Sulfur: At the Crossroads of Energy, the Environment, and Agriculture

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Abstract

The success of the Clean Air Act has created evidence of sulfur deficiency on the farm, and a surplus sulfur stockpiles elsewhere. Hondo Chemical has shown that sulfur products derived from a particular process, the iron-redox (i.e. LO-CAT®) sulfur removal plant, produces sulfur-based agricultural products with superior results compared to products based on sulfur from more conventional sources, such as Claus plants.

Introduction

As our world and economy has developed, so has our need for energy, in all its forms. However, not all energy is created equal, and it has come at a cost, in economic and environmental terms. This is true for oil, gas, coal, and even geothermal energy. Each has its advantages and disadvantages in a given situation. Ironically all of these energy sources have one common problem that remaining world energy supplies bear in ever increasing quantity: sulfur.

Sulfur isn't necessarily bad. Without it, no life that presently exists on the planet could have come into being. While people and plants both need sulfur to survive, we have been experiencing cases of sulfur being present in the wrong places, at the wrong times, in the wrong chemical forms, and in the wrong quantities.

Where the need for energy, life, and sulfur collide is in the production and consumption of energy. The conversion of energy converts the sulfur, often in the form of toxic hydrogen sulfide, into oxides of sulfur (SO_x). Sulfur oxides are key culprits in the formation of photochemical smog and acid rain; unpleasant side effects of our industrial society.

Driven by the Clean Air Act and other similar local, state, federal, and even international legislation, industries around the world have searched for better ways to remove various sulfur byproducts from exhaust gases for the past 30 years. Numerous processes were developed to remove sulfur from both gas and liquid hydrocarbon streams, including Claus, LO-CAT® and Stretford processes for gas streams, and Mericat and Merox units for liquid streams. Ironically, these processes were so effective at removing sulfur compounds from exhaust gas streams that the agricultural industry, which previously attained almost all the sulfur it needed from the atmosphere via smokestacks and automobile exhaust, suddenly found itself desperately short of sulfur and experiencing crop losses due to sulfur nutrient deficiencies for the first time since the industrial revolution.

The other impact of this success is in the area of sulfur production. So much by-product sulfur is being produced, that the on-purpose production of sulfur has been virtually shut down while huge sulfur stockpiles of excess product continue to build. A solution has begun to develop over the past several years: the discovery that much of the sulfur that has pulled from many exhaust gas streams can be used in agriculture.

Role of Sulfur in Agriculture:

The success of the Clear Air Act, and the huge reduction of sulfur emissions from energy production and generation facilities, has had important side effects in agriculture and industry.

1. Evidence of sulfur deficiency in agriculture.
2. Creation of new sulfur-containing fertilizer products to address the sulfur deficiency.
3. Replacement of all on-purpose sulfur production with by-product sulfur production.

Sulfur's role in agriculture was not fully appreciated when sulfur was "free," in the form of sulfur dioxide emissions to the atmosphere, and falling to earth in the form of acid rain. With the huge reduction in sulfur dioxide emissions, it is now clear that sulfur plays three roles in agriculture:

1. Soil amendment for pH adjustment
2. Plant nutrient
3. Fungicide

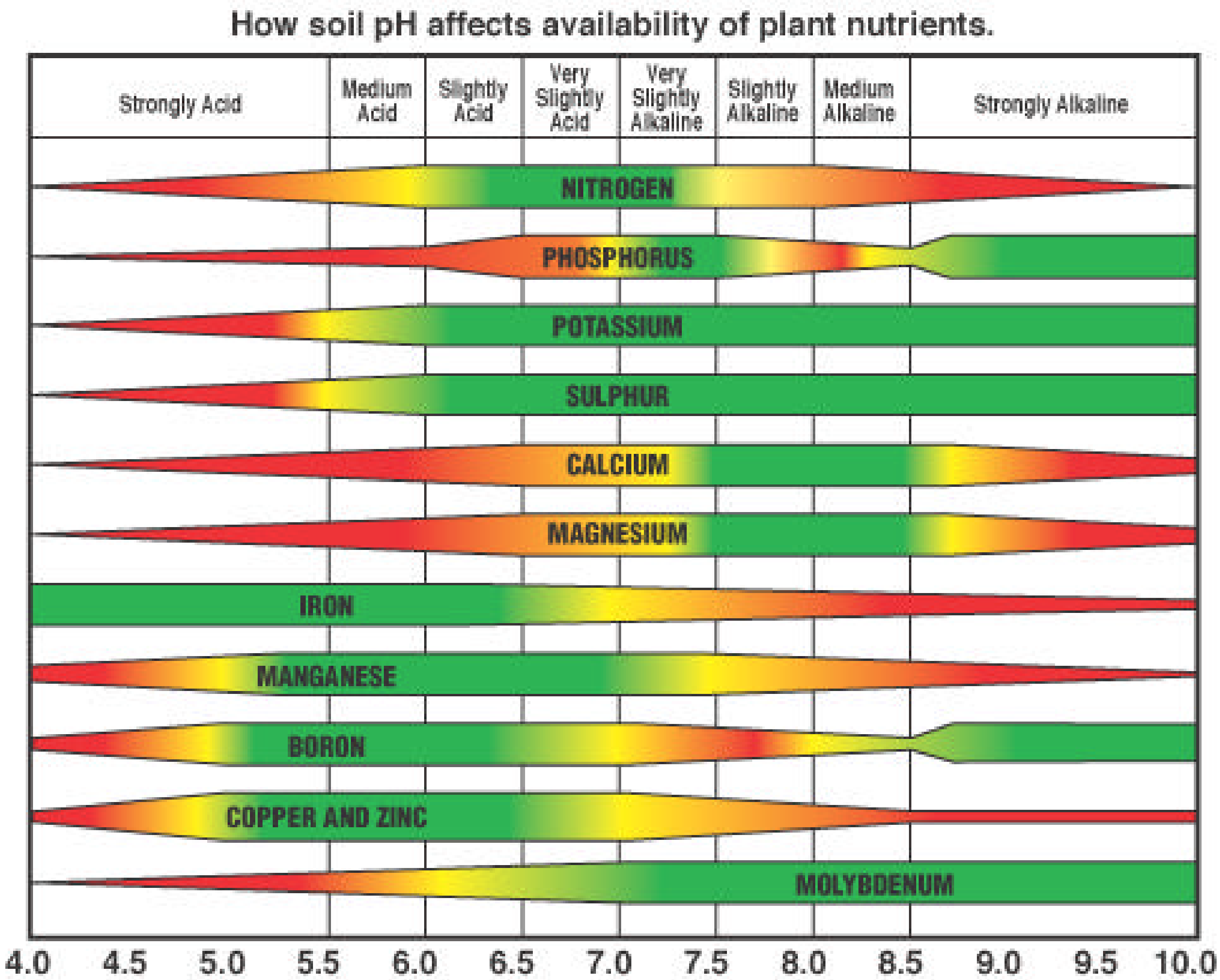
Soil amendment:
Soil pH can affect the efficiency of virtually every other nutrient. Nitrogen, phosphorus, potassium, three most prevalent fertilizer ingredients, or macronutrients, as well as all the essential micronutrients, are affected by soil pH.

Plants use nitrogen to synthesize amino acids, which form proteins, which stimulate plant growth. At too high of a pH, the plant will form nitrates. The problem with nitrates is that the plant cannot absorb nitrates. The plant can absorb nitrates in the form of sulfates, which occurs at a lower pH. Nitrates not only waste nitrogen by "locking" the nitrogen in an unusable form for the plant, nitrates are also a waste and environmental concern as they are susceptible to leaching into the water table, creating problems for the water supply.

Phosphorus stimulates early growth and root formation, and may be the most expensive of the primary macronutrients. However, at a soil pH of 7.5, virtually all of the phosphorus will be tied-up in the soil by calcium, becoming unavailable to the plants, and a waste of money.

