SUL4R-PLUS®, LLC: Fact Sheet

Benefits of Ammonium Lignosulfonate (ALS)

Compiled by Greg Parris: APRIL 01, 2019

At SUL4R-PLUS® LLC, we are committed to using the highest quality ingredients to produce our pelletized calcium sulfate that supplies sulfur as a Controlled Release Technology. In this process we bind our micronized calcium sulfate with Ammonium Lignosulfonate (ALS). ALS is an organic certified, water-soluble, anionic polymer ingredient derived from plant material.

Adding ALS to our high purity, synthetic calcium sulfate micronized powder (90% < 44 microns) allow us to manufacture a uniform pellet with high performance characteristics. They are: 265 SGN, 50+ UI, crush strength approaching 8 lbs and density of 60 lbs per cubic foot. These characteristics allow SUL4R-PLUS® products to blend well with other dry fertilizers, and spread uniformly.

What are the benefits of ALS for the soil and plants?

There are many benefits that are associated with ALS. ALS has the following key attributes:

- Complexing agent to hold root desired nutrients near the root zone. Stronger CEC for soil fertility
- Root Anatomy: Humus like material (Fulvic Acid) that can stimulate cell division and increase permeability of membranes for adsorption
- Increases soil fertility: Loosens compaction and water bridging for nutrient transportation
- Nitrogen N_2 Fixation
- Cozy environment in the soil for the growth of biologicals, Microbes and Mycorrhizas Fungi, increasing by 10 to 100 fold
- Reduce soil bourn pest and pathogens

Lignosulfonates (LS) are the byproducts of the pulp and paper industry, derivates of lignin: an organic compound found naturally in softwood and hardwood plants. To be specific, LS are anionic polyelectrolyte polymers.

LS have very broad ranges of molecular mass (they are very polydisperse: have a range of particle sizes). A M_w range from 1,000 – 140,000 da has been reported for softwoods and with lower values reported for hardwoods. [11] SUL4R-PLUS® products contain hardwood [20] LS and therefore, smaller M_w molecules.

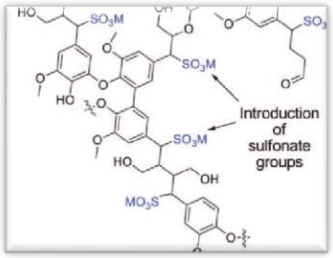

Fig 1: Lignin with Sulfonate groups [12]

Is ALS safe for my soil?

At 8 lbs per acre there are only benefits from the addition of ALS. Studies at 1000x to 4000x have shown to have some impacts but recoverable.

LS has been exhaustively studied based on use for road dedusting. Rates were applied as high as 20+ tons of solids per acre with no effect to Douglass fir trees. Studies for insecticides at 1% (12 tons solids/ha) and 0.1 % solids in water were studied with some impacts to Tomato leaves and roots. [15]

ALS was also used to investigate microbial activity in potatoes [16] at 0.5% (v/w) levels (6 tons solids/ha) with recoverable phytotoxicity. [7]

SUL4R-PLUS® product is applied at levels that will only be beneficial to the crop and nonphytotoxic, ~8 lbs. per acre. 1,500x less that the previous studies.

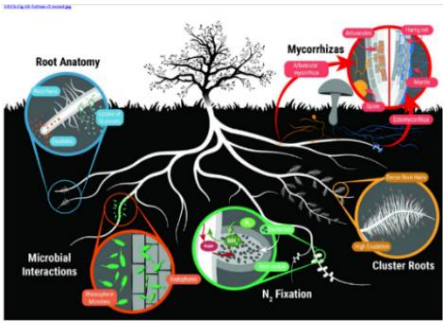

Fig 2: Soil Fertility Areas of SUL4R-PLUS® product [1]

Is ALS a complexing agent?

LS have been used for a long time as a carrier for critical cations needed for plant growth. LS come available in many salt forms already complexed with cations such as Iron, copper, magnesium, calcium, potassium, zinc, nitrate nitrogen (Ammonium), chloride, and phosphorous. We at SUL4R-PLUS®, LLC use the ammonium salt LS that provides a small amount of Nitrogen to the soil <0.5%.

