

Technical Bulletin:

Oxidation of Elemental Sulfur in Soils

EXECUTIVE SUMMARY

- » Sulfate-based fertilizers are immediately available to crops but are prone to leaching below the root zone in high rainfall environments. They are low in sulfur (S) content compared to elemental S fertilizers so transport costs are comparatively higher.
- » Fertilizers containing elemental S can provide higher S content, resulting in less dilution of other nutrients compared to sulfate-containing fertilizers. They also provide S in a form that is not leached out of the root zone. However, to be plant available, the elemental S must first be oxidized to sulfate in the soil.
- » In soils, oxidation of elemental S is a biologically-mediated process and a wide range of soil organisms are able to perform this oxidation, not just autotrophic soil microorganisms like the *Thiobacillus* species. Hence all soils have the inherent biological capability to oxidize elemental S.
- » Oxidation of elemental S in soils is increased at higher soil temperatures, in moist soils and in soils with higher pH and higher amounts of soil organic matter.
- » The smaller the particle size of elemental S, the faster its oxidation when dispersed in soil.
- » Co-granulation of elemental S with macronutrient fertilizers (nitrogen, phosphorus or potassium), e.g. MicroEssentials®, can enhance oxidation rates over granules containing only S.
- » Granulation of elemental S slows oxidation compared to elemental S particles dispersed throughout soil.
- » Oxidation of co-granulated elemental S is affected by the total elemental S content of the granule (reducing as S content increases) and granule size (reducing as granule diameter increases), as both these affect the surface area of elemental S available for oxidation. Particle size of the co-granulated elemental S only significantly affects oxidation when fertilizer granules have low contents of elemental S.
- » An Excel-based model has been developed to predict oxidation rates of elemental S in a range of co-granulated fertilizers for various soil and climatic environments.

BACKGROUND

Sulfur (S) is one of the 17 elements essential for plant growth and the fourth most important after nitrogen (N), potassium (K), and phosphorus (P) in terms of amounts required by crops. Elemental S is the most concentrated form of S, and hence will have lower transport costs and less dilution effects on other nutrients in fertilizers compared to sulfate-based fertilizers. Elemental S is not taken up by crops in the applied form, and must be converted in the soil to sulfate-S before uptake by plants or microorganisms.

This factsheet describes how elemental S is oxidized in soil, and the factors that affect the rate of oxidation. An example of results from a model predicting rates of S oxidation from granulated fertilizers containing elemental S is provided to illustrate the key factors affecting oxidation in soils.

OXIDATION OF ELEMENTAL S IN SOILS

Oxidation of elemental S (or thiosulfates) in soil is a microbial process requiring the presence of both water and oxygen (Figure 1). The converted sulfate can be taken up by crops, taken up by

microorganisms in the soil, or leached below the root zone in coarse textured soils or if rainfall is high.

There is a very wide variety of microorganisms in soil that are capable of oxidizing elemental S, both bacteria and fungi (Lawrence and Germida 1988; Tourna et al. 2014), hence oxidation is not solely dependent on the presence of specific S-oxidizing organisms e.g. *Thiobacillus* species.

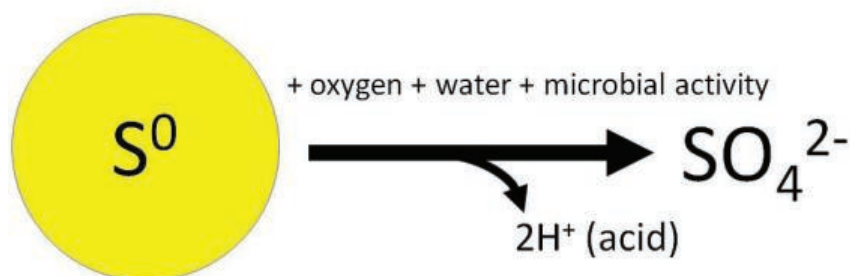


Figure 1. The reaction of elemental S (S^0) oxidation in soils to sulfate (SO_4^{2-}).

ENVIRONMENTAL FACTORS AFFECT OXIDATION OF ELEMENTAL S IN SOILS

As oxidation is a microbial process, soil or environmental factors that affect activity of soil microorganisms will influence the rate of elemental S oxidation. Oxidation is more rapid in warm, moist soils with high organic matter (OM) contents (Germida and Janzen 1993). Oxidation reactions of elemental S are also faster in alkaline soils than in acidic soils (Germida and Janzen 1993; Zhao et al. 2015) (Figure 2). Of the soil and environmental factors affecting oxidation rate, temperature and soil pH have the largest effect (Janzen and Bettany 1987; Watkinson and Blair 1993).

