

## **Sulphur-enhanced triple superphosphate as a substitute for single superphosphate**

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### **Abstract**

Single superphosphate (SSP) production in Australia and New Zealand is declining due to the ageing of production facilities, the high transport costs of a relatively low nutrient density fertiliser and the generally unbalanced P: S ratio in the fertiliser. A process has been developed by Shell to add elemental S to triple superphosphate (TSPS) which can vary the P:S ratio and the ratio of sulphate to elemental S. A feature of the Shell "Thiogro" process is the ability to incorporate microfine elemental S into the fertiliser granule.

Previous research at UNE has found that a ratio of 2P:1S and 1 sulphate: 3 elemental S to be generally appropriate for pastures. Growth chamber, glasshouse and field trials in Australia, and field trials in Brazil, have demonstrated the efficacy of this new fertiliser. The development of this TSPS fertiliser follows on from similar developments where S has been added to di-ammonium phosphate (DAP) and mono-ammonium phosphate (MAP). As sulphur deficiency becomes increasingly evident in Australia, and throughout the world, these fertilisers are anticipated to play an increasing role in sustaining crop and pasture production.

### **Key Words**

phosphorus, fertiliser, oxidation, elemental sulphur, sulfur

### **Introduction**

There are three major drivers of change in SSP usage. The first is the variation in returns from wool and meat in traditional pasture areas. This, together with the observation that responses to single superphosphate (SSP) are not as noticeable after several years of application due to increased soil P and S levels. Producers are often heard say "My pastures don't need P because I have applied 20 cwt of SSP over 30 years" not realizing that the application rates used, and the infrequency of applications, was generally below maintenance. Because of the poor uptake of soil testing in pastures many producers do not know the P and S status of there soils.

The second reason is the increased transport and spreading costs. Cartage to the New England region of NSW from Newcastle costs \$59/t and ground spreading \$45/t so that these costs are lower/unit P for more concentrated P sources.

The third reason is the move from pasture rotations in cropping areas to continuous cropping with the SSP in the pasture phase being replaced by ammonium phosphates in the crops. Incitec Pivot has closed the Cockle Creek and Geelong SSP plants and this is having a major impact on the supply of SSP in Australia. Given the trend in the world fertiliser industry of capital investments being made in DAP, MAP and TSP plants it is unlikely that substantial capital will be put into the current SSP plants in Victoria, Tasmania and Western Australia as they age. TSP could potentially be used to replace SSP but current availability in Australia is low, and it contains little S.

Although DAP and MAP are widely available, both from domestic production and imports, the lack of value placed on the N it contains for pastures, and the lack of S, means that they are unlikely to substitute for SSP even when S is added to them.

*The alternative*

There is a significant world TSP production capacity to supply the total phosphate needs of Australia and New Zealand and adding S to this could provide an SSP substitute. The S can be added either as sulphate or elemental S. The model of C, N, P and S cycling in grazed pastures developed by McCaskill and Blair (1988) indicates that a P:S ratio of 2:1 in pasture fertiliser would meet the P and S needs in most situations.

This can be done by coating with elemental S or gypsum, incorporation of elemental S into TSP during manufacture or physical mixing with elemental S/bentonite or granulated gypsum prills.

If sulphate S in a form such as gypsum was added to TSP to achieve this 2P:1S ratio the P concentration in the TSP would be reduced by one third, thus losing the concentrated nutrient benefits of the TSP. This leaves elemental S as the candidate material to add to the TSP. For the elemental S to become available to the plant soon after application it must be applied in fine particles ( $<75\mu\text{m}$ ), and preparation of this material is difficult because of the potential explosion risk. This has led to a number of elemental S/Bentonite products, commonly containing 10% bentonite, being developed. These are generally ineffective because the amount and quality of the bentonite used is compromised by the need to avoid it absorbing water and expanding in the bag or pile prior to application and releasing the S particles in the soil for S oxidation.

Another attraction of elemental S is the likely future marked reduction in price for this commodity. Increased recoveries of S from refineries needing to make cleaner petrol and diesel, together with increased recoveries from new gas fields being opened up in the Middle East and Central Europe will likely increase supply dramatically.

#### *Development of Shell "Thiogro" fertilizers*

Elemental S is an almost ideal fertilizer as it contains 100% nutrients. The elemental S must be oxidized to sulphate before it is available to plants and since microorganisms carry out this process it is moisture and temperature dependant, as is the crop demand for S. The rate of oxidation is also dependent on the particle size of S. This means that there is great scope to manage the release rate of sulphate to the plant to maximize plant uptake and minimize losses by surface runoff and leaching.