Likewise potassium, which encourages root growth, resistance to disease, and increases the size and quality of crops, will unavailable for plant use at higher pH.

The target pH for optimum absorption of plant nutrients is 6.5. Figure 1 shows the optimum pH for the major soil nutrients.



Sulfur application lowers the pH of alkaline soil, increasing the uptake and efficiency of all of the other plant nutrients. The pH adjustment takes place through the bacterial conversion (primarily by the Thiobacillus species) of sulfur to sulfuric acid by the equation:

$$S + 3/2\ O_2 + H_2O \Longrightarrow H_2SO_4$$

The reaction rate that produces sulfuric acid is a function of the sulfur particle size and crystal structure. The impact of these features on reaction rate will be further developed in the context of different forms of sulfur.

<u>Plant nutrient:</u>
In a world where NPK are the three “macronutrients,” sulfur is becoming the fourth “macronutrient.” Sulfur is a component in three amino acids, and therefore essential for protein synthesis. Crops from “fruits to nuts” require nutrient sulfur. Nuts, such as almonds and pistachio require 40 pounds of sulfur per acre, while citrus fruits, such as lemons and oranges require 30 pounds per acre. This compares to nitrogen consumption of 200 to 260 pounds per acre, 250 to 300 pounds per acre of potassium, and phosphorus consumption closer to 50-75 pounds per acre.

Fungicide:
Because sulfur is an acid-producing element, it has a devastating effect on molds, fungus, and mildew. For centuries farmers in Italy have applied sulfur to their vines after exposure to rain and fog. Were it not for these "dusting sulfurs" that are routinely sprayed in vineyard and orchards around the world, a bottle of wine would be beyond the reach of all but the richest among us.

Differences in Sulfur Production:

The technological developments of the energy industry, including hydrocarbon processing, geothermal energy, and unconventional sources such as tar sands and bitument, are bringing to market energy from various resources with various processing requirements. Many of these sources contain hydrogen sulfide, which must be removed prior to conversion of the energy. The hydrogen sulfide is converted to elemental sulfur in the most common processes. The result of these developments is that:
1. There is a surplus of sulfur.
2. Different processes are producing sulfur.
3. Sulfurs produced by different processes have very different properties.

Not all by-product sulfur is suitable for use in agriculture. Hydrocarbon-based processes, and aqueous-based processes with vanadium catalysts, produce sulfur products that are unsuitable for agriculture. Most of the by-product sulfur finding use in agriculture are produced by the Claus method, and the low-temperature, aqueous, iron-redox process (i.e. LO-CAT® and Sulferox®). However, these two processes produce sulfur with very different properties, with very different results.