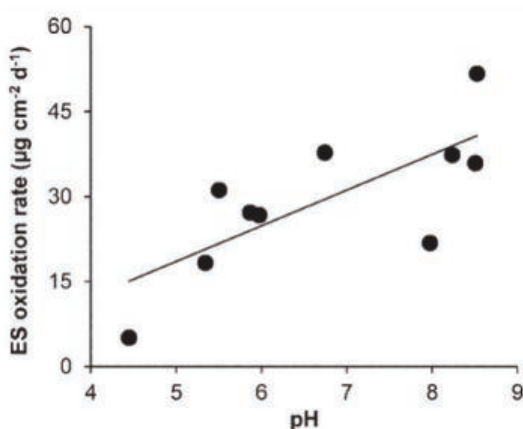


Figure 2. Effect of soil pH on oxidation of elemental S (ES) across ten soils at 25°C (77°F) where particles (average diameter 48 µm) were dispersed through soil. The line represents: $\text{Rate} = 6.29 \text{ pH}_{\text{water}} - 12.7$; $r = 0.75$, $P < 0.05$ (Zhao et al. 2015).

FERTILIZER ATTRIBUTES AFFECT OXIDATION OF ELEMENTAL S IN SOILS

Oxidation of elemental S fertilizer is also affected by the characteristics of the fertilizer. When elemental S is dispersed through soil, the oxidation of elemental S is faster as the particle size of the elemental S decreases (Figure 3). This occurs because oxidation is a surface-based process and surface area increases dramatically as particle size decreases.

In co-granulated elemental S fertilizers, (i.e. where elemental S particles are co-granulated with macronutrients (N, P or K) or with binders/dispersants such as bentonite), the oxidation is much reduced compared to the elemental S particles of the same size dispersed through soil (Friesen 1996). This is not because the macronutrients reduce the oxidation rate, in fact the presence of macronutrients can enhance the oxidation rate as the nutrients can stimulate microbial growth in deficient soils (Friesen 1996). The reduction of oxidation rate due to co-granulation (Figure 4) is rather due to the

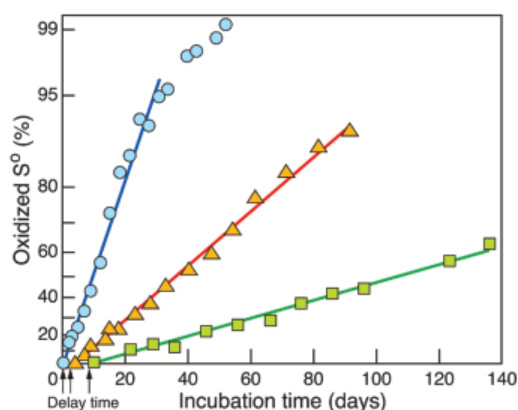


Figure 3. Effect of elemental S (S^0) particle size on the rate of oxidation in soil at 30°C and where particles were dispersed throughout the soil (Watkinson and Blair 1993). \circ - 38-75 µm diameter, \triangle - 125-150 µm, and \square - 212-250 µm.

reduction in surface area of elemental S available for oxidation when dispersed in soil (Degryse et al. 2016a).

MODELLING OXIDATION OF ELEMENTAL S IN CO-GRANULATED FERTILIZERS

As oxidation of elemental S is a surface-based process, the rate of oxidation is proportional to the surface area of the particles if they are dispersed through soil. The specific surface area (SA, the surface area per unit mass) of a spherical particle equals:

$$SA = A/(\rho \cdot V) = (\pi d^2)/(\rho \cdot \pi d^3/6) = 6/(\rho \cdot d) \quad [1]$$

where A , V and d are the area, volume and diameter of the spherical particle, respectively, and ρ is the particle density. Hence, the oxidation rate of elemental S particles dispersed in soil is predicted to be inversely proportional to the particle diameter.

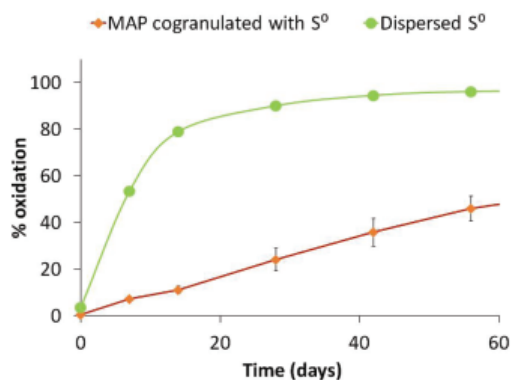


Figure 4. Effect of co-granulation of elemental S (S^0) on the rate of oxidation in soil (pH(water) 5.6, 3.8 %OM) at 25°C (77°F) and where particles (17 µm diameter) were dispersed throughout the soil or co-granulated with monoammonium phosphate (Mosaic Fertilizer Technology Research Centre, unpublished data).

The lower oxidation rate of co-granulated elemental S can be explained by a reduction in the surface area of S in contact with the soil. A model was produced which assumes that as the granulated soluble fertilizer nutrients (N, P) dissolve and diffuse away from the granule, this leaves a collapsed “cavity” (Figure 5) with a surface area in contact with soil corresponding to the surface area of the original granule (Degryse et al. 2016b). Thus, if the area covered by the individual elemental S particles combined exceeds the surface area of the original granule, the area of elemental S actually exposed to soil is equal to the granule surface area (Figure 5a).

