Understanding Limestone, pH & Calcium

by Craig Dick

As the sales manager and agronomist for Calcium Products, I have interacted with thousands of agronomists and farmers. One of the most common things we find is a general confusion on limestone, pH and calcium. Many think these refer to the same thing. This article is meant to be an introduction to the difference in pH and calcium as well as an overview of how limestone reduces soil acidity. While seasoned *Acres U.S.A.* readers may find the information provided fairly basic, it's my hope that newer readers will find this helpful as they try and determine how to improve their soils.

WHAT IS LIMESTONE?

Limestone makes up about 10 percent of the total volume of all sedimentary rocks on Earth and is largely comprised of the mineral calcite (calcium carbonate: $CaCO_3$). High-quality limestone contains skeletal fragments of marine organisms and coral. Calcium magnesium carbonate or dolomitic lime is also considered limestone.

Because of impurities, such as clay, sand, organic remains, iron oxide and other materials, limestone can exhibit different colors and neutralizing values. Limestone is mainly used in agriculture to change soil pH, but high-calcium lime can also be a source of calcium, an important nutrient for soil and plant health.

HOW SOIL BECOMES ACIDIC

The nitrification process converts ammonium to nitrate. This process releases hydrogen (H+) ions. Nitrate further increases acidity by leaching cationic nutrients like calcium and potassium with it. As alkaline ions are removed more hydrogen can be held in the soil causing low pH.

Synthetic nitrogen has recently been shown to burn out soil carbon. This loss of carbon lowers soil buffering capacity, speeding acidity caused by rainfall. Since rainfall is nearly pure water once it hits the soil, it's hungry for basic ions. This is why soft water works better for cleaning than hard water. The combination of low carbon (buffer capacity) of soils, application of synthetic nitrogen and rainfall can quickly lower soil pH.

Raw limestone from the Gilmore City, Iowa quarry.

Crop removal of nutrients also lowers pH. As the alkaline ions (Ca++, Mg++, K+) are removed, they need to be replaced or H+ will steadily increase, lowering pH. Decomposition of organic matter also increases soil acidity.

POTENTIAL HYDROGEN (PH)

The term "pH" stands for "potential Hydrogen" and defines the relative acidity or alkalinity of a substance. The scale ranges from 0 being acid to 14 being alkaline and a pH value of 7.0 is neutral. The hydrogen ion (H+) is what is measured to give an acid reading. The more H+ held in the soil, the greater its acidity. The hydroxide ion (OH-) is present when a test shows a soil has an alkaline reading.

Many people confuse calcium and pH, however pH only measures hydrogen and it has nothing to do with calcium! Having a high or low pH reading tells you nothing of calcium availability.

Since pH is expressed in logarithmic terms, each unit change on the scale is a tenfold change in the acidity or alkalinity. A soil with a pH of 6 is 10 times more acid than a soil with a pH of 7. A soil that has a pH of 5 is 100 times more acidic than a soil with a pH of 7. A soil with a pH of 4 is 1,000 times more acidic than a soil with a 7 pH. This is why low pH can have devastating effects on yield.

According to Midwest Laboratories, a pH of 5.0 reduces the potential yield of corn by 27 percent, soybeans by 21 percent and alfalfa by 91 percent. At a pH of 5.0, 50 percent of nitrogen, 33 percent of phosphorus, and 50 percent of potassium is unavailable for plant uptake. Additionally at a pH of 5.0, nodulation in soybeans is reduced up to 40 percent. The University of Wisconsin has stated that bringing pH into optimal range can increase yield by 10-40 percent.

HOW LIME REDUCES SOIL ACIDITY

Once limestone (calcium carbonate) is applied to the soil, it must be dissolved into the soil solution to affect a change. The carbonate molecule (CO3--) reacts with two H+ ions on the soil exchange site. This process creates more water (H_20) and carbon dioxide (CO_2). As the H+ concentration is lowered soil acidity decreases. One calcium ion (Ca++) ion from the lime (calcium carbonate) replaces two hydrogen ions on the exchange site. The calcium does not affect the pH change, it is the carbonate molecule that does the work.

WHAT IS BUFFER pH?

Soil pH measures the active acidity, while the buffer pH indicates the potential acidity. The amount of potential acidity for any given soil pH will depend upon the amount and type of clay and the level of organic matter in that soil. It is possible to have two soils with the same soil pH but with different buffer pH's. A lower buffer pH represents a larger amount of potential acidity and thus more limestone is needed to increase the soil pH to a given level.

