A Review on the Oxidation of Granular Fertilisers Containing Elemental Sulphur with or without Ammonium Sulphate in Soils

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ABSTRACT

Sulphur (S) is an essential plant nutrient. S deficiency slows down the formation of all amino acids which are required for optimal plant growth and final maximum crop yield. Recent research has shown that many agricultural soils worldwide are increasingly suffering (S) nutrient deficiency for crop production. Various types of granular fertilisers containing elemental sulphur (ES) with or without ammonium sulphate (AS) have been commercialised. Since plants cannot absorb ES directly, ES oxidation to SO_4-S by soil microbes must occur to enable ES to provide plants available S. In this paper, the results of several literature reports from laboratory soil incubation studies with granular

(ES±AS) products were extracted and reviewed critically. Granulation of micronised ES particles result in a locality effect on dispersion of ES particles after granule disintegration, limiting contact between ES surface and ES oxidising microbes in the soil. It is concluded that ES oxidation of these granular S fertilisers often is too slow or inadequate to provide initial available SO_4-S. Therefore, granular ES products are generally inferior to SO_4-S fertilisers for agronomic effectiveness.

Keywords: **Granular elemental Sulphur, oxidation of elemental Sulphur, available Sulphur, Sulphur response**

INTRODUCTION

Sulphur (S) is an essential plant nutrient. A S deficiency slows down the formation of all amino acids which are required for optimal plant growth and final maximum crop yield. In recent years, soil S deficiency has become a major problem for crop production in many countries due to the extensive and popular use of high-analysis NP fertilisers, e.g., urea, mono-ammonium phosphate (MAP), di-ammonium phosphate (DAP), and triple superphosphate (TSP), which contain little or no S nutrient (Chien *et al*., 2009). Reduction of SO_2 emissions from industry to the atmosphere by the environmental laws also has a significant effect on S deposition from air to soils. The major S fertiliser sources have been gypsum ($CaSO_4$) in

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SSP, ammonium sulphate (AS), and elemental S (ES). Natural gypsum and phosphogypsum, a by-products of H_3PO_4 production, are used as soil amendments and supply S nutrient as well. Recently, flue gas deSulphurised (FGD) gypsum, a by-product from coal-generated power plants, has been introduced to the farmers.

Given that powdered ES particles are dusty, difficult to apply to soils and potentially explosive, the use of ES as an S source normally is in granular form. For example, a granulated product of powdered ES with10% bentonite has been introduced to farmers for some time. Recently, several fertiliser companies have developed and marketed high-analysis granular NP fertilisers such as TSP, MAP and DAP containing ES. Since ES is almost 100% S, N and P contents are not significantly reduced compared to incorporating AS or gypsum. However, ES is not plant available unless it is oxidised to SO_4-S by soil microbes. Since the oxidation rate of ES particles increases with decreasing particle size of ES (Boswell and Friesen, 1993), some fertiliser companies have developed and marketed granular ES or NP fertilisers containing micronised ES particles (< 100 µm) (Table 1). It has been assumed that once the fertiliser granules disintegrate and the ES particles are released back to the original very fine particle size, the rate of ES oxidation in the soils may be rapidly enhanced. In order to make up for a potentially slow ES oxidation from granular ES and NP-ES fertilisers to provide available SO_4-S early in the first crop, products containing a mixture of (ES + AS) at various S ratios have been marketed. It is assumed that AS of granular NP-(ES+AS) products supplies initial available S while ES provides available S at later stages of crop growth up to maturity for season-long or first crop nutrition compared to sulphate-based S fertilisers within the year of application. However, manufacturers of these products have not provided scientific evidence that granular ES products can provide available S as effectively as SO_4-based sources during the first cropping season (Chien *et al*., 2016a).