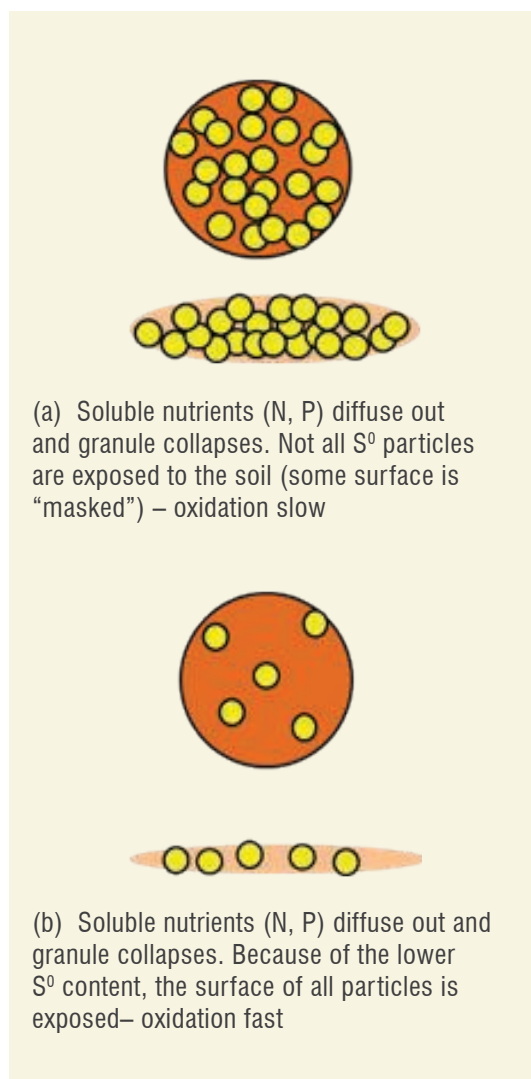


Figure 5. Schematic of dissolution of granulated fertilizers containing elemental S (S⁰), for a granule with (a) high or (b) low ES concentration (McLaughlin et al. 2015).

- = elemental S particles
- = macronutrient carrier (MAP/TSP/ urea)

Hence the effective surface area (SA_{eff}) per mass of elemental S in this case is:

$$SA_{\text{eff}} = 6/(f_{\text{ES}} \times \rho_{\text{gran}} \times d_{\text{gran}}) \quad [2]$$

where d_{gran} is the diameter of the fertilizer granule, ρ_{gran} the density of the granule, and f_{ES} the mass fraction of elemental S in the granule (Degryse et al. 2016b). If the area covered by the individual elemental S particles is less than the original granule surface area, the particles act as dispersed particles (Figure 5b). Hence, the surface area available for oxidation for a given amount of S depends on the concentration of elemental S in the granule, the original granule size and the particle size of the elemental S within the granule. The last factor is only important at low concentrations of elemental S.

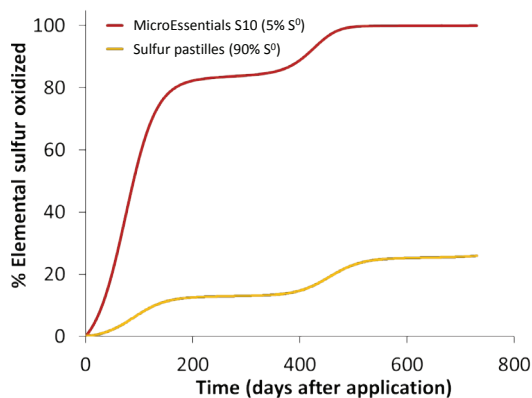


Figure 6. Effect of elemental S content of granule on oxidation for co-granulated products over two seasons. The model simulation integrates climatic data for Kansas and a soil having a pH of 7.5 and an organic matter content of 4% (Mosaic Fertilizer Technology Research Centre, unpublished data).

An Excel-based model has been produced by the Mosaic Fertilizer Technology Research Centre that integrates all soil, environmental and fertilizer granule factors that affect the oxidation of elemental S in soils to allow predictions of oxidation rates in various locations with defined fertilizer types. The graphical output provides a quick visual appreciation of the factors that govern elemental S oxidation. An example of model output is shown in Figure 6.

The oxidation of the sulfur pastilles is predicted to be much slower than for the sulfur in the MicroEssentials® granules. This is due to the much higher content of the sulfur pastilles, resulting in less surface area exposed to the soil.

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Further information

The Fertiliser Technology Research Centre was established in 2007 via a partnership between The University of Adelaide and The Mosaic Company. The scope of the centre was further expanded in 2009 via a partnership between The Mosaic Company and Australian Grains Research and Development Corporation (GRDC). The centre has expertise in soil chemistry, fertiliser technology and plant nutrition, specifically in developing novel fertiliser formulations, advanced isotopic and spectroscopic investigations of fertiliser efficiency, and field scale agronomy trials.

CONTACT:

Prof. Mike McLaughlin
Fertilizer Technology Research Centre
The University of Adelaide, School of Agriculture Food and Wine
Phone: +61 8 8313 8433
Email: michael.mclaughlin@adelaide.edu.au

