

# SUL4R-PLUS® Fertilizer: Fact Sheet



## Soil pH & Buffering Capacity

March 2019

Compiled by Greg Parris

The concept of pH was first introduced by the Danish chemist Søren Peder Lauritz Sørensen at the Carlsberg Laboratory in 1909 and revised to the modern pH in 1924 to accommodate definitions and measurements in terms of electrochemical cells. [1]

### What is the pH Buffering Capacity (pHBC)?

Buffering Capacity is the resistance of soil to change in pH because of the addition of acidic or basic material. The measure of the pHBC of a soil, for a soil type, increases as the CEC increases. Hence, pure sand has almost no buffering ability, while soils high in colloids have high buffering capacity. "Soil Colloids" are the most active portion of the soil and determine the physical and chemical properties of a soil. Buffering occurs by cation exchange and neutralization.

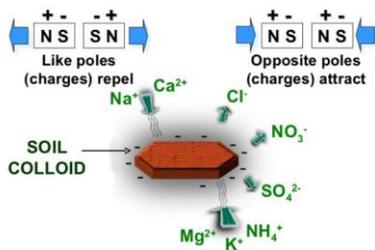


Fig 1) Soil Colloid chemical properties [2]

Let's review two examples of the buffering of soil pH:

1) The addition of a small amount highly basic aqueous ammonia to a soil will cause the ammonium to displace hydrogen ions from the colloids, and the end product is water and colloiddally fixed ammonium, but little permanent change overall in soil pH.

2) The addition of a small amount of lime, Ca(OH)<sub>2</sub>, will displace hydrogen ions from the soil colloids, causing the fixation of calcium to colloids and the evolution of CO<sub>2</sub> and water, with little permanent change in soil pH.

The general principal is that an increase in a specific cation in the soil water solution will cause that cation to be fixed to colloids (buffered) and a decrease in solution of that cation will cause it to be withdrawn from the colloid and moved into solution (buffered).

"The degree of buffering is often related to the CEC of the soil; the greater the CEC, the greater the buffering capacity of the soil." [3]

Simply stated buffering is the number of constituents in the soil that can hold charges, H<sup>+</sup> (anions) and OH<sup>-</sup> (cations) in that soil type. Whereas the pH of the soil can be thought of as amount of free H<sup>+</sup> ions in the soil and pOH as the amount of free OH<sup>-</sup> in the soil.

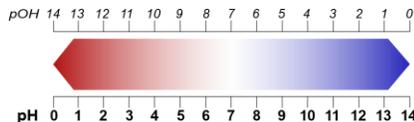


Fig 2) Red is acidic region and blue is basic region. [4]

**pH scientific definition:** pH is defined as the decimal logarithm of the reciprocal of the hydrogen ion activity, a<sub>H<sup>+</sup></sub>, in a solution.

$$\text{pH} = -\log_{10}(a_{\text{H}^+}) = \log_{10}\left(\frac{1}{a_{\text{H}^+}}\right)$$

### What makes buffering capacity important?

Soil acidification (low pH) is a major problem for agriculture sustainability and alkalization (high pH) is a problem for drier irritated regions. [5] Understanding the soil pH and pHBC can facilitate assessments of acidification risks, acidification rates, and potential management interventions. For a plant to uptake nutrients those nutrients must be dissolved. Changes in pH can affect a plants nutrient uptake such that pH will:

- ❖ Diminishing the fraction of nutrients in soil that are available to the plants
- ❖ Increasing uptake of undesirable minerals like aluminum.

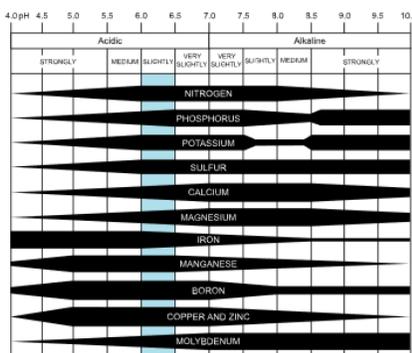


Fig 3) Nutritional elements availability within soil varies with pH. Light blue color represents the ideal range for most plants. [10]

The soils buffering capacity helps to stabilize the pH and provides the best environment for high yielding crops.

