of drought stress rather than low soil Ca levels. However, if the supply of available soil Ca is inadequate (exchangeable Ca less than 250 to 500 mg/kg, Jones, 2003; Simmons and Kelling, 1987), supplemental Ca can improve plant nutrition. In this case, any *soluble* Ca material can be used to alleviate Ca deficiency. Lime (in acidic soils only) and gypsum are the most widely used soil-applied Ca fertilizers, whereas  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$  are often used for foliar application.

## How much gypsum do I need to apply?

The amount of gypsum that should be applied is best determined by a soil analysis. Soil analyses should be conducted to determine soil sodium status, either as “sodium adsorption ratio” (SAR) or as “exchangeable sodium percentage” (ESP). Either provides a good indication of the need for gypsum and the two measures are roughly equivalent. Approximate amounts of gypsum to add, based on soil analyses, are shown in Tables 3 and 4. These values were calculated based on cation exchange values of 15 cmol<sub>c</sub>/kg coarse soil, 25 cmol<sub>c</sub>/kg medium-textured soil, and 35 cmol<sub>c</sub>/kg of fine-textured soil, bulk density 3.33 g/cm<sup>3</sup>, soil depth 6 inches, and assume replacement of all the exchangeable Na. Application rates may need to be adjusted for actual soil conditions.

## Summary

In soils with weak structure resulting from an imbalance between  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , increasing soluble  $\text{Ca}^{2+}$  can improve aggregation, water infiltration, soil drainage, and root penetration. Acid or acid-forming amendments are acceptable additives for increasing soluble  $\text{Ca}^{2+}$  in calcareous soils only. In all soils, regardless of pH, gypsum is a good  $\text{Ca}^{2+}$  additive when  $\text{Ca}^{2+}$  is needed. Calcium sulfate anhydrite will also supply  $\text{Ca}^{2+}$ , but it will dissolve more slowly than gypsum. With either gypsum or calcium sulfate anhydrite it is important to know the composition of the material you select, which can vary considerably depending on source. Soil analysis can help determine how much of these materials to apply to your soil.

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Table 3. Gypsum requirements in tons per acre as influenced by soil texture and exchangeable sodium percentage.

Soil Texture	Exchangeable Sodium Percentage					
	10	15	20	30	40	50
	Gypsum (tons per acre)					
Coarse	1.1	1.7	2.3	3.4	4.6	5.7
Medium	1.9	2.9	3.8	5.7	7.7	9.6
Fine	2.7	4.0	5.4	8.0	10.7	9.6

Table 4. Gypsum requirements in pounds per one thousand square feet as influenced by soil texture and exchangeable sodium percentage.

Soil Texture	Exchangeable Sodium Percentage					
	10	15	20	30	40	50
	Gypsum (lbs per 1000 ft <sup>2</sup> )					
Coarse	55	80	105	160	210	265
Medium	90	130	175	265	350	440
Fine	125	185	245	370	490	615



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Issued in furtherance of Cooperative Extension work, acts of May 8 and June 30, 1914, in cooperation with the U.S. Department of Agriculture, Jeffrey C. Silvertooth, Associate Dean & Director, Economic Development & Extension, College of Agriculture and Life Sciences, The University of Arizona.

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