The buffer pH is the sample pH after the laboratory has added a liming material. The laboratory adds the buffering solution, which acts like an extremely fast-acting lime. Each soil sample receives the same amount of buffering solution; therefore the resulting pH is different for each sample.

To determine a lime recommendation, the laboratory looks at the difference between the original soil pH and the ending pH after the buffering solution has reacted with the soil. If the difference between the two pH measurements is large, it means that the soil pH is easily changed, and a low rate of lime will be sufficient. If the soil pH changes only slightly after the buffering solution has reacted, it means that the soil pH is difficult to change and a larger lime addition is needed to reach the desired pH for the crop.

	SuperCal 98G	8 mesh lime	60 mesh lime
CCE (purity)	95.15	99.6	99.03
ECCE (finess+purity)	92.3	9.96 *	39.81

** not a misprint, it's actually that ineffective. Source: Midwest Labs*

The reasons that different soils may require differing amounts of lime to change the soil pH relates to the soil CEC (cationic exchange capacity) and the "reserve" acidity that is contained by the soil. Soil acidity is controlled by the amount of hydrogen (H+) that is either contained in, or generated by the soil and soil components. Soils with a high CEC have a greater capacity to contain or generate these sources of acidity. Therefore, at a given soil pH, a soil with a higher CEC (thus a lower buffered pH) will normally require more lime to reach a given target pH than a soil with a lower CEC.

FINDING HIGH-QUALITY LIME

Much of the limestone in the Midwest either has too many inert ingredients (clay, sand, marl, etc.) or is not crushed fine enough to get results in your lifetime.

To determine what liming material is best, you need to know:

Percent purity (CCE), and

Grind fineness (ECCE) of the material.

Each state has a different name for purity and for fineness and a different testing procedure to determine fineness.

The purity of limestone is expressed as calcium carbonate equivalent (CCE). It is a measure of how much of the material can react with the soil to neutralize acidity under ideal conditions compared to pure calcium carbonate.

Limestone should have a neutralizing value of at least 90 percent. Liming material purity can range from 50-175 percent. One needs to be cautious when working with liming agents that have a CCE of more than 100 percent. These products are generally caustic and can cause burns to skin and eyes.

Much of the country's Ag Lime contains many impurities; such as sand, clay, iron, and lead, which lower its CCE.

EFFECTIVE CALCIUM CARBONATE EQUIVALENT (ECCE)

The Effective Calcium Carbonate Equivalent (ECCE) is a measure of the limestone's effectiveness and is based on the combined effect of chemical purity (CCE) and fineness of the product. It also can be referred to as *effective neutralizing value* (ENV), *total neutralizing power* (TNP), *effective neutralizing material* (ENM) and in one state as the "*lime score.*"

Because limestone is fairly insoluble, the fineness of lime is almost more im-

Chart of Lime Surface Area

Size in Mesh	Size in Micron	Surface Area (sphere) in microns	Volume (sphere) in microns	Surface area to Volume Ratio	X times more effective than 30 mesh	X times more effective than 60 mesh
30	590	1,093,588.40	107,536,192.93	0.01	1.00	0.42
60	250	196,349.54	8,181,230.87	0.02	2.36	1.00
100	150	70,685.83	1,767,145.87	0.04	3.93	1.67
170	90	25,446.90	381,703.51	0.07	6.56	2.78
200	75	17,671.46	220,893.23	0.08	7.87	3.33

Relative Neutralizing Values (CCE) of Common Liming Materials

Calcitic Limestone	85-100
Burned Lime	150-175
Hydrated Lime	120-135
Oyster Shells	90-110
Dolomitic Limestone	95-108
Basic Slag	50-70
By-product	Variable
Gypsum	None

Efficiency Factors for Liming

Particle Size	Within 1 Year of Application	After 4 Years of Application
Greater than 8 mesh	5	25
Between 8 & 10	20	45
Between 20 & 60	50	100
Smaller than 60 mesh	100	100

Source: National Stone Association

portant than the CCE. For example you can have three lime sources.

The reason grind fineness is more important than purity of calcium carbonate is, large pieces of lime will not dissolve in the soil. Even very pure calcium carbonate (limestone) is not very soluble in water so it must be finely ground to effectively neutralize soil acid. Only limestone that goes into solution can change pH.

The finer the particle, the more quickly and completely it will react to neutralize soil acidity. Most states consider the effective portion of lime to consist of the 30 to 60 mesh particles. Some ag lime is ground even finer to increase the ECCE. While grinding finer increases effectiveness this also increases cost and drift loss. The finer the particle size is, the more susceptible it is to drift. Finely ground lime is only effective if it reaches your field. The majority of fine ag lime is lost to drift, making it ineffective.