### What are the key factors impacting soil buffering capacity?

There are many key factors that can increase or decrease the pHBC of a soil. Here are a few:

- ❖ Cationic Exchange Capacity (CEC) adsorption & desorption of exchangeable cations.
  - Soil Types: Sandy, Loam, & Clay
  - Soil Colloidal Quantities
    - Clay
    - Organic Materials (OM)
- ❖ Aluminum concentration: complexation & decomplexation of Al by organic matter
- ❖ Oxides O<sup>-</sup> and hydroxides OH<sup>-</sup>
- ❖ Dissolution & precipitation of carbonates;
- ❖ Protonation & deprotonation of acidic groups on organic matter,
- ❖ longer time scales, soils with high contents of weatherable minerals

The amount of H<sup>+</sup> in solution is small compared with the H<sup>+</sup> & Al<sup>+++</sup> adsorbed on the soil colloids, (reserve) 1:99 ratio Soil is made up of many components and a significant percentage, of most soil types, is clay. Organic matter, while a small percentage, 0% to 7%, is also a very important factor for pHBC. Both of these soil fractions have a large number of negative charges on their surface, thus they attract cation elements and contribute to a higher CEC. At the same time, they can repel anion nutrients ("like" charges).

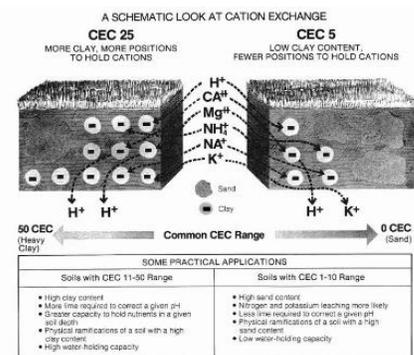


Fig 4) Common CEC Range [6]

For a plant to uptake nutrients they need to be in the dissolved state. When nutrients are dissolved, they are in a form called "ions". This simply means that they have electrical charges. As an example, gypsum is calcium sulfate dihydrate (CaSO<sub>4</sub>·2H<sub>2</sub>O), when it dissolves it becomes two ions plus water; one of calcium (Ca<sup>++</sup>), one of Sulfate (SO<sub>4</sub><sup>-</sup>) and 2 waters (H<sub>2</sub>O). The small + and -

# SUL4R-PLUS® Fertilizer: Fact Sheet

## Soil pH & Buffering Capacity

March 2019

Compiled by Greg Parris



signs with the Ca and the SO<sub>4</sub> indicate the type of electrical charges associated with these ions. In this example, the calcium has a plus charge and is called a "cation". The Sulfate has a negative charge is called an "anion". Since, in soil chemistry "opposites attract" and "likes repel", nutrients in the ionic form can be attracted to any opposite charges present in soil. CEC, as reported by nearly all soil testing laboratories, is a calculated value that is an estimate of the soils ability to attract, retain, and exchange cation elements. It is reported in milliequivalents per 100 grams of soil (meq/100g).

### What does the Buffering pH mean on my laboratory test?

Buffer pH (pHB): This is a value that is generated in the laboratory, it is not an existing feature of the soil. Laboratories perform this test in order to develop lime recommendations, and it actually has no other practical value. [7]

But according to Kissel, pHBC can be used in making ag lime recommendations for acid soils, can be potentially useful in making S recommendations for decreasing the pH in some soils, i.e. Blueberries and is a valuable soil property for estimating pH changes from some nitrogen reactions in soils such as urea hydrolysis, nitrification or soil retention of ammonia [8]

In basic terms, the pHBC is the resulting sample pH after the laboratory has added a liming material. In this test, the laboratory adds a chemical mixture called a buffering solution. This solution functions like 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 suffice. If the soil pH changes only a little 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. [7]

### Why do soils require differing amounts of buffering agents (lime)?

To change the soil pH relates to the soil CEC and the "reserve" acidity that is contained by the soil. Soil acidity is controlled by the amount of hydrogen (H<sup>+</sup>) and aluminum (Al<sup>+++</sup>) 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 higher charge retention) will normally require more lime to reach a given target pH than a soil with a lower CEC.

Some important elements with a positive electrical charge in their plant-available form include potassium (K<sup>+</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), magnesium (Mg<sup>++</sup>), calcium (Ca<sup>++</sup>), zinc (Zn<sup>++</sup>), manganese (Mn<sup>++</sup>), iron (Fe<sup>++</sup>), copper (Cu<sup>+</sup>) and hydrogen (H<sup>+</sup>). While hydrogen is not a nutrient, it affects the degree of acidity (pH) of the soil, so it is also important.

Some other nutrients have a negative electrical charge in their plant-available form. These are called anions and include nitrate (NO<sub>3</sub><sup>-</sup>), phosphate (H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>--</sup>), sulfate (SO<sub>4</sub><sup>-</sup>), borate (BO<sub>3</sub><sup>-</sup>), and molybdate (MoO<sub>4</sub><sup>--</sup>).

