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 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, a function of their charge and size, is shown in Table 1. In this table the flocculating power of Na\(^+\) is assigned a value of 1, and the other cations 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. Calcium is clearly the cation of choice for flocculating soil clays.

We generally consider Na\(^+\) to be the major ‘weak’ flocculator, and Ca\(^{2+}\) and 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).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Chemical Symbol</th>
<th>Relative Flocculation Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>Na(^+)</td>
<td>1.0</td>
</tr>
<tr>
<td>Potassium</td>
<td>K(^+)</td>
<td>1.7</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg(^{2+})</td>
<td>27.0</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca(^{2+})</td>
<td>43.0</td>
</tr>
</tbody>
</table>
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 solublize 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:

\[
\text{H}_2\text{SO}_4 + \text{CaCO}_3 \rightarrow \text{CO}_2(\text{gas}) + \text{H}_2\text{O} + \text{Ca}^{2+} + \text{SO}_4^{2-}
\]

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\(_2\)O), 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\(_2\)SO\(_3\)) 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.

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 (SO\(_4^{2-}\)) for calcium sulfates, carbonate (CO\(_3^{2-}\)) for calcium carbonate, chloride (Cl\(^-\)) for calcium chloride, and nitrate (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 CaSO\(_4\)2H\(_2\)O. This means that each gypsum molecule contains one Ca\(^{2+}\) cation, one SO\(_4^{2-}\) 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 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 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 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 CaCO$_3$. In acidic soils, supplemental CaCO$_3$ will dissolve, but in alkaline soils it will not; adding CaCO$_3$ to calcareous soils accomplishes nothing in terms of increasing soluble Ca levels.

Calcium chloride and calcium nitrate

Calcium salts that contain Ca$^{2+}$ and a monovalent anion such as chloride (CaCl$_2$) or nitrate (Ca[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.

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 CaCl₂ and Ca(NO₃)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 cmolₑ /kg coarse soil, 25 cmolₑ /kg medium-textured soil, and 35 cmolₑ /kg of fine-textured soil, bulk density 3.33 g/cm³, 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 Na⁺ and Ca²⁺, increasing soluble Ca²⁺ can improve aggregation, water infiltration, soil drainage, and root penetration. Acid or acid-forming amendments are acceptable additives for increasing soluble Ca²⁺ in calcareous soils only. In all soils, regardless of pH, gypsum is a good Ca²⁺ additive when Ca²⁺ is needed. Calcium sulfate anhydrite will also supply Ca²⁺, 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.

References