The presence of a considerable number of anionic groups including sulfonic, carboxylic acid and phenolic hydroxyl groups [2] which can form coordinated bonds with metals, converts the LS into an appropriate micronutrient's complexing agent. "The degree of sulfonation increased with decreasing M_w for the fractions as previously found for fractions of spruce lignosulfonate." [13] The more sulfonic groups the more sites the LS has and therefor the more complexing that can be achieved. Further for SUL4R-PLUS® products, the ALS has ~5% of Acidic Acid, by weight of binder, that is a known complexing agent.

ALS is an organic acid/humus material: Does size matter?

"Apart from supplying micronutrients at controlled rates to the crop, lignosulfates also restore the carbon balance in soils." [10] Our ALS supplies 13.5% Carbon by weight.

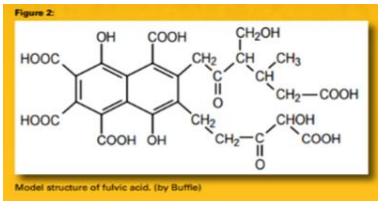

Fig 3: Example of a Fulvic Acid Chain [10]

Humates (Organic Acids) have two specific groups, Humic Acid (HA) and Fulvic Acid (FA). Tests of ALS have consistently shown our source of ALS composition to be ~95% FA as measured by Waters lab. ALS is an organic acid and functions like a FA. The easiest type of organic acid for roots to up-take are FA because they are smaller in size than HA, allowing it to be taken up by the plant.

As you can see from figures 1 and 3, the main difference of ALS to FA is the Sulfonic group ($SO_3^{2-}+M^{2+}$) that replaces the carboxyl group (C=O, C-OH) that are more water soluble. H^+ are the reactive sites.

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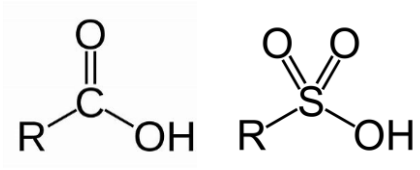

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Are all LS the same size? Some LS can have a variety of chain sizes from 10,000 to 140,000 da. Where the humates are:

- HA long chains: 100,000 to 150,000 da
- FA shorter chains: 10,000 to 15,000 da

"Lignosulfonates obtained from spruce (Picea abies), aspen (Populus sp.) and two species of Eucalyptus (E. globulus and E. grandis) were characterized by aqueous size exclusion chromatography (SEC) combined with in-line multi-angle laser light scattering (MALLS).

In general, the hardwood lignosulfonates were shifted to lower molecular weights (Mw = 5,700 – 12,000 da) as compared to softwood lignosulfonates (M_w = 36,000 – 61,000 da). Lignosulfonates from E. grandis were further fractionated to obtain fractions of different molecular weights (3,500 – 30,000 da)." [14]

SUL4R-PLUS® products use a hardwood lignosulfonate that show to have M_w range of 5,700 to 12,000 da and are like FA. (test ordered)

What are the benefits of hardwood LS?

All LS can complex nutrients, stimulate microbes in the rhizosphere and have high CEC. But hardwood LS, works in the rhizosphere to increase the pore sizes of the root system, enabling the plant to take up more and larger nutrients that are available in the soil. Further it can be absorbed by root tissue and provide hormone-like stimulation to the plant. Also aids in the efficiency of other plant metabolic reactions.

How does ALS impact soil?

Humate loosens soil: allowing roots penetrate more easily. Humic acid's effect on clay soil is more evident as time passes. In heavy clay soils, six months or more may be needed before you will see a noticeable improvement in the soil's density.

Water bridging: is an important function of HA and FA. Water bridging is believed to improve the mobility of nutrient ions through the soil solution to the root. These mechanisms also help reduce leaching of plant nutrients into the subsoil. The same can be said for ALS.