TABLE 1
Some commercial-grade granular fertilisers containing elemental S (ES)
with or without ammonium sulfate (AS)

Chemical Composition	Total S (%)	ES-S (%)	AS-S (%)
(Bentonite + ES)	90	90	0
(Bentonite + ES)	85	85	0
(Bentonite + ES) + (AS)	46	32	14
(MAP + ES + AS)	9	4.5	4.5
(MAP + ES + AS)	10	5	5
(MAP + ES + AS)	15	7.5	7.5
(TSP + ES)	12	12	0

While several reviews of factors affecting oxidation of powdered ES in soils are reported in literature (Johnson, 1975; Palmer *et al*., 1983; Hagstrom, 1986), plus a comprehensive one by Boswell and Friesen (1993), there are no reviews or discussions available on the issue of ES oxidation of granular ES products in soils. The purpose of this paper is to examine and discuss some published results of the ES oxidation of granular fertilisers containing (ES±AS). The review will be focus mainly on the results of ES oxidation from laboratory soil incubation studies reported in literature. A review of agronomic results from the greenhouse and field studies that have shown little or inadequate available S from oxidation of granular (ES±AS) products compared to AS for crop growth can be found in Chien *et al*. (2016a).

ES Oxidation in Laboratory Soil Incubation Study without Leaching
Biological ES oxidation requires colonisation of soil oxidising bacteria on the surface of the ES particles (Janzen and Bettany, 1987). Therefore, the rate of ES oxidation increases with the specific surface area of ES particles which increases with decreasing ES particle size (Boswell and Friesen, 1993). While very fine micronised ES particles (< 100 μm) can oxidise rapidly in soils, granulation of the same fine micronised fine ES particles may not have the same oxidisation effect as claimed by some researchers and fertiliser companies. This is due to the so-called negative "locality effect" on the ES oxidation as discussed by Chien *et al.* (2009;, 2011). The concept implies that when the ES granules disintegrate and release micronised ES particles in the soil, the very fine ES particles still in cluster form, localise with limited dispersion around the applied granule site due to the fact that ES is water-insoluble. Furthermore, ES is hydrophobic and the released micronised ES particles tend to coalesce to form larger aggregates that further decrease ES oxidation (Friesen, 1996). Consequently, little S oxidation of granular (ES + bentonite) and MAP-(ES+AS) products occurs during soil incubation compared to the powdered ES which goes on up to 10 weeks (Chien *et al.*, 2016b; Fig. 1).

Janzen (1990) used a unique technique to demonstrate the importance of dispersion of ES particles (mean 87 μm) and the minimum soil volume (or equivalent soil weight) that is required to mix the ES particles to begin the ES oxidation in a Chernozemic and Luvisolic soil. The ES particles (64 mg S) were thoroughly mixed with varying amounts of moist soil ranging from 0 to 64 g (oven-dry basis). Untreated moist soil was then placed in the bottom of incubation vials, the ES-soil mixture was placed in an indentation in this layer, and additional untreated soil was placed on the surface. In this way, the ES-soil mixture was placed in the centre of a volume of soil weighing a total of 64 g. The uncovered vials were incubated at 80% of field capacity in a sealed, humidified incubation chamber at room temperature. During the course of the incubation, the samples were aerated and watered to weight as required. After 35 days, the ES concentration in the soils was determined by extraction with acetone and colorimetric assay.
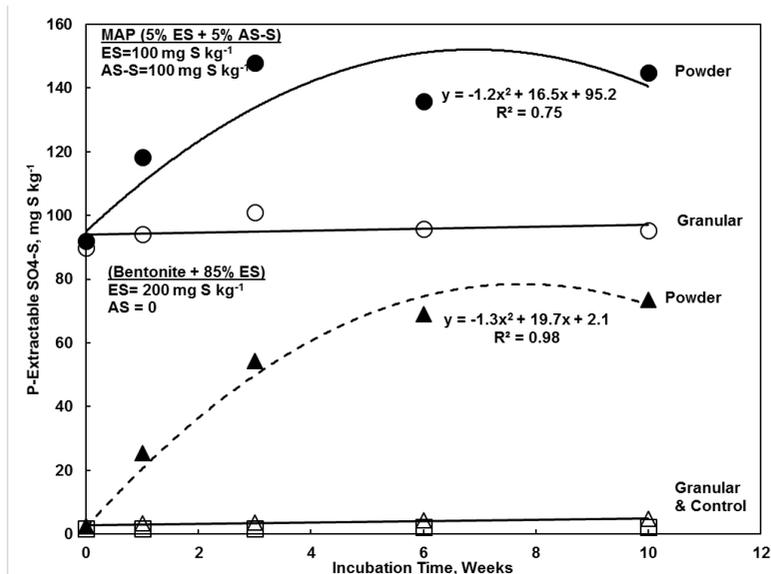
Fig. 1: Oxidation of ES of granular MAP-(5% ES + 5% AS-S) and (Bentonite + 85% ES) and their same but finely ground powder (< 0.15 mm) in a sandy loam soil (pH 6.4) during incubation (Chien et al., 2016b).