Phosphates are unique among the negatively charged anions, in that they are not mobile in the soil. This is because they are highly reactive, and nearly all of them will combine with other elements or compounds in the soil, other than clay and organic matter. The resulting compounds are not soluble; thus, they precipitate out of soil solution. In this state, they are unavailable to plants, and form the phosphorus "reserve" in the soil. [7]

### Advancements in pHBC methods?

Soil pH buffering capacity:

Calculation of soil acidification rates requires knowledge of pH buffering capacity (pHBC), which is measured using titration methods. The pHBC is often quoted as a single value for a particular soil, implying a linear relationship between pH and the amount of acid or alkali added. However, over its whole range, the relationship is sigmoid rather than linear, and in many soils the pH is low or high enough to be outside of the linear range.

Using the function, the contribution of variable charge to pHBC was calculated for the PNG soils; on average it was 93% at the pH buffer curves' inflection point, which corresponds with the soil's minimum pHBC. Factors other than variable charge became important at pH (1 : 5, 0.002 M CaCl<sub>2</sub>) values <4.8 or >6.0. **The relationship between pHBC and soil organic**

**matter content was closest at pH 6.0–6.5. The relative significance of these processes varies with pH. Over the approximate pH range 4.0–6.5, there is a close relationship between soil pHBC and organic matter content, and to a lesser extent with clay content** (e.g. Magdoff and Bartlett 1985; Aitken et al. 1990a; Helyar et al. 1990; Dolling et al. 1994; Noble et al. 1997). [5]

**Metal Oxides:** The oxide mineral class includes those minerals in which the oxide anion (O<sup>--</sup>) is bonded to one or more metal ions. The hydroxide-bearing minerals are typically included in the oxide class. The minerals with complex anion groups such as the silicates, sulfates, carbonates and phosphates are classed separately.

**Base Saturation:** The concept of base saturation is important, because the relative proportion of acids and bases on the exchange sites determines a soil's pH. As the number of Ca<sup>++</sup> and Mg<sup>++</sup> ions decreases and the number of H<sup>+</sup> and Al<sup>+++</sup> ions increases, the pH drops. Base Saturation: It is the summation of exchangeable bases divided by CEC. [8]

$$BS = \frac{(\text{exch Ca} + \text{Mg} + \text{Na} + \text{K})}{(\text{exch Ca} + \text{Mg} + \text{Na} + \text{K} + \text{Al} + \text{H})}$$

You can find an example calculation below showing both % base saturation and % hydrogen saturation:

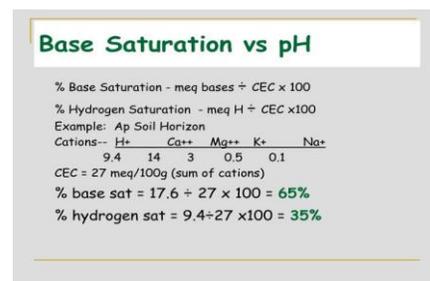


Fig 5) Example Calculation [9]

- **SUL4R-PLUS® fertilizer uses an ALS binder, providing 6 units of OM when applied at 100lbs/acre, that will increase the CEC/AEC of the soil and facilitate nutrient absorption.**

- **High concentrations of dissolved Ca<sup>+</sup> ions will replace H<sup>+</sup> and Al<sup>+++</sup> on the colloidal sites thus increasing the Base Saturation but the net CEC will remain the same.** [10]

- **In acidic subsoil ligand exchange: SO<sub>4</sub> can free up hydroxyls (OH).** [11]

