

# In situ acidulation of rock phosphate

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## Abstract

The ability to utilize local rock phosphate (RP) deposits is often limited by the availability of the P they contain. Application of fine elemental S (ES) with ground rock phosphate is a potential way to alleviate this problem and to supply S to the plants. An experiment was conducted, using North Carolina rock phosphate, to examine the impact of incorporation of fine elemental S into the fertilizer granule. The application of a sulfate basal allowed the impact of P availability to be studied. There was an almost doubling in the yield in the first six weeks after application of rock phosphate + elemental S compared to rock phosphate alone which was attributable to the increased P availability (4.6% with RP, 10.3% with RP+ES) brought about by in situ acidulation of the rock phosphate. In the second six week period, where basal P was applied, the S in the fertilizer granule was shown to continue being oxidized. These rock phosphate/elemental S assemblages could prove very beneficial in remote areas and in developing countries where fertiliser production facilities are limited.

## Key words

Phosphorus, sulfur, sulphur, fertilizer, fertiliser

## Introduction

There are many rock phosphate deposits in developing countries which would be useful to local agriculture if there was a local facility to convert the slowly soluble octacalcium phosphate to plant available orthophosphate. One of the earliest reports on rock phosphate/elemental S fusions is that of Kittoe and Attoe (1965). Swaby (1975) found that the effectiveness of rock phosphate/elemental sulfur (S) assemblages (Biosupers) was dependent on the reactivity of the rock phosphate (RP), to a certain extent on the granule size, the P retention capacity of soil, the duration of cropping and soil moisture and temperature as they effect S oxidation. Freisen et al. (1987) showed that addition of elemental S to various rock phosphates resulted in acidulation of the rock over time.

One of the main factors which affects S oxidation rate and hence potential acidulation rate, is the particle size of the elemental S. Dry grinding of elemental S can be hazardous due to the explosivity of the fine dust. Recent advances in wet grinding technology (eg. US Patents 4372872A, US8679219 B2) have reduced this hazard and it is now feasible to safely prepare fine elemental S. As an alternative molten elemental S can potentially be added to crushed RP during granulation. The aim of the study reported here was to examine the impact on P availability from North Carolina rock phosphate resulting from the addition fine elemental S.

## Materials and Methods

The study was undertaken in a glasshouse at the University of New England, Armidale, NSW, Australia. A Tenosol soil of granitic origin, known to be S deficient was collected from the Kirby Experimental Station of the University. The soil was collected from the 0-30 cm horizon, dried, ground, and passed through a 2.0 mm sieve. The total S concentration in the soil was 204 µg/g and KCl-40 S was 1.3 µg/g.

PVC plastic pots with an inside diameter of 15 cm and 12 cm depth were filled with 1.3 kg of soil and watered gradually over two weeks to leach out sulfate. The pots were allowed to stand until the soil was drained to field capacity. The solid fertilizer treatments shown in Table 1, along with a small amount of soil which previously received elemental S to act as an inoculum for *Thiomonas* (an elemental S oxidizing bacteria), were applied to the surface of this soil layer and an additional 200 g of soil and placed on top of the 1.3 kg soil. There were 4 treatments (Table 1) with three replicates. All treatments received P at a rate equivalent to 45 kg/ha either in the fertiliser or as an addition of DAP in the SSP and ES treatment. S was applied at 15 kg/ha (27 mg/pot) in the SSP and ES treatments based on pot surface area. Additional S was

applied as ammonium sulfate in the RP and RP+ES treatments to remove S nutritional effects so differences in P availability could be detected. N, P, K and Mg were applied to all treatments at rates of 80, 45, 40 and 10 kg/ha, respectively as Urea, DAP, KCl, and MgCl<sub>2</sub>. The rock phosphate used was from the North Carolina deposit which was ground to <250 µm and the elemental S had a particle size <75 µm. The RP and RP+ES fertilisers were granulated into 2-3 mm granules using calcium lignosulfonate as the binder and elemental S was added at the rate of 10.7%. The rock phosphate and RP+ elemental S treatments received 26 mg per pot of as ammonium sulfate S to remove any nutritional effects of S.

**Table 1. Fertilisers used in the experiment**

Treatment	Analysis				
	N	P	S	Sulfate	Elemental
Control (+P-S)					
Single superphosphate (SSP)	0	8.6	11	11	0
Rock phosphate (RP)	0	13	0	0	0
RP+ elemental S (RP+ES)	0	11	10.7	0	10.7

The pots were set up in the glasshouse and the soil maintained at field capacity for two weeks to initiate S oxidation before the first planting. Four 4-day old pre-germinated seeds of maize were sown in each pot to a depth of 2-2.5 cm. The pots were then watered to near field capacity within one week. After one week plants were thinned to two healthy plants per pot and the moisture content adjusted to field capacity and maintained with tap water for the majority of the experiment. Excess water was applied at intervals to leach out sulfate to simulate field conditions. The temperature of the glasshouse was maintained at 20-30°C throughout the first crop in the experiment which was grown for 5 weeks.

After this first crop the soil in the pots was allowed to air dry and the pots containing the soil were stored for 10 weeks before the second crop was planted. At the commencement of the second crop the pots were first watered to above field capacity and to leach out sulfate before being replanted with maize as in the first planting. P was applied at a rate equivalent to 45 kg/ha as diammonium phosphate to all treatments. This was done to remove P limitations to growth to see if S was still being oxidized in the RP+ elemental S treatment. The crop was grown for 6 weeks. Additional urea was applied throughout both trials to ensure that nitrogen deficiency did not limit plant growth.