The study by Janzen (1990) showed that the non-mixed ES particles with soil could be considered to mimic the disintegrated ES granule without dispersion. The only contact between ES particles with soil would be limited to a very small surface area of outer ES particles. In this study, ES oxidation rate was < 8 µg S cm^{-2} day^{-1} in the two soils. The ES oxidation rate did not increase with increasing soil volume (or weight) until ES particles were mixed with soil weight higher than 50 g (Fig. 2). Assuming the soil bulk density was 1.25 Mg m^{-3}, it suggests that 1 g of ES particles must be mixed with a minimum of 40 cm3 of soil to initiate an increase in ES oxidation. After that, a steady, almost linear increase in ES oxidation rate to 40 – 50 µg S cm^{-2} day^{-1} was observed with 1 g of ES particles mixed with 1 kg or 800 cm^3 of the soils (Fig. 2b). For commercial-grade granular fertilisers containing ES with or without AS, the granule sizes generally passed a sieve opening of 3.35 mm but we retained on an opening of 1.00 mm with an average diameter = 2.22 mm or radius (r) = 1.11 mm and granule volume = (4/3) x π r^3 = (4/3) x 3.1416 x $(1.11)^3$ = 5.73 mm^3. The specific gravity of solid ES is 1.92 – 2.07 Mg m^{-3} with an average of 2 Mg m^{-3} (or 2 g cm^{-3}). Therefore, 1 g of granular ES has a volume of 0.5 cm^3 (or 500 mm^3) with about 500/5.73 ≈ 87 granules. After disintegration, the ES particles must disperse within a soil volume equivalent to at least (40 x 103) / (5.73 x 87) ≈ 80 times the volume of 1 g of ES granules before a significant ES oxidation could begin to occur in 35 days. In commercial application, unless the soil is mixed with the ES particles by ploughing, this dispersion of ES particles from ES granules is limited even when granulated with bentonite. According to the manufacturers, the bentonite-
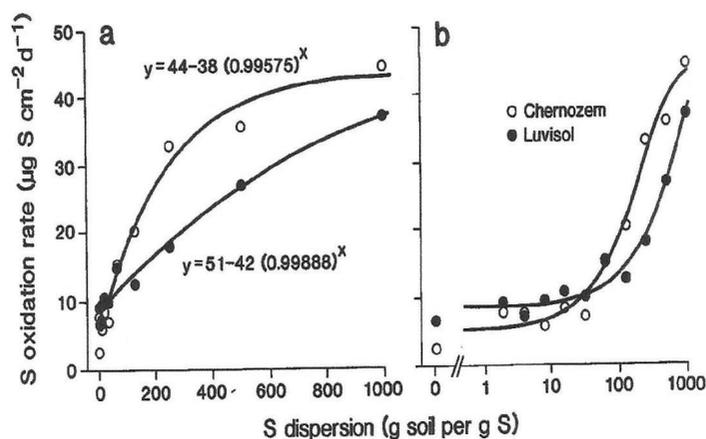
Fig. 2: Oxidation rate of fine ES particles (87 μm) mixed with various amounts of two soils during soil incubation (a) regular S rate and (b) log scale of S rate (Janzen, 1990).

ES granules could expand up to a range of 5-7 (mean = 6) times higher than its volume (no supported data). For example, a volume of 1 g of bentonite-ES granules could expand to 0.5 cm³ x 6 = 3 cm³. This is way below the minimum 40 cm³ of soil volume that is required for 1 g of bentonite-ES granules to begin ES oxidation as shown in Fig.. 2b. The theoretical calculation thus supports the lack of oxidation of granular (ES±AS) products due to the localised ES particles even after the disintegration of ES granules, whereas the ground ES particles rapidly oxidised in the sandy loam soil as shown in Fig. 1.