What are the microbial benefits of ALS?

Plants are threatened by various pathogenic micro-organisms like fungi, viruses and bacteria. To overcome the problem of infections with these micro-organisms, large quantities of anti-microbial compounds (in particular synthetic pesticides, such as fungicides and bactericides) are applied. From an environmental and health point of view it is desirable to reduce the amount of chemicals that are applied to the plants and the soil, [3] making us good environmental stewards.

It is known that certain compounds of natural origin can protect the plant against pathogenic micro-organisms. These so-called natural crop protection compounds (NCP's) are organic substances derived from natural organisms (e.g. pheromones, plant extracts), or organic compounds found in the natural environment (e.g. phosphates, sulfur). [3] ALS has many sulfonic groups that make it a suitable NCP.

Can ALS reduce soil bourn pest and pathogens?

Nematodes: Lignosulfonate, it is believed that it is the sulfonates that function as the NCP. When it comes into contact with pests or pathogens in the soil, it is absorbed through the cuticles and affects the pseudocoelomic fluid which renders the pests or pathogens more amenable to attack by soil microbes such as soil fungi and soil bacteria. ALS contains nutrient material, sugars (10% by binder weight), [20] to feed the soil fungi and soil bacteria. [5]

Benefits to potatoes: wilt and scab:

"Laboratory and greenhouse experiments indicate that ALS, while increasing soil microorganisms by 10x to 100x, reduces populations of important soil borne pathogens of fungal and bacterial species. This suggests that ALS could become a component for plant disease control and an alternative to fumigants for the control of soil borne plant pathogens.

Numbers of soil microorganisms increased two- to eight-fold at all sites within weeks of ALS application, (6 t/A). Fungal numbers increased the most and remained elevated for two seasons … compared with control plots." [6]

ALS is an effective treatment for potato scab disease caused by bacteria, Streptomyces.

Does ALS aid seedling to fungus interaction?

When placed in row with the seed, there is a significant chance that LS will aid seed development by reducing early plant stress. In a 2005 study with Fe-LS they concluded that LS: "may be a potential tool to improve the efficiency of fungal inoculations, thus, facilitating the early interaction between an ECM fungus and host seedling." **[19]**

Nitrogen N_2 fixation

As shown in the example below there is a need to convert Ammonium (NH_4) to Nitrites (NO_2) to Nitrates (NO_3) for plant assimilation. ALS can be a direct and indirect contributor to plant health and sustainability. ALS supplies 4.8% Ammonia Nitrogen and 10% sugar by binder weight. [20] Research suggests that ALS, supplies the sugars to feed the bacteria, the small M_w polymers (like FA) for dilation of the root cell for more symbiotic bacteria interaction and improves nitrogen efficiency overall. [12]

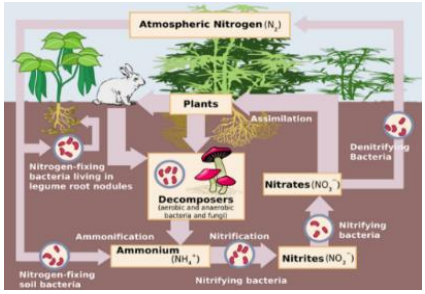

Fig 4: Nitrogen Cycle [17]

This can be thought of as follows: "The symbiotic nitrogen-fixing bacteria invade the root hairs of host plants, where they multiply and stimulate formation of root nodules, enlargements of plant cells and bacteria in intimate association. Within the nodules, the bacteria convert free nitrogen to ammonia, which the host plant utilizes for its development. To ensure sufficient nodule formation and optimum growth of legumes (e.g., alfalfa, beans, clovers, peas, soybeans),

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seeds are usually inoculated with commercial cultures of appropriate Rhizobium species, especially in soils poor or lacking in the required bacterium." [12]

In row fertilization, SUL4R-PLUS® products can aid in Rhizobacterial proliferation, root development and root bacteria colonization.

Can ALS help my Carbon levels in the soil?