# SUL4R-PLUS® Fertilizer: Fact Sheet

## Soil pH & Buffering Capacity

March 2019

Compiled by Greg Parris



### Reference:

- 1) Sørensen, S. P. L. (1909). "Über die Messung und die Bedeutung der Wasserstoffionenkonzentration bei enzymatischen Prozessen". Biochem. Zeitschr. 21: 131–304. Two other publications appeared in 1909 one in French and one in Danish
- 2) <https://www.slideshare.net/guest89ce50/week-7-clay-and-ion-exchange-1>
- 3) Adapted from <https://en.wikipedia.org/wiki/Soil#Buffering>
- 4) [https://en.wikipedia.org/wiki/PH#pH\\_in\\_soil](https://en.wikipedia.org/wiki/PH#pH_in_soil)
- 5) Nelson, Paul & Su, Ninghu. (2010). Soil pH buffering capacity: A descriptive function and its application to some acidic tropical soils. Australian Journal of Soil Research. 48. 201-207. 10.1071/SR09150. [https://www.researchgate.net/publication/236878026\\_Soil\\_pH\\_buffering\\_capacity\\_A\\_descriptive\\_function\\_and\\_its\\_application\\_to\\_some\\_acidic\\_tropical\\_soils](https://www.researchgate.net/publication/236878026_Soil_pH_buffering_capacity_A_descriptive_function_and_its_application_to_some_acidic_tropical_soils)
- 6) [https://www.spectrumanalytic.com/support/library/ff/CEC\\_BpH\\_and\\_percent\\_sat\\_files/image003.jpg](https://www.spectrumanalytic.com/support/library/ff/CEC_BpH_and_percent_sat_files/image003.jpg)
- 7) Adapted from [https://www.spectrumanalytic.com/support/library/ff/CEC\\_BpH\\_and\\_percent\\_sat.htm](https://www.spectrumanalytic.com/support/library/ff/CEC_BpH_and_percent_sat.htm)
- 8) David E. Kissel, University of Georgia <https://www.slideserve.com/camille/rapid-determination-of-the-ph-buffering-capacity-of-soils>
- 9) Reese & Waters, Lecture 12b, Soil CEC <https://www.slideserve.com/reese-walter/lecture-12-b-soil-cation-exchange-capacity>
- 10) <https://www.agvise.com/educational-articles/gypsum-magic-part-3/>
- 11) GYPSUM AS AN AMELIORANT FOR THE SUBSOIL ACIDITY SYNDROME Prepared by University of Georgia Department of Agronomy Under a Grant Sponsored by the Florida Institute of Phosphate Research Bartow, Florida; December 1990
- 12) <https://www.maximumyield.com/can-i-use-gypsum-to-buffer-the-coco-peat/7/1768>
- 13) [https://www.ctahr.hawaii.edu/MauiSoil/c\\_acidity.aspx](https://www.ctahr.hawaii.edu/MauiSoil/c_acidity.aspx)
- 14) Adapted from [www.hunker.com/12450132/buffering-capacity-of-soils](http://www.hunker.com/12450132/buffering-capacity-of-soils)

### Extended Benefits of Gypsum:

#### GYPSUM AS AN AMELIORANT [11]

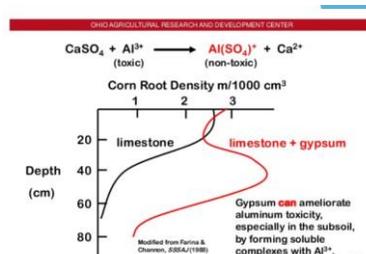
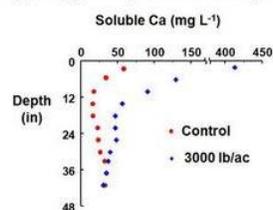
- The ameliorative effects of gypsum on subsoil acidity stem from one or more of the following mechanisms:
  - (a) increased levels of subsoil Ca,
  - (b) complex formation between Al and sulfate (SO<sub>4</sub>) ... which detoxifies the Al,
  - (c) ligand exchange of SO<sub>4</sub> for hydroxyls (OH) on sesquioxide surfaces resulting in the so-called "self liming" effect,
  - (d) precipitation of basic aluminum sulfate minerals which renders the labile Al insoluble and
  - (e) salt sorption in which SO<sub>4</sub> is specifically adsorbed which causes the removal of some Al from solution.

Dr. Malcolm Sumner, et.al. at the University of Georgia has shown that gypsum is highly effective as an ameliorant for low pH soils that have high levels of exchangeable aluminum. His research revealed that even 16 years after the initial application of gypsum the yields of both corn and alfalfa were higher where the gypsum was applied.

It is theorized that the gypsum reacts in these low pH soils to form ion pair AlSO<sub>4</sub> which renders the aluminum non-toxic to plant roots. The calcium in the gypsum is also thought to create a better balance between aluminum and calcium in soil solution.

A benefit of finely ground gypsum is that it is 200 times more water soluble than lime and so calcium will move more easily downwards through the soil profile. In one study water soluble calcium was increased to a depth of 36 inches in a silt loam soil in just two years. <http://soilsolutions.net/crop-responses/university-research/>

Within 2 years, water-soluble Ca from surface applied gypsum is present at 36 in depth.



(Ohio State)

When Liming a case can be made that adding Gypsum with the lime would result in a better soil ameliorant. Could flocculation of hardpan clays by gypsum help water removal to permit flushing out the sodium Na<sup>+</sup> and aluminum Al<sup>+++</sup> sulfate salts? This type of root growth would benefit crop drought tolerance.