ES Oxidation in Laboratory Soil Incubation Study with Leaching

In another study, Degryse *et al.* (2016a) applied a column study to minimisze possible immobiliszation of SO_4-S by soil organic matter after ES oxidation by mixing three soils with granular (ES±AS) sources at 24 mg total S per soil column. The soil columns were immediately leached to remove SO_4-S and then the soil columns were incubated at 25 ºC and leached at regular time intervals to remove SO_4-S that was produced by ES oxidation. Three S sources used were: (1) ES particles, (2) granulated bentonite-ES (ES pastille) containing 90% ES and 10% bentonite, and (3) co-granulated MAP-(ES+AS) containing (5% ES + 5% AS-S). The results with the Edmonton soil (Fig. 3) show that the ES oxidation increased in the order of ES particles > granular MAP-(ES+AS) > (bentonite+ ES) pastille. Although ES particles of both (bentonite +ES) pastille and MAP-(ES+AS) were in granular form, ES oxidation of ES pastille was much lower than MAP-(ES+AS) (Fig. 3).

It should be pointed out that percentage of S recovered in leachate for SO4-S for MAP-(ES+AS) granules was based on 12 mg ES per column because MAP-(ES+AS) contained only 50% of total S as ES whereas it was based on 24 mg ES
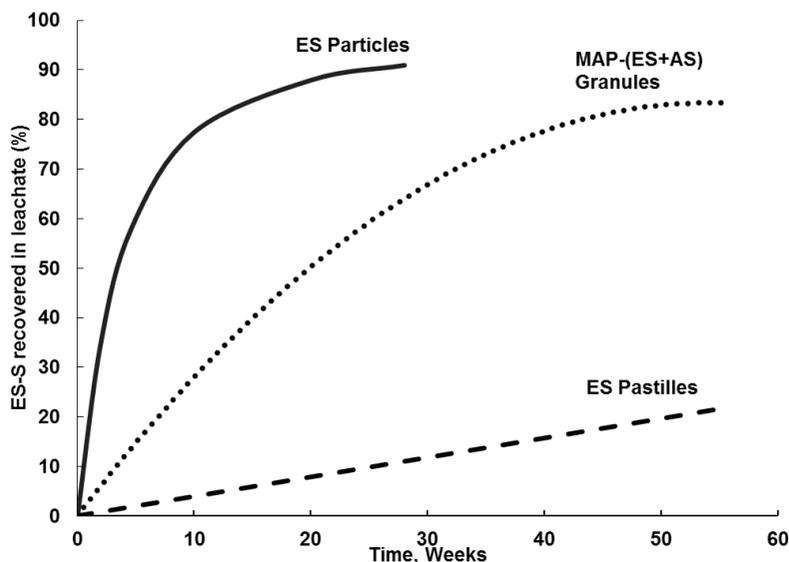
Fig. 3: Recovered SO4-S in leachate from ES oxidation of ES particles, granular ES pastilles and granular MAP- (5%ES+5%AS-S) in soil columns under leaching conditions (adapted from Degryse et al., 2016a).

per column for ES particles and ES pastilles as shown in Fig. 3. This is important when comparing ES oxidation of ES particles with that of MAP-(ES+AS) granules. For example, about 90% of 24 mg of ES added for ES particles and 50% of 12 mg of ES added for MAP-(ES+AS) granules were oxidised after 20 weeks (Fig. 3). The actual amount of ES oxidation from ES particles was 0.90 x 24 = 21.6 mg SO_4-S whereas the amount of ES oxidation from MAP-(ES+AS) granules was 0.50 x 12 = 6.0 mg SO4-S. Therefore, it is incorrect to compare 90% of ES oxidation from ES particles with 50% of ES oxidation from MAP-(ES+AS) granules at 20 weeks. The best unbiased comparison should be based on the same amount of ES applied. In this case, 48 mg of total S per soil column of granular MAP-(ES+AS) that provided 24 mg ES per soil column should be compared with the same amount of 24 mg of ES particles per soil column in terms of ES oxidation so that both S sources provided the same amount of 24 mg ES per column in order to study the effect of particle-size or granule-size on ES oxidation in soils.