Research carried out by Blair et al (1979) has shown that plants require S and P early in growth and that oxidation rates are enhanced by intimate mixing of P and elemental S (Lefroy et al 1997), which makes S inclusion into P containing fertilizers an attractive proposition.

Shell Canada invented the Shell "Thiogro" process to include microfine elemental S into DAP and MAP and TSP. A significant feature of the process is that different proportions of elemental S and sulphate can be included in the fertiliser and elemental S is distributed throughout the fertilizer granule.

A series of trials have been conducted to evaluate the performance of TSPS, and other sulphur enhanced DAP and MAP fertilizers, and the results of some of them are reported here.

### **Methods**

#### *S oxidation from elemental S*

S oxidation from sized elemental S was determined by incubation of triplicate samples in soil maintained at field capacity in a cabinet set at 28/18°C (14 hour day/10 hour night) over an 87 day period. The amount of sulphate S produced from oxidation was determined by extraction in water and measurement by ICP.

#### *Growth chamber*

S oxidation from Shell “Thiogro” was determined in plant growth chambers at the University of New England (UNE), Armidale using the carrier free  $\text{Ca}^{35}\text{SO}_4$  reverse dilution technique. Triplicate pots of Ryegrass (*Lolium perenne*) and rhodes grass (*Chloris gayana*) were grown at temperatures of 22/14 °C and 34/26 °C (14 hour day/10 hour night), respectively, for 9 weeks.

#### *Glasshouse trial*

A glasshouse trial was undertaken at UNE using an S deficient soil of granitic origin. S was applied at a rate equivalent to 15 kg/ha in the forms shown in Table 1 and N, P and K balanced between treatments.

All fertilisers were mixed throughout the entire soil volume and the soil was maintained near field capacity in a glasshouse set at 30°C day, and 20°C night temperatures and the maize grown for six weeks.

#### *Pasture trial*

A pasture trial, supported by Shell, comparing SSP and TSPS was established in January, 2010 by over sowing white clover and fescue on an old pasture area that had been sprayed with glyphosate. SSP was applied at the commonly used application rate of 18 kg P/ha and TSPS (0:19.2:0:10S) was applied to either supply the same rate of P/ha or on the basis of an equal on-ground cost as SSP.

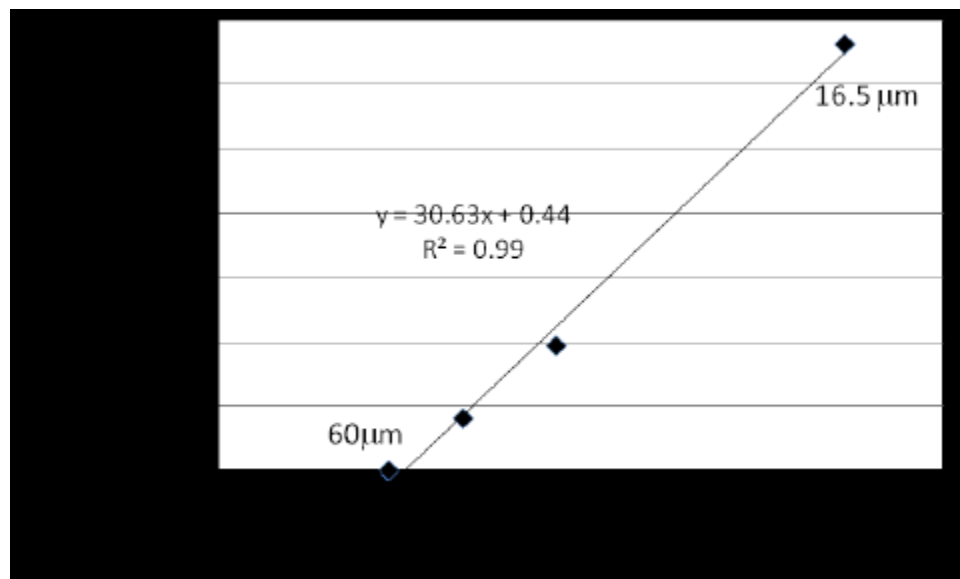
#### *Cropping trial*

A relay cropping trial, supported by Shell, has been undertaken on a virgin soil at the Embrapa, Cerrado Research Station, Brazil. Fertilisers were applied to a soybean/wheat/ soybean/wheat rotation to measure initial and the residual effects of a range of S containing fertilizers, including gypsum and TSPS.

## Results

### *S oxidation from elemental S*

The importance of particle size in determining S oxidation rate is highlighted by the data in Figure 1. Particle sizes ranged from a mean of 16.5 µm to 60 µm and oxidation rate was linearly related to 1/particle diameter, which is a measure of surface area. There was a more than doubling of daily S oxidation rate over this particle size range.