To avoid drift many quarries will only grind limestone to an average of 30 mesh. This is to ensure that it can be applied to the field with a minimum of drift loss. However, lime that is not ground to at least 30 mesh will not make a significant impact on soil pH. It is too coarse to make a change in soil pH.

ONE LAST THOUGHT ON ECCE

Most ag lime has fineness on average of 30 mesh. Most lime laws give 60 mesh lime an effective score of 100 percent. However reactivity (rate of dissolution, how fast it goes into solution) should be based on the surface area of the particle to volume ratio of the particle. A clay particle is smaller than a sand particle yet the clay particle holds more nutrients due to its higher reactivity.

A 100 mesh particle is 1.6x more reactive than a 60 mesh particle but according to the ag lime laws a liming product cannot claim more credit for being ground finer than a 60 mesh.

WHAT ABOUT DOLOMITIC LIME?

Calcium magnesium carbonate (dolomite) is often used for liming. Dolomite is less soluble than calcium carbonate, and reacts more slowly. Dolomite supplies magnesium, a consideration if you are trying to increase magnesium content. The more magnesium applied the fewer sites you have to hold calcium. Unless your soils need additions of magnesium, dolomite should be avoided. While pH has nothing to do with calcium, high quality limestone can provide calcium.

Calcium should be considered the most important nutrient. It plays a major role in the physiology of the plant, strengthening its physical structure, increasing nutrient uptake and protecting from disease. The importance of calcium in the soil includes the reduction of soil compaction, increased water infiltration, and helping to provide a better environment for the proliferation of beneficial bacteria. Some research even suggests that calcium plays a role in weed populations.

ADDITIONAL NOTES ON CALCIUM

A common misconception is that if there is adequate calcium present in the soil, pH is high. Remember that pH only measures hydrogen. Calcium, while found in many mineral soils, is relatively insoluble. It is not considered a mobile soil nutrient but can leach with excessive nitrogen use. Over-fertilization of nitrogen and potassium will reduce calcium availability. High potassium levels can also reduce the uptake of calcium.

Calcium is a very important nutrient. Only nitrogen and potassium are required in larger amounts by plants. While nitrogen and potassium are critical, there is growing evidence that the amount of available calcium has important consequences for plant production, soil health and animal health. Plant available calcium determines the uptake of all other nutrients into the plant.

Calcium stimulates soil life, including nitrogen-fixing bacteria, which creates a healthy environment for plants and stimulates root growth. Large roots will ensure that the plant has adequate access to soil, water and nutrients. Small, weak and shallow roots are more apt to be impacted by dry weather, reducing transpiration, growth, and sugar formation.

A reduction in transpiration causes the calcium supply to growing tissues to become inadequate. As calcium content in the plant drops the protein, mineral and energy levels of the plant drop also. Calcium is not mobile in the plant. If the plant's supply of calcium is depleted it cannot remobilize calcium from older tissues.

Calcium needs to be kept available. Calcium neutralizes cell acids and increases the plant's resistance to diseases. Multiple studies have shown calcium at the optimal level will decrease disease in most plants. Yield, disease resistance, quality, taste and shelf life are all functions of good calcium uptake.

Craig Dick is a blogronomist and sales and marketing manager at Calcium Products. He writes "Yield Starts Here" a blog for farmers, focusing on increasing yield and profitability by focusing on the soil. For more articles visit http://blog.calciumproducts.com. He can be reached at *craig@calciumproducts.com* or by phone at 800-255-8196.

200-500 lbs. of Finely Ground Lime Applied Annually

- Helps prevent weeds such as dandelion, plantain, chickweed and buttercup.
- Helps with the movement and absorption of phosphorus, nitrogen and magnesium.
- Benefits bacteria, fungi, protozoa and other soil life so important for nutrient cycling.
- Releases important trace and growth nutrients by its pH-altering effect.
- Helps clover, which requires twice the calcium of grass.
- Abundant calcium is necessary for clover nodulation. No lime, little clover.
- Improves the palatability of grass and clover, makes the pasture softer for animals to graze, and lessens grass-pulling in new stands.
- Creates soil tilth and structure so that air and water can move more freely through soil by causing clay particles to stick together. Soil must be able to breathe to grow great grass.
- Allows pastures to hang on longer in a drought.
- Reportedly makes an animal more docile and content.

Source: Nation, Allan. 1995. Quality Pasture-Part II. *Stockman Grass Farmer.* January. p. 13.