The poorer ES oxidation of granular MAP-(ES+AS) than that of ES particles shown in Fig. 3 is due to the negative locality effect on ES oxidation as discussed previously. The granular ES pastille that had the least ES oxidation was due to, in addition to the locality effect, the physical hardness of the ES pastilles that did not significantly break down or disintegrate into the ES particles as revealed by nearly intact pastilles in the soil columns at the end of incubation (Degryse *et al.*, 2016a). The data of % ES oxidation with the three soils treated with S sources at 20 weeks are shown in Table 2. ES pastilles were found to have very poor ES oxidation to SO4-S (0-5%), similar to the results shown in Fig. 3. Oxidation of

TABLE 2

ES-S recovered in the form of SO_4-S in leachate from soil columns treated with different soils and S sources following incubation for 20 weeks (estimated from Degryse *et al.*, 2016a)

Soil	S Source	ES-S Recovered in Leachate, % of ES
Edmonton, Canada	ES Particles	90
	Granular MAP-(5%ES+5%AS-S)	50
	ES Pastilles	5
Beardstown, USA	ES Particles	95
	Granular MAP-(5%ES+5%AS-S)	10
	ES Pastilles	0
Sorriso, Brazil	ES Particles	95
	Granular MAP-(4.5%ES+4.5%AS-S)	40
	Granular MAP-(7.5%ES+7.5%AS-S)	40
	ES Pastilles	5

granular MAP-(ES+AS) products in the soils at 20 weeks (equivalent to 5 months of maximum general annual crop growth to maturity) was much lower (10-50%) than that of ES fine particles (70-90%). This suggests that these granular MAP-(ES+AS) products are not effective as SO_4-S sources for the initial S effect on crop growth.

Zhao *et al*. (2016) estimated that the rates of ES oxidation after 20 weeks in an incubated sandy soil (90% sand) mixed with 200 mg S kg^{-1} were 36% and 95%, for co-granulated (DAP+ES) and powdered ES products, respectively. They explained that the slow oxidation of co-granulated ES was due to the limited access of S oxidisers to the interior of the granule because of inadequate dispersion of ES particles in the soil. Therefore, the findings of Degryse *et al*. (2016a) and Zhao *et al*. (2016) suggest that the oxidation of granular NP-ES products could hardly provide adequate available S at the latter stages of crop growth to maturity and put in at risk the strategy of using granular NP-(ES±AS) to supply S for the whole cycle.

General Discussion on ES Oxidation

Soil leaching may confound the evaluation of the degree of ES oxidation for the granular NP-(ES+AS) products in soil incubation. Under leaching conditions,

mass flow of water may carry small clay particles which may intermix with very fine ES particles from top to bottom in the soil columns. Thus, ES particles may be dispersed wider under leaching than that of the same soil without leaching. If so, the degree of ES oxidation of the granular NP-(ES+AS) products may be higher with leaching than without leaching. Research is needed to test this hypothesis so that a proper comparison of ES oxidation may be made.

It has been claimed by manufacturers that granular ES and NP-ES products can provide available S through ES oxidation during the season of application. Regarding granular NP-(ES+AS) products, it has been claimed that AS provides available S during the crop vegetative stages while ES oxidation provides available S during the later reproductive stages to maturity. For cereal crops such as maize, the average vegetative growth to VT stage (tassel fully extended) is around 65-72 days after seeding and around 128-135 days to maturity for harvest at R6 stage. Therefore, oxidation of granular ES would be expected to provide available S at least before 20 weeks to maturity. However, data from Degryse *et al.* (2016a) in Table 2 indicate that the ES oxidation of different granular bentonite-ES or MAP-(ES+AS) products at 20 weeks in different soils under favourable leaching conditions for ES oxidation ranged only between 0 and 5% or 10 and 50% of ES applied, respectively. They estimated that with yearly applications, 40% of ES applied in the current year would be expected to oxidise under these soil and climate conditions, but also circa 30% of ES added in the previous year and circa 20% of ES applied in the year before that, i.e., after three to four years, the ES that oxidises within a growing season would be expected to approach the added ES rate. In other words, it is questionable that the ES oxidation of granular bentonite-ES or NP-(ES+AS) products would be able to provide adequate available S to the first season or in the first year after application. The limited agronomic field results presented by Chien *et al.* (2016a) tend to confirm this suggestion.

