

Gypsum and Other Calcium Sources

Their properties and chemical processes when applied to soil.

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

IS CALCIUM EFFECTIVE?

In this brief article there is not space to provide a thorough review of the interactions between cations and soil particles. In brief, 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 (Na^+) and potassium (K^+), and the divalent cations (two charges per molecule) magnesium (Mg^{2+}) and calcium (Ca^{2+}). In highly acidic soils the trivalent aluminum cation (Al^{+3}) may be present.

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



Golf course soils may become dispersed when sodium (Na^+) accumulates in relation to calcium and magnesium. Dispersed soils have very poor water infiltration properties and may ultimately result in turf loss. Calcium can help stabilize the aggregate structure of such soils.

Calcium is clearly the cation of choice for flocculating soil clays.

In soils without adequate *soluble* Ca^{2+} , increasing the Ca^{2+} in solution will help to flocculate clay particles. There are two methods that can be used to accomplish this process. One is to solubilize calcium already present in the soil; the other is to add a supplemental calcium source.

CALCIUM ALREADY PRESENT

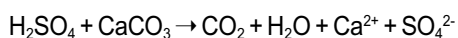
Let's look at the first option, solubilizing existing soil calcium. This strategy works only if there is an excess of calcium carbonate minerals in the soil. Soils with excess or solid-phase calcium carbonate (CaCO_3) are referred to as *calcareous* soils. They can be identified through a soil analysis. Look for *free lime* on the soil test. It will

Table 1		
Relative flocculating power of major soil cations		
Ion	Chemical Symbol	Relative Flocculating Power
Sodium	Na^+	1.0
Potassium	K^+	1.7
Magnesium	Mg^{2+}	27.0
Calcium	Ca^{2+}	43.0



Sulfuric or sulfurous acid applied directly to a calcareous soil creates a reaction whereby lime is dissolved, producing calcium sulfate, carbon dioxide (seen as the fizzing bubbles), and water.

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 (fizz) as the CaCO_3 reacts with the acid (sulfuric acid in the equation below) to produce carbon dioxide (CO_2) gas:



In calcareous soils, acid can be applied to dissolve soil calcium carbonate. The products of the reaction of calcium carbonate 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 calcium carbonate and release the bound calcium. 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, and it 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.

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.

BEST CALCIUM ADDITIVE

Now let's look at calcium additives. There are several calcium-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 (a negatively charged molecule). Calcium salts, of course, contain Ca^{2+} as their cation. The anion could be sulfate (SO_4^{2-}) for calcium sulfate, carbonate (CO_3^{2-}) for calcium carbonate, chloride (Cl^-) for calcium chloride, nitrate (NO_3^-) for calcium nitrate, etc.

GYPSUM AND CALCIUM SULFATE ANHYDRITE

The most widely used calcium 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 calcium cation, one sulfate anion, and two waters. There are other calcium

sulfates, such as calcium sulfate anhydrite (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 calcium on a weight basis than gypsum. Calcium sulfate anhydrite contains 29.4% calcium, whereas gypsum contains 23.2% calcium.

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

Gypsum is a good choice for calcium addition because it is inexpensive, non-toxic, 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 (Bolan et al., 1991). 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 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 also can be used as a calcium supplement. The



The pH of calcareous soils is typically greater than 8.0 and they often contain generous deposits of calcium carbonate (lime). Much of the calcium in the lime is insoluble, especially when the pH value is greater than 8.2. Acid and acid-forming materials can increase the available calcium by chemically reacting with the lime.

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 calcium 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 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 quite insoluble. This is why most soils with a pH above this threshold are also calcareous, meaning that they contain solid mineral calcium carbonate. In acidic soils, supplemental calcium carbonate will dissolve, but in alkaline soils it will not; *adding calcium carbonate to calcareous soils accomplishes nothing.*

CALCIUM CHLORIDE AND CALCIUM NITRATE

Calcium salts that contain Ca^{2+} and a monovalent anion such as Cl^- (calcium chloride) or NO_3^- (calcium nitrate) are very highly soluble. They are not usually used as calcium 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.

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 calcium 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. As such, calcium deficiencies are usually the result of drought stress rather than low soil calcium levels. However, if the supply of available soil calcium is inadequate, supplemental calcium can improve plant nutrition. In this case, any *soluble* calcium material can be used to alleviate calcium deficiency. Lime (in acidic soils only) and gypsum are the most widely used soil-applied calcium fertilizers, whereas calcium chloride and calcium nitrate are often used for foliar application.

SUMMARY

Acid or acid-forming amendments are acceptable additives for increasing soluble Ca^{2+} in calcareous soils only. In all soils, regardless of pH, gypsum is a good Ca^{2+} additive. Calcium sulfate anhydrite will also supply 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.

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Table 2
Calcium additives and their appropriate use as affected by soil pH

Material	Soil pH		Comments
	<7.0	>7.0	
Acids	NO	YES*	Only effective in calcareous soils (*calcareous soils contain lime and usually have a pH>8.0)
Gypsum	YES	YES	Will not change soil pH
Lime	YES	NO	Raises soil pH; not soluble in higher-pH soils
CaSO_4 (Anhydrite)	YES	YES	Dissolves more slowly than gypsum; will not prevent surface crusting
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