

CHAPTER 1

INTRODUCTION

Sulfur (S) is one of the major nutrients required by plants for their growth. Generally, it is referred to as the fourth essential nutrient in crop production after nitrogen (N), phosphorus (P) and potassium (K) (Olson and Rehm, 1986). S is a major constituent of three amino acids, viz; cystine, cysteine and methionine, and various other compounds in plants (Russell, 1973; Anderson, 1975; Thomson *et al.*, 1986). Its deficiency results in reduced crop growth and yield, as well as poor crop quality (Blair and Till, 1981). S deficiency can also affect enzyme synthesis.

Despite its importance as an essential plant nutrient, it has received little attention compared to N, P and K and only in the recent past, has its significance been recognized. Evans (1975), advanced a number of reasons as to why there is increasing recognition of S deficiency. He pointed out that many cereals and other crops remove more than 20 kg S/ha/yr, while Cruciferae and Liliaceae remove as much as 70 kg S/ha/yr and with the reductions in S inputs, the incidence of S deficiency is becoming widespread. Sulfur deficiency has now been widely recognized in many countries (Morris, 1987) and in rice, S deficiency is widespread in most rice growing regions, particularly in Southeast Asia (Blair, 1983; Ismunadji *et al.*, 1983; Mamaril *et al.*, 1983; Hoult *et al.*, 1983), Latin America (Wang *et al.*, 1976), and Africa (Osiname and Kang, 1975). Blair *et al.* (1979a), attributed the increasing incidence of S deficiency to the following factors:

- The increasing use of high analysis, low S containing fertilisers;
- The increase in crop yields obtained as a result of other technological advances;
- The decreasing use of S containing pesticides and fungicides;
- The environmental control of sulfur dioxide emissions in industrial areas;
- Where responses to fertilisers such as $(\text{NH}_4)_2\text{SO}_4$, K_2SO_4 , ZnSO_4 and superphosphate have been attributed solely to N, K, Zn and P. This has led to the fact that the potential responses to S have largely been ignored.

In the past, the so-called "low analysis" fertilisers such as single superphosphate and ammonium sulfate were the principal sources of sulfur for most agricultural crops. However, recently there has been a growing shift away from the use of these fertilisers to the so-called "high analysis" fertilisers such as urea, triple superphosphate (TSP), mono- and di-ammonium phosphate which contain little or no sulfur (Blair, 1979; Morris, 1987). Elemental sulfur (S^0) can be considered as a high analysis straight fertiliser (Tandon, 1987). This is in view of the fact that it contains 100% S.

As the need for S increases to counter the S deficiencies resulting from the increased use of high analysis fertilisers, many attempts have been made to use S° to supply crop demand (Fisher *et al.*, 1984). However, since plants use only sulfate S, S° needs to be oxidized before a plant can utilize the S.

Coating of fertiliser materials with S° has been introduced to deliberately supply S to plants and according to Bixby and Kilmer (1975), these employ finely divided S bound to granular products with various binders such as lignosulfonates, formaldehyde, etc. Most of these materials contain 10-100% S (Tandon, 1987). Because of the important role granules and particle sizes play in so far as the efficiency of fertilisers is concerned the literature review presented in Chapter 2 describes firstly the effects of granule and particle sizes of some of the common fertilisers (N, P, K and Mg) on nutrient release, and crop and pasture yields. Secondly, since the aim of this study is to investigate the effectiveness of the different S coated materials as sources of S for rice under flooded and non-flooded conditions, a large section of the literature review is devoted to discussing S, particularly in relation to the sources and forms it is found in soils, as well as factors that are involved in the mineralization and immobilization of S. The literature review also examines elemental S as a plant nutrient and the factors that contribute to its oxidation. Finally, the literature review discusses the effectiveness of some of the elemental S containing fertilisers that are currently available in the market or are still in the experimental stages as sulfur sources for crops and pastures.