Soil respiration is a key ecosystem process that releases carbon from the soil in the form of carbon dioxide. LS "improves soil respiration for improved soil NH_4-N levels and possibly leading to nitrogen efficiency. This improved reparation leads to CO_2 production and the loss of C. Also LS decreased urea hydrolysis slightly and reduced the proportion of added N volatilized from the LS+U treatment." (Meier et al 1993) [8] However: the net balance of C supplied from vs C lost is a net gain.

SUL4R-PLUS® product, ALS and Calcium Sulfate can reduce anaerobic organism activity, that can use nitrogen instead of oxygen, thus improving the overall N efficiency and plant yield.

How are Lignosulfonates made?

"LS are obtained from sulfite pulping processes wherein cellulose is extracted from wood in the pulp industry. The so-called sulfite pulping process involves mixing sulfur dioxide (SO_2) with an aqueous solution of base to generate the raw liquor for cooking the wood. In water, the sulfur dioxide forms sulfurous acid (H_2SO_3), which degrades and eventually sulfonates the lignin by replacing a hydroxyl group with a sulfonate group, allowing it to be solubilized and separated from the cellulose in non-precipitated form. The spent sulfite liquor contains LS and sugars." [9]

Resources:

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20. Lab Analysis of Lignosulfonate

SUL4R-PLUS, LLC: *Tech Brief:*

Title: Benefits of ALS

Daron Bell, Nick Rhea and Greg Parris: Feb 28, 2018

ALS - Quick Facts

- ALS will supply 8 units for 100 lbs per acre of SUL4R-PLUS® product applied
- ALS will complex iron, copper, magnesium calcium, potassium, zinc, sulfur, nitrate nitrogen, chloride, phosphorous
- Source of added organic carbon and soluble sulfur, which are necessary nutrients for good soil microbiology and healthy plant growth
- Stronger CEC will largely increase the fertility of the soil and water holding capacity
- Its Fulvic Acid can stimulate cell division and increase permeability of membrane to increase plant growth through magnified absorption of a group of Micro nutrients by strong root system
- Can create a kind of cozy environment for microbial to grow thus promote plant growth
- Strong complexing capacity to complex mineral ions into the form absorbable by plants
- Non-ionic surfactant (wetting agent) made from hydrophilic sulfonic acids added to dissolve lignin
- A natural forestry bi-product and a natural crop protection compounds (NCPs)
- Lignosulfonates have generally a wide molecular weight ID distribution, typically in the range of about 500 to about 150,000 da where FA is from 10,000 to 15,000 da & HA is 100,000 to 150,000 da

ALS - Role of Nutrient

- From an agronomic perspective, the most interesting observation was that LS significantly increased soil NH4-N levels throughout the experiment, suggesting that LS has the potential to increase fertilizer N efficiency
    - LS may inhibit nitrification
- These organic carbon acids also play a useful role in vascular mineral transport
- Impacts DOC (Dissolved Organic Carbon) excretion at the plant root
- Supplies additional N, S, & C

ALS - Nutrient in Soil

- Coarse-textured soils that have low organic matter, “C” content may be improved with ALS at point of use
- Improves microbial growth: Microorganisms in the soil are speedily activated.
- Also treating potato scab disease caused by bacteria Streptomyces
- ALS also has surfactant and dispersant properties which make it a great fertilizer aid
- Improves Fungi growth that supplies nutrient to the root
- Green natural origin can protect the plant against pathogenic micro-organisms (NPCs)
- Improved mobilization and nutrient utilization by the plant
- Increases the biomass
- Increases P availability to the plant thru indirect pathways (AM Fungi) (mychoriza)
- Improves N fixation (rhizobia)
- Assists in pathogen suppression
- Increases phospholipid fatty acids
- Hold S in the soil (1% organic matter will release 2.8 lbs of sulfur per acre.)
- Perhaps the most dramatic impact of Humate is on urea because it will hold and slow release the nitrogen, leading to much higher (greater than 40 percent) dry matter and more volume