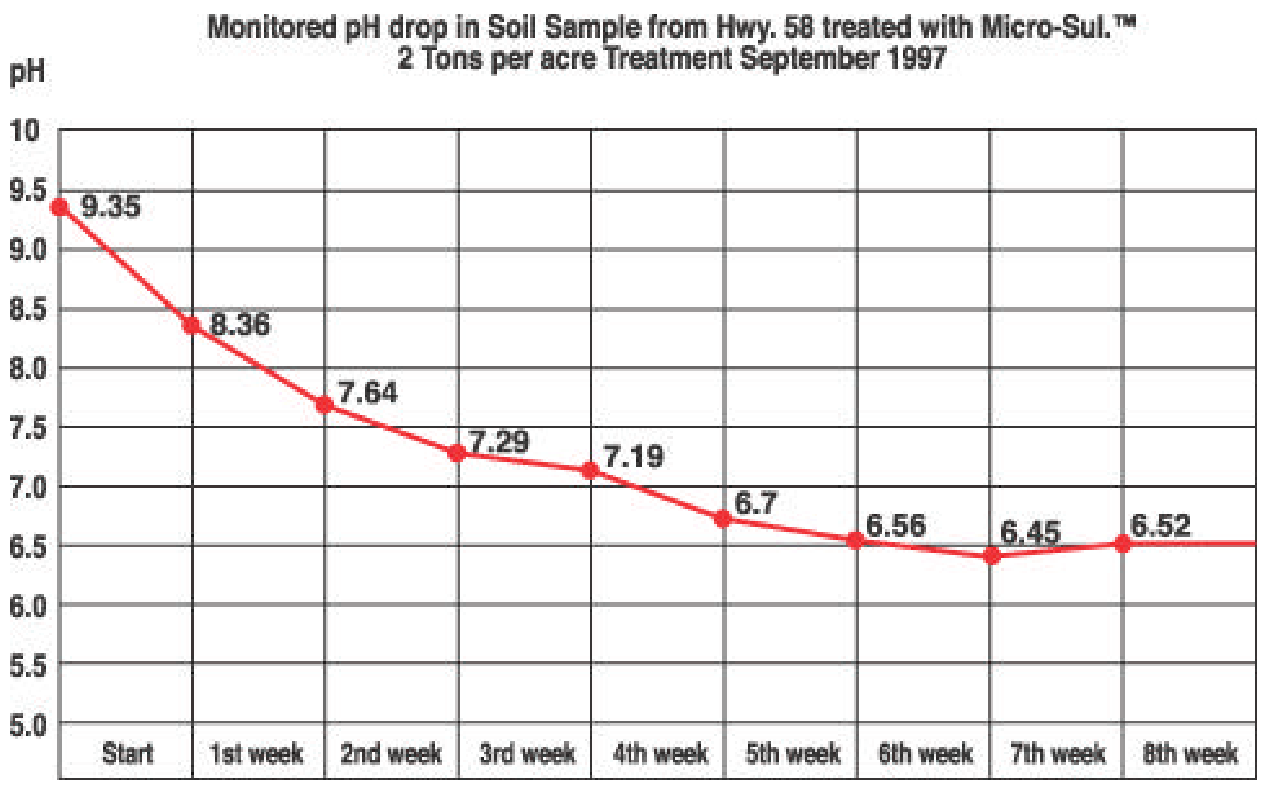
Most by-product sulfur is produced by the Claus process. The Claus process is a catalytic process that operates at about 700^{o}F and produces pure, molten sulfur. The sulfur is then prilled to create small sulfur particles. Since the sulfur is derived from molten sulfur, the sulfur particle is a glassy, orthorhombic crystal. For the orthorhombic crystal to be useful in agriculture, the sulfur particles must be processed to very small particle size to promote biological conversion in the soil, and coated with bentonite, a dispersible clay, to reduce the flammability hazard associated with pure sulfur.

The iron-redox process, which operates at about 140^{o}F, produces an amorphous sulfur particle size between 8 and 45 microns. The particle is in a "cake" form that includes about 25% water. The differences in sulfur form make for profound differences when applied to agriculture. Hondo Chemical Company of Bakersfield, California, is the world's leader in the research and development of the iron-redox-based sulfur fertilizer. Hondo's Micro-Sul™-based fertilizer product demonstrates the benefits in the resulting fertilizer products. These differences in crystal structure lead to profound differences in:
- Reactivity
- Fertilizer application
- Safety

The above lead to a profoundly different value proposition compare to sulfur-based fertilizer products based on sulfur from traditional processes.

Reactivity:
As stated earlier, the rate at which the thiobacillus organism converts the sulfur particle to sulfuric acid is a function of particle size. The smaller the particle, the more surface area, the faster the reaction, and the faster the crops will benefit. Most Claus sulfur processed for fertilizer application is prilled to create a particle size range of 50 to 200 mesh. This equates to a particle size range of 75 to 300 microns. The iron-redox sulfur particle, by comparison, is 8 to 45 microns; five to six times smaller than the traditional "hard" particle, with 25 to 36 times more surface area per unit weight. In addition to the reduced surface area, the "glassy" orthorhombic particle is slower to react than the relative soft amorphous particle produced by the iron-redox process.