The study reported in Chapter 3 was undertaken to investigate the effectiveness of some of the sulfur coated fertiliser materials as S sources in terms of rice growth and yield, S concentration and content and the recovery of fertiliser S in the various plant components, under the flooded and non-flooded conditions in a glasshouse.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

It is well documented that the agronomic effectiveness of fertilisers is related to their water solubility, granular and particle sizes (Owens *et al.*, 1955; Thomas and Prasad, 1982; Mortvedt and Kelsoe, 1988). Generally, highly soluble fertilisers will dissolve soon after soil application and tend to defuse from the application site into the surrounding soil (Mortvedt and Kelsoe, 1988). Decreased fertiliser particle size may expedite the process of dissolution thereby immediately rendering the nutrients contained in the fertiliser material available for plant uptake. However, although this may be beneficial in terms of nutrients release, it may not be beneficial in terms of plants' requirements, that is, the release of nutrients may occur at a time when they are not required by the plant. Granule size may influence fertiliser effectiveness by affecting the placement pattern or distribution of the fertiliser material in the soil. Moreover, it determines the effective surface area and the reactivity of the material (Phillips and Webb, 1971). Granular fertilisers can more easily be placed using a seed-cum-fertiliser drill than a powdered fertiliser which, in most instances, tends to clog drills. Hence, the granular and particle size of fertiliser materials, timing of fertiliser application, and placement of fertilisers are important factors which must be considered if fertilisers are to be efficiently utilized by plants.

2.2 GRANULAR AND PARTICLE SIZE OF FERTILISERS

Granulation of fertilisers, whereby the particles are converted into spheroids of nearly uniform size and composition, promotes good physical condition in the fertiliser. Granular products are needed because, during handling and application, segregation of individual products occur, unless particle sizes of the materials are well matched (Mortvedt and Kelsoe, 1988). Owing to variations in the specific gravity, and especially in the particle size of ingredients, a mixed fertiliser may segregate when it is agitated during transportation or application. In short, granulation of fertilisers enables users to use the products more efficiently.

2.2.1 Effect of Granular and Particle Size on the Effectiveness of Fertilisers

(i) Nitrogen Fertilisers

According to Achorn and Cox (1971) granule size is of little importance for readily soluble N fertilisers. Common solid N sources such as NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ are water soluble and highly mobile in soil. Nelson and Terman (1963), indicated that immediately after application to a moist soil, the concentration of N around the granule increases, however, soon dissolution and diffusion into a relatively large volume of the soil occurs. The authors also indicated that granule size is not an important factor in the effectiveness of the N component of fertilisers formulated with these water-soluble sources. They further pointed out that in the case of N sources of low water solubility, granule size can be an important factor in the effectiveness of the N component of the fertiliser.

Using high and low NH_4^+ -fixing soils, Nõmmik (1966) found that with the low-fixing soils the rate of nitrification of the different N fertiliser materials (ammonium sulfate, monohydro- and dihydro-ammonium phosphates, and urea) was higher as the particle size of the fertiliser material was decreased. Also, the rate of nitrification was reduced when the N fertiliser materials were added in coarse-particle form (3–4 mm). Furthermore, he observed that dihydro- ammonium phosphate was nitrified slower than monohydro- ammonium phosphate and ammonium sulfate. The author ascribed the reduced rate of nitrification of coarse-particle N fertiliser materials to high osmotic concentration in the vicinity of fertiliser particles and also as a consequence of high acidity formed in the oxidation of ammonium to nitrate. In the case of urea, Nõmmik (1966), observed that it was nitrified faster than ammonium sulfate of comparable particle size. With respect to the high NH_4^+ -fixing soils, Nõmmik (1966) observed that NH_4^+ -fixation decreased dramatically with increasing particle size of the N material (ammonium sulfate). He also showed that when added in coarse-particle form, both the rate of nitrification and, as a consequence of this, the rate of release of fixed NH_4^+ were low compared with treatments with fine-texture or aqueous sources of N.