The lack of a significant increase in powdered ES oxidation from 6 to 10 weeks in the sandy loam soil (Fig. 1) is probably, in part, due to an increased soil acidity induced by ES oxidation. It is known that the rate of ES oxidation decreases with increasing soil acidity as described by Barrow (1971). In the a soil incubation study with the sandy texture soil at pH 6.7 (Zhao *et al.*, 2016), soil pH values after 20 weeks were: control = 6.3, granular (DAP+ES) = 5.8, and powdered (DAP+ES) = 5.0. To remove excess salt and protons generated by the ES oxidation, leaching was performed at 5 weeks by adding artificial rain water. Despite the lower pH with the powdered ES than the granular ES, % of ES oxidation of powdered ES (95%) was much higher than that of granular ES (36%). Thus the extent of ES oxidation of the granular ES products may be influenced by the pH-buffering capacity of the soils (sandy versus clayey) used, in addition to other factors such as temperature, aeration, moisture and biological activity.

Degryse *et al*. (2016b) developed a conceptual model to predict the "effective diameter" for the ES oxidation of granular NP-(ES±AS) products including MAP-(ES+AS) discussed in the present article. The "effective diameter" was defined as an imagine(imagined??) diameter of ES particles mixed through soil that would

oxidise at the same rate as the granulated ES by taking into account the effect of granulation on the effective surface area available to the ES in the granule cavity after the soluble macronutrient compound in the granule has diffused.

One application of the model to commercial products is to predict the effect of granule size on ES oxidation (Degryse *et al.*, 2016b). For example, comparing small and large granules of ES with diameter = 1.8 mm (10-mesh) and 3.4 mm (6-mesh), the predicted "effective diameters" are 81 and 153 μm, respectively, based on the same ES particle-size (25 μm) and mass fraction of ES (0.05 or 5%) in the MAP-(ES+AS) granule. After 140 days (20 weeks), the estimated ES oxidation rates of the smaller and larger granules would be about 90% and 50% of ES applied, respectively. Therefore, the MAP-(5%ES+5%AS-S) product with a granule size of 3.4 mm would have only 50% of applied ES oxidised, which may not provide adequate available SO_4-S during the later stages of crop growth to reach maturity, or the S rate would have to be increased to compensate the partial oxidation of ES.

It is noted that large granular MAP/DAP products are often bulk-blended with other large granular N (e.g., urea) and K (e.g., KCl) sources to form popular N-P-K compound fertilisers (Schultz, 1998). Thus smaller granular MAP/DAP-(ES+AS) products (e.g., 1.8-mm granule size), which may increase ES oxidation rate, may be incompatible with other larger granular N and K fertilisers (e.g., 3.4-mm granule size) for bulk-blending because of potential segregation problem.

CONCLUSIONS

Oxidation of ES from the granular NP-ES or NP-(ES+AS) products was nil (0-5%) or low (40-50%) for up to 20 weeks in laboratory studies using procedures of static soil incubation or soil columns under leaching conditions. The results of greenhouse studies also showed very low or inadequate ES oxidation of granular NP-ES or NP-(ES+AS) products to provide available S to first crops compared with SO4-S sources such as gypsum and AS. The nil or inadequate ES oxidation from the granular NP-ES or NP-(ES+AS) products is due to locality effect, which significantly reduces surface area of ES particles in contact with ES oxidising microbes. The reason is that following granule disintegration and release of the fine ES particles, these clusters in large aggregates around the granule's application site within the soil. These granular ES products, however, may have long-term residual S effect, especially under field conditions. In this review article, the initial, not residual, S effect is the main issue for discussion since the fertiliser producers have claimed that these ES products are as effective as SO_4-S sources even in the first year for the season-long or first crops. It is concluded that ES oxidation of these granular S fertilisers is often is too slow or inadequate to provide initial available SO_4-S. Therefore, granular ES products are generally inferior to SO_4-S fertilisers in agronomic effectiveness.

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