**Figure 1. Effect of elemental S particle size on relative S oxidation**

### *Plant uptake of S from Shell “Thiogro”*

At the end of the 9 week growth period in the growth chamber study an average of 23.6% of fertilizer S was recovered in the plant tops from DAP and MAP based Shell “Thiogro” with no significant effect of temperature. This compares with 73.2% from gypsum in rhodes grass and 54.1% in ryegrass. This luxury uptake of sulphate early in the growth cycle often ends up in urine patches and animal camps and is effectively lost from the system. The more metered uptake of oxidised sulphate reduces this problem.

### *Glasshouse trial*

There was a significant yield response to P (TSP v control) and all S sources produced higher yields than TSP (Table 1). Yields from gypsum and TSP-S were not significantly different from each other despite them being an approximate fourfold difference in S uptake between the two treatments.

The importance of elemental S particle science is highlighted by the data from the two particles size treatments Shown in Table 1. Yield and S uptake was higher in the 53µm than the 106µm treatment.

**Table 1. Yield and S uptake of maize grown in an S deficient soil in a glasshouse at the University of New England.**

Treatment	Maize tops yield (g/pot)	S uptake (mg/pot)
Control (-P,-S)	3.25 e	2.1 f
TSP (-S)	4.12 d	3.2 e
Gypsum	4.79 bc	11.6 a
TSPS	4.58 c	3.9 d
Elemental S 106µm <sup>A</sup>	5.07 b	5.9 c
Elemental S 53µm <sup>A</sup>	5.43 a	7.2 b

<sup>A</sup> mean particle size

### *Pasture trial*

There was a significant increase in pasture yield to the S in both the SSP and TSPS treatments in the harvest made on April 21, 2010 (Table 2) and there was no significant difference between SSP and TSPS when applied at the same dollar value as SSP. The TSPS treatment received 3 kg P/ha more and 11 kg S/ha less than the SSP treatment. When TSPS was applied at the same the rate/ha as SSP there was a marked reduction in yield due to the lower S application rate (Table 2). Pasture S uptake rate did not differ significantly between the minus S control and TSPS applied at the same rate as in SSP. There was no significant difference in S uptake between SSP and TSPS when applied at the same dollar value, although the uptake in SSP tended to be higher. When the uptake is expressed as apparent S recovery approximately 5% of the fertiliser S in SSP had been taken up compared to 1% from TSP-S, applied at the same dollar value (Table 2).

**Table 2. Pasture yield (kg/ha) in the first cut taken after fertiliser application and Armidale, NSW**

Fertiliser	P applied (kg/ha)	S applied (kg/ha)	Pasture dry matter yield (kg/ha)	S uptake (kg/ha)	Apparent S Recovery (%)
Control (-S)	0	0	521 c	1.70c	
SSP	18	22	694 ab	2.82ab	5.1
TSPS 7-946, P=P in SSP	18	9	494cd	1.70c	0.0
TSPS 7-946, \$=\$ in SSP	21	11	616 bc	1.81bc	1.0

*Cropping trial*

There was no response to TSP S in the wheat crop grown after the first application (Table 3). The fertiliser used was a prototype material which contained only 0.1% sulphate sulphur and the site had never been fertilised with elemental sulphur and hence the sulphur oxidising bacterial population would be expected to be low. When soybeans were grown on residual fertiliser there was no difference in yield between the gypsum and TSPS treatments indicating that oxidation of the elemental S in the TSP had commenced.

**Table 3. Response of wheat and soya beans to applications of gypsum and TSP-S in Brazil.**

Fertiliser crop 2	Relative wheat grain yield	Fertiliser crop 3	Relative soybean grain yield
MAP	100a	MAP	100a
Gypsum	138b	MAP	114b
TSPS	103a	MAP	115b

**Conclusion**

As existing single superphosphate plants in Australia age it is unlikely that they will be replaced. World capacity for SSP production has declined significantly in the past 20 years or so importation of SSP is unlikely. This, together with increased transportation and spreading costs of a relatively low analysis fertiliser like SSP make it in its continual use less attractive.

Technology is available to incorporate microfine elemental S into triple superphosphate and laboratory, growth chamber, glasshouse and field research research has shown that this S oxidises to plant available sulphate provided it is in a microfine form. The Shell "Thiogro" technology provides such microfine elemental S in TSP and has the technology has the capacity to be able to vary the sulphate/elemental S

ratio in the fertiliser. These characteristics, together with its high nutrient density, make it a good candidate to replace SSP

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