Urea is the major dry N fertiliser in world agriculture (Yadvinder-Singh *et al.*, 1994) and in most arable soils it is readily hydrolyzed to NH_3 and CO_2 by soil urease activity. Ammonia volatilization loss of N can be minimized by deep placement or incorporation into the soil. The use of large urea granules (LUG) is one of the methods of controlling nitrification. Yadvinder-Singh *et al.* (1994) indicated that granulation and compaction processes can be used to produce urea granules that are larger than the commercial fertiliser grade prilled urea (1–2 mm diameter). The authors found that the rate of nitrification was reduced when urea was applied as LUG. They observed that by using LUG, the contact between the nitrifying bacteria and the NH_4^+ released upon urea

hydrolysis, was reduced. Furthermore, they observed that N was more efficiently retained in the soil as NH_4^+ and therefore, more effectively utilized by plants if formation of NO_2 and NO_3 was reduced or curtailed by inhibiting nitrification. Yadvinder-Singh and Beauchamp (1988), observed that LGU, as compared with fall-incorporated commercial urea prills, was effective in conserving N over the winter period, especially when applied a month after planting. They also observed that yields of winter wheat and N recovery were greatly increased.

In laboratory and field experiments where the use of large granular urea (LGU, 6 to 8 mm diameter) in wetland rice cultivation was investigated, Prins and Rauw (1989) found that N concentrations in the floodwater were lower when LGU was dropped from a height of 2 m or when shot with force into the puddled soil compared with prilled urea or LGU placed on the soil surface. They also found that when the LGU was placed at 1 and 4 cm depths, N concentration in the floodwater decreased even further and as a consequence N uptake by grain and straw increased significantly. From these results, the authors indicated that the efficiency of broadcast urea can be improved by using large urea granules provided favorable conditions for penetration into the puddled soil are present. That is, by placing the LGU 1 to 4 cm below the surface of the puddled soil, the rice plants were able to utilize the available N, hence, less N was found in the floodwater.

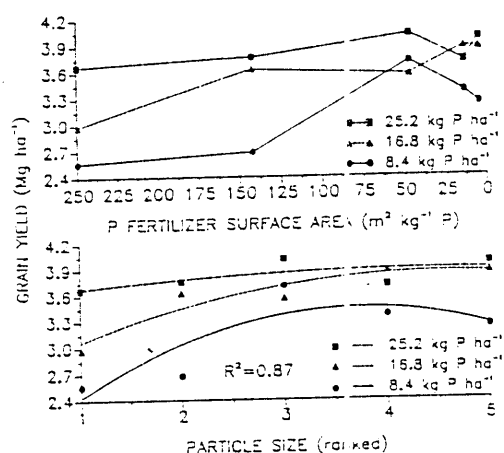
Urea supergranules (USG) are the latest addition to the list of new N fertilisers suggested for rice (Thomas and Prasad, 1982) and have been found to be more efficient than commercial prilled urea (Prasad and Prasad, 1981). An experiment conducted to study the nature of mechanisms responsible for the higher efficiency of USG (Thomas and Prasad, 1982) showed that hydrolysis of urea was slower when applied as USG (1 g weight) compared to the commercial urea prills. They also found that this resulted in the applied N remaining as NH_4^+ in the soil for a longer period. The concentration of NO_2 was also found to be much less with USG. These were considered to be the principal mechanisms responsible for the higher efficiency of USG over urea prills.

(ii) Phosphorus Fertilisers

Achorn and Cox (1971) stated that for P, incorporation in granular fertiliser of 1000 to 2000 μm , delays the reaction with the soil and the reversion to less soluble forms sufficient to improve utilization by the immediate crop. According to Tisdale *et al.* (1993), the relative effectiveness of phosphorus fertilisers is influenced by the size of the granule and the water solubility of the P fertiliser. Therefore, plant response to P is improved with water-insoluble or slightly soluble phosphates on both acid or calcareous soils when they are applied in powdered form or as a very fine granule (<420 μm) and mixed thoroughly with the soil of the root zone. Furthermore, they indicated that increasing granule size of the fertiliser will decrease soil-fertiliser contact thereby maintaining a higher solution P concentration for a longer time than for fine particle size.

Lawton *et al.* (1956) reported that for phosphate fertilisers the ability to supply P to a specific crop is largely determined by (i) particle size, (ii) percentage of the fertiliser P soluble in water, (iii) method of fertiliser placement, and (iv) certain soil properties including level of available soil P, soil texture, and soil pH. Sander and Eghball (1988), reported that particle size of P fertiliser influences the utilization of applied P in that it affects the distribution of fertiliser in soil particularly in relation to its reactivity which, in turn, affects availability. The authors found that in two of the soils under investigation, the grain yield of winter wheat (*Triticum aestivum* L.) was significantly affected by fertiliser particle size. Furthermore, they observed significant particle size by P rate interactions in both soils existed which means that the particle size effect varies depending on P rate (Figure 2.1a and b).

(a)



(b)

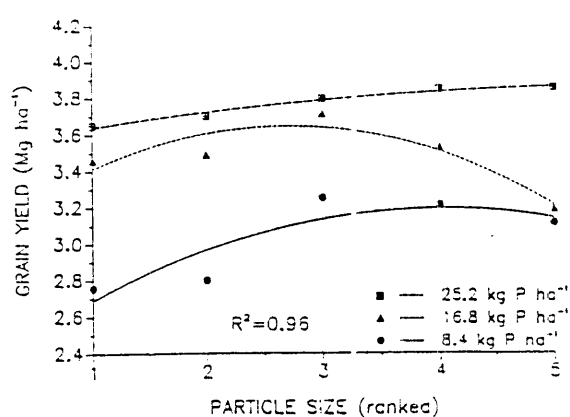


Figure 2.1 Effect of P fertiliser particle size on grain yield of winter wheat at three P rates in Holdrege (a) and Ascalon (b) soils (Source: Sander and Eghball, 1988).

In an experiment where the availability of P in granulated fertilisers (superphosphate and dicalcium) was investigated, Starostka *et al.* (1954) found that the optimum size for superphosphate granules was >800 µm for banded placement, 1700-2000 µm for mixed placement while that of dicalcium phosphate was <420 µm for both placement. However, they found that regardless of placements, the 800-1200 µm superphosphate resulted in the highest percentage of plant P derived from fertiliser of any of the superphosphate granule sizes applied at 29 kg P/ha. In the case of dicalcium phosphate, the authors found that the <420 µm material resulted in the highest percentage of plant P, irrespective of placement or soil (Table 2.1).

Table 2.1 Phosphorus uptake (mg/pot) by wheat in final harvest when P was applied at 29 kg/ha.

Granule Size (µm)	Total P taken up (mg/pot)							
	Evesboro soil				Davidson soil			
	Superphosphate		Dicalcium phosphate		Superphosphate		Dicalcium phosphate	
	Banded	Mixed	Banded	Mixed	Banded	Mixed	Banded	Mixed
<420	11.1	9.0	10.8	10.1	9.5	7.5	7.8	6.9
420-500	10.4	8.9	12.2	11.1	10.3	6.3	8.3	8.4
800-1200	11.6	9.6	9.5	9.6	8.8	11.1	7.6	7.5
1700-2000	10.8	9.5	6.7	7.3	9.2	10.4	7.6	7.0
2800-4000	11.1	8.8	5.8	5.5	9.0	10.2	8.6	7.3
No P	3.6				7.1			

LSD 1% = 2.2 mg, 5% = 1.6 mg

(Source: Starostka *et al.*, 1954)

As P fertilisers, rock phosphates are relatively insoluble in water, hence their effectiveness as fertilisers is strongly influenced by their particle size. In glasshouse experiments, where the effects of particle size on the response of subterranean clover were examined, Alston and Chin (1974) reported that dry matter yield and P concentration in the clover tops were increased by increasing the fineness of grinding of rock phosphate (Figure 2.2). They also found that Florida rock phosphate was a better P source for subterranean clover than the Christmas Island rock when the samples were coarsely ground. However, when both rocks were ground to give 70 percent <150 µm, both rocks were found to be equally effective as sources of P for subterranean clover.

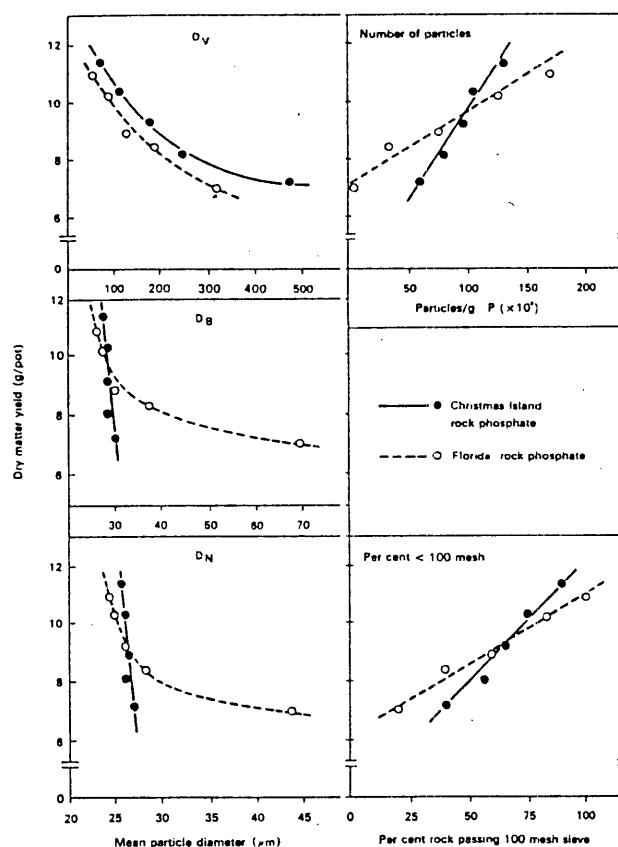


Figure 2.2 Relations between the dry matter yield of the tops of subterranean clover and estimates of the mean particle size of Christmas Island and Florida rock phosphates (Alston and Chin, 1974).

A pot trial was undertaken by Rajan (1982) on the influence of phosphate rock reactivity and granule size on the effectiveness of 'biosuper'. Biosuper is a granulated phosphate rock sulfur mixture that has been inoculated with *Thiobacillus spp* bacteria (Swaby, 1975). The study showed that increasing the biosuper granule size from 0.2-0.5 mm to 0.5-1.0 mm or 1.0-2.0 mm lessened the effectiveness of the North Carolina/S (NC/S = biosuper) granules slightly although the calculated maxima were the same. However, the size of granules did not influence the effectiveness of Florida/S (FI/S=biosuper) (Figure 2.3). The author found that with regard to the influence of granular size of biosuper on its effectiveness, the benefit to the smaller granules with NC/S was realized in the first two cuts (Figure 2.3). In view of the above scenario, Rajan (1982) pointed out that in practice it might be better to apply a mixture of granule sizes which would ensure that the possible differential dissolution from the different sizes meet the plants' phosphate needs.

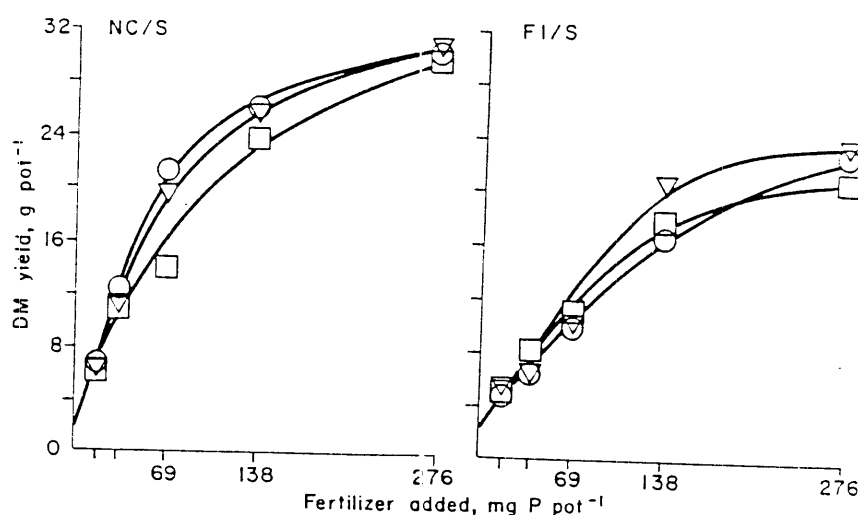


Figure 2.3 Ryegrass dry matter yield (total of 6 cuts) as influenced by biosuper granule size. ○=0.2-0.5 mm; ▽=0.5-1.0 mm; □=1-2 mm (Rajan, 1982).

(iii) Potassium Fertilisers

According to Barber *et al.* (1971), and Achorn and Cox (1971) granule size is of minor significance for readily soluble K. However, Barber *et al.* (1971) pointed out that granular size of potassium chloride (KCl) is considered to be important in the United States of America due principally to the large fertiliser bulk blending industry. There is a high tendency for finely divided KCl fertilisers towards caking on storage, dust formation during handling and segregation of fertiliser blends. Because of the above problems Loganathan *et al.* (1992) indicated that demands by consumers for coarser particle sizes and/or granular forms of KCl are increasing rapidly. Using 8 different granulating agents to granulate the finely divided red KCl (particle size distribution: 79% <0.5 mm, 20% 1-0.5 mm and 1% 1-2 mm) fertiliser, Loganathan *et al.* (1992) found that of the 8 different granulating agents tested, 5 of them [(i) urea + formaldehyde, (ii) pulp and paper waste liquor containing lignosulphonate, (iii) ammonium sulphate, (iv) Ferritin waste liquor containing ammonium sulphate and (v) ammonium sulphate + pulp and paper waste liquor] were shown to produce KCl granules of high critical relative humidity (65-70%), high crushing strengths (2.0-2.5 kg for 2-3 mm granules), better storage quality, higher K content (46-50% K and 42-47% Cl) and better agronomic effectiveness and good size distribution.

(iv) Magnesium Fertilisers

According to Mortvedt and Kelsoe (1988), the main magnesium fertilisers for soils which do not need lime application or where dolomite cannot be obtained, are MgSO_4 , langbeinite (a double salt of K_2SO_4 and MgSO_4), and MgO . In an experiment where crop responses to fine and granular magnesium fertilisers were examined, Mortvedt and Kelsoe (1988) found that corn forage yields were similar with finely ground (<0.2 mm) MgSO_4 , MgO , MgCO_3 , and a partially acidulated MgO product (Mg -oxysulfate). Moreover, they found that granular MgSO_4 (100 % water-soluble) was as effective as the finely ground products and that the small granules (1.4-2.0 mm) were almost as effective as the finely ground fertilisers. They also found that granule size of 2.4 to 3.4 mm (medium granule size) and 3.4 to 4.8 mm (coarse granule size) were less effective (Table 2.2).

Table 2.2 Granule-size effects of Mg fertilisers on corn forage yields and Mg uptake.

Mg fertiliser	Granule size (mm)	Mg applied (mg/pot)	Crop 1		Crop 2	
			Yield (g/pot)	Mg uptake (mg/pot)	Yield (g/pot)	Mg uptake (mg/pot)
-	-	0	26.8	17	9.6	11
MgO	1.4-2.0	30	38.7	28	7.7	10
		90	50.8 a*	52 a	13.8 a	19 a
	2.4-3.4	30	23.2	17	8.4	9
		90	34.6 c	32 c	13.5 a	19 a
	3.4-4.8	30	22.7	17	8.3	10
		90	32.2 c	26 c	10.9 ab	14 ab
Mg oxysulfate	1.4-2.0	30	41.0	31	8.6	8
		90	50.8 a	47 a	12.2 ab	17 a
	2.4-3.4	30	33.9	28	8.2	10
		90	41.1 b	40 b	12.7 a	18 a
MgSO ₄	1.4-2.0	30	40.2	29	8.9	10
		90	51.0 a	53 a	11.3 ab	15 ab
	2.4-3.4	30	42.5	32	7.3	7
		90	49.7 a	46 a	9.1 b	11 b

* Values for yield and Mg uptake in each column with the same letter, are not significantly different at the 0.05 probability level (Source: Mortvedt and Kelsoe, 1988).

It is evident from the above discussions, that both the granule and particle sizes play an important role in the efficiency of fertiliser materials. Apart from influencing nutrients release, granule and particle sizes can also facilitate handling, storage and application processes.

2.3 SULFUR IN SOILS

2.3.1 Sources of Sulfur

According to Tisdale *et al.* (1993), S is the 13th most abundant element in the earth's crust with an average ranging between 0.06 and 0.10%. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), mirabilite ($\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$), pyrite (FeS_2), sphalerite (ZnS), chalcopyrite (CuFeS_2), and cobaltite (CoAsS) are the main S-bearing minerals in rocks and soils (Tisdale *et al.*, 1993). Sulfur content in silicate minerals is less than 0.01% but in such minerals as biotites, chlorites, and layer-type clay minerals S content can be high. Igneous and sedimentary rocks contain about 0.02-0.07% and 0.02-0.22% S, respectively (Tisdale *et al.*, 1993). Elemental sulfur occurs in deposits over salt domes, in volcanic deposits and in deposits associated with calcite and gypsum.

Another important source of S is the atmospheric sulfur that originates from sea water. Robinson and Robbins (1968) as cited by Evans (1975) indicated that the natural supply of S to the atmosphere is 142×10^6 tonnes/yr and about half of that comes from the sea, that is, 44×10^6 tonnes as SO_4 in spray and 30×10^6 tonnes as H_2S from oceanic decay. When coal and other S-containing products are burned, SO_2 is released thereby contributing to atmospheric S. Tisdale *et al.* (1993), reported that in 1990, about 100 million tons of SO_2 was liberated into the atmosphere by the so-called industrial nations as a result of burning of fossil fuels. They also reported that industrial processes such as ore smelting, petroleum refining, and others contributed about 20% of the total amount emitted. Figure 2.4 shows the simplified version of the overall S cycle in nature.

2.3.2 Forms of Sulfur in Soils

Sulfur is present in the soil in both organic and inorganic forms, however, in many soils the organic S component is the predominant one (Evans, 1975; Scott and Anderson, 1976; Tisdale *et al.*, 1993).

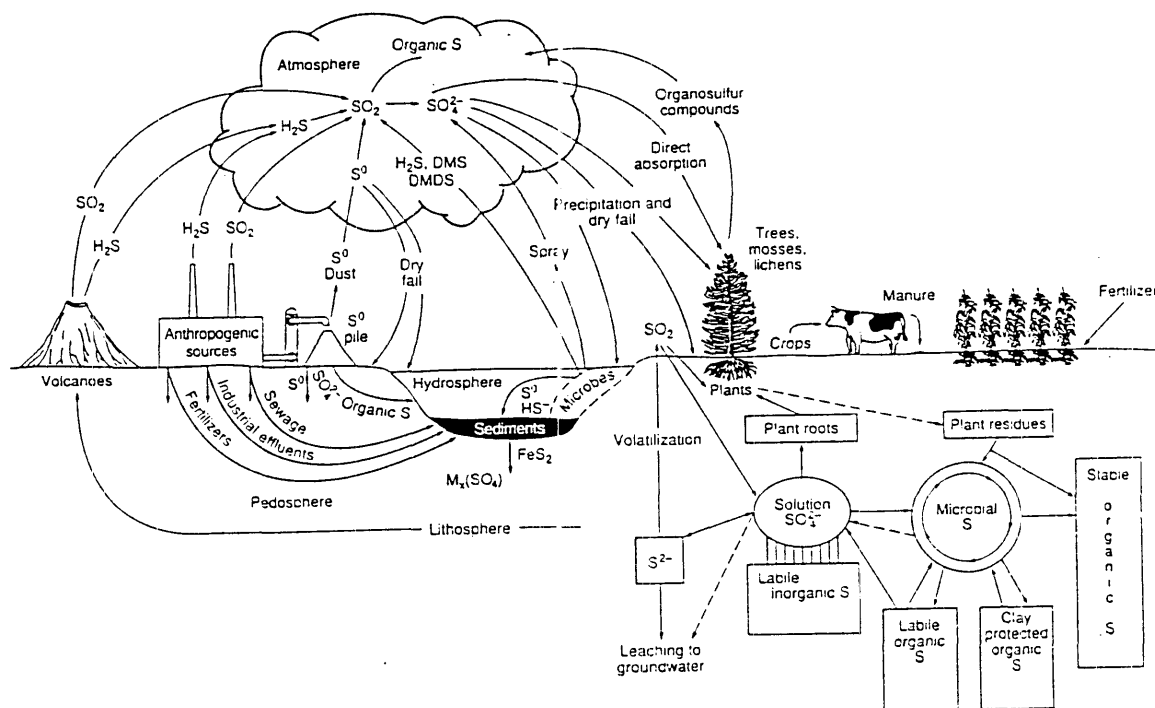


Figure 2.4 Simplified version of the overall S cycle in nature (Sources: Krouse and McCready, 1979; Tisdale *et