Maize tops were harvested cutting plants 1.5 cm above the soil surface. The harvested tops were dried in an oven at 60°C until constant weight. The dry plant tops were weighted and ground to pass a 1 mm screen and analyzed using Ultrawave Microwave Digestion with nitric acid. Total P and S, as well as other macronutrients and micronutrients were measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). P and S recovery was determined from chemical analysis of the harvested tops.

## Results and discussion

There was a substantial response to S, applied as sulfate, in the first crop (compare control and SSP treatments in Table 2). Although the same amount of P and S were applied to the SSP, RP and RP + ES treatments yields were significantly lower in the latter two treatments than in the SSP treatment indicating a lower availability of P in the RP treatment which was supported by P content data. The yield in the RP+ES treatment was significantly higher than in the RP treatment although the same amount of S had been applied to both treatments (basal ammonium sulfate applied) indicating that the elemental S in the RP+ES treatment increased P availability. This is supported by the P content data for these two treatments. Despite the same amount of S being applied in the SSP and RP treatments the highest S content was in the SSP treatment which was the result of the higher P availability in this treatment. The higher P and S contents in the RP+ES treatment compared to the RP alone treatment are the result of increased P availability in the RP+ES resulting from the acidulation of the RP from elemental S oxidation.

**Table 2. Tops dry weight yield (g/pot) and tops P and S contents (mg/pot) of maize in crops 1 and 2.**

Treatment	Tops DWt (g/pot)	P content (mg/pot)	S content (mg/pot)
<i>Crop 1</i>			
Control (+P-S)	8.46 b <sup>A</sup>	26.9 b	4.9 c
Single superphosphate (SSP)	17.40 a	35.3 a	19.5 a
Rock phosphate (RP)	3.09 c	3.7 d	4.8 c
RP+ elemental S (RP+ES)	6.93 b	8.3 c	14.1 b
<i>Crop 2</i>			
Control (+P-S)	2.71 b	26.2 c	2.1 b
Single superphosphate (SSP)	5.11 a	36.2 bc	5.8 b
Rock phosphate (RP)	4.69 a	43.4 a	4.0 b
RP+ elemental S (RP+ES)	5.57 a	39.5 ab	16.5 a

<sup>A</sup> Within a crop numbers in a column followed by the same letter are not significantly different according to DMRT

In the second crop the maize tops yield was significantly higher in the three fertiliser treatments than in the control (Table 2) indicating that the soil was S deficient. When P was applied to all treatments in the second crop there was no significant difference in yield between the three fertiliser treatments (Table 2) indicating that P and S availability was adequate for plant growth in each treatment. The highest S content was found in the RP+ES treatment which is the only treatment where ES had been applied. This suggests that the sulfate in the SSP and in the ammonium sulfate applied as a basal in the RP and RP+ES treatments had been leached.

In the first crop there was a higher percent P recovery in the SSP treatment than in the control despite both having the same P application rate presumably because a lack of S in the control limited yield. The apparent S recovery from SSP treatment was 56% (Table 3). The % P recovery in the RP and RP +ES treatments was significantly lower than from SSP. The % P recovery and apparent fertilizer S recovery was higher in the RP+ ES treatment compared to RP alone suggesting that the oxidation of elemental S in the fertilizer granules had increased the availability of P.

**Table 3. P and S recovery in plant tops**

Treatment	% P recovery	% Apparent fertiliser S recovery
<i>Crop 1</i>		
Control (+P-S)	33.7 b <sup>A</sup>	
Single superphosphate (SSP)	44.2 a	56.0 a
Rock phosphate (RP)	4.6 d	0.0 c
RP+ elemental S (RP+ES)	10.3 c	8.9 b
<i>Crop 2</i>		
Control (+P-S)	16.3 b	
Single superphosphate (SSP)	22.6 a	14.2 a
Rock phosphate (RP)	27.2 a	7.2 b
RP+ elemental S (RP+ES)	24.9 a	14.0 a
<i>Crop 1+2</i>		
Control (+P-S)	50.0 b	
Single superphosphate (SSP)	66.8 a	70.2 a
Rock phosphate (RP)	31.7 c	6.7 c
RP+ elemental S (RP+ES)	35.3 c	22.9 b

<sup>A</sup> Within a crop numbers in a column followed by the same letter are not significantly different according to DMRT

In the second crop the %P recovery was higher in the three fertiliser treatments compared to the control because of higher yields in these treatments. The apparent fertiliser S recovery was not significantly different between the SSP and RP+ES treatments and both were higher than the RP treatment (Table 3) suggesting again that the elemental S in the fertiliser granules was being oxidized to plant available sulfate.

The results for crop 1 clearly showed that elemental S added to the RP had oxidized and that this led to an increase in % P recovery. The application of P to all treatments in crop 2 allowed an examination of the fertilizer S supply and the approximate doubling in the % apparent fertilizer S recovery indicated that S oxidation continued through this growth period.

Although the % P recovery in the RP treatments was only approximately 50% of that from SSP over this short experimental period the results are encouraging and indicate the need for further studies. Such studies are under way using rocks of different reactivity. Improved procedures for producing fine elemental S potentially make it possible to produce agronomically attractive fertiliser at the phosphate mine site without the need for expensive infrastructure. This is particularly important in remote areas of Australia where phosphate deposits occur and in developing countries.

### References

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