Hondo Chemical demonstrated the increased reactivity in a field trial in Arvin California in 1994 (Figure 1). The small, soft, amorphous sulfur particle in Hondo's Micro-Sul™ fertilizer product is completely assimilated and converted to sulfuric acid and calcium sulfate, effectively reducing the soil pH, within 45 days. The comparable assimilation time required for the more conventional, larger, "glassy" orthorhombic crystal, typical of most sulfur-based fertilizer products, typically takes one to three years to completely convert to sulfates.



Since the sulfur is being applied to amend the soil and adjust pH, this fast reaction means that not only is the sulfur available as a plant nutrient in a matter of weeks, but every other nutrient in the soil is similarly made more available in only weeks.

One might suggest that sulfates, such as ammonium thiosulfate, could be applied directly to the crop, and be absorbed even faster. That is partially true. A sulfate compound is ready for absorption almost immediately. In fact, bentonite is often applied as a coating for a "time-released" effect of the sulfate, providing nutrient value to the crop over time. However, the sulfate products are quickly absorbed and have little impact on the soil pH, and therefore, have little impact on the availability of the other crop nutrients being made available to the crop.

Applicability:

Pure sulfur particles are not suitable for application as a soil ingredient. The pure sulfur particles, due to heat and friction generated by the application spreader, have a tendency to catch fire. In addition, the fine particle size that enhances reactivity in the soil, can result in the sulfur being picked-up by the wind. The airborne sulfur particle is not only a waste of sulfur, as it is unavailable for the crop, but it becomes an environmental issue as well.

To address the flammability issue, most typical sulfur products coat the sulfur particle in bentonite. The sulfur:bentonite ratio is typically 10:1. This is the same bentonite that is applied to some sulfate products to reduce reaction rates for a "time-release" effect.

Hondo's Micro-Sul™ product has a superior solution. The soft, amorphous particle is "packed" in water. The fertilizer "cake" handles like a dry power, but it has 25% water. This means that there is no fire hazard. It also means that the Micro-Sul™ product has a dual personality. It is a tiny, soft sulfur particle to the bacteria that "digest" the sulfur. Yet for the purpose of application, it is a safe, heavy particle. The best of both worlds.

Fungicide:

It would stand to reason that the same features present in iron-redox sulfur that lead to superior products in soil amendment and nutrient functions, would lead to superior results in fungicide products.

"Dusting sulfur" is applied to grapes after rain and fog to control fungi and bacteria growth. Hondo Chemical is in the process of commercializing a new dusting sulfur product called "Dusting-O". The product has been certified by the Federal Department of Agriculture (required of all pesticide products), and Oregon's Department of Agriculture. Certification has been applied for in California, Texas and Arizona.

The application of "dusting sulfur" involves making a very fine sulfur dispersion in water. The sulfur/water dispersion is spayed or "dusted" on the crop in a very fine mist. The iron-redox basid sulfur is dispersed much more readily than the conventional sulfur based products. An example of the difference in dispersibility of sulfur in water can be readily seen in the photographs in Figure 3.

It stands to reason that the more stable sulfur/water dispersion would allow for a more even, better controlled application of the dusting sulfur. It also stands to reason that the smaller, softer sulfur particle will react faster, provide protection sooner, than "dusting" products based on conventional sulfur. Finally, it stands to reason that there will be measurable benefits in the performance and efficiency in the iron-redox based fungicide products.

Superior Value Proposition

As more strict environmental standards are being implemented, there is increasing evidence that sulfur-deprivation in crops is becoming more widespread.

Hondo Chemical has shown that it's iron-redox-sulfur-based Micro-Sul™ product is safe and easy to apply. They've also been able to show superior results from application of Micro-Sul™ sulfur product. Not only because the sulfur nutrient is absorbed faster from Micro-Sul™, but also because, when applied to alkaline soil, the Micro-Sul™ sulfur will "unlock" virtually every nutrient in the soil faster than other sulfur-based products. The "unlocking" of the soil nutrients to the crops not only benefits the crops, it also benefits the environment as it reduces the leaching of expensive "locked-up" nutrients into the surrounding environment. A good deal for the farmer, the plants, as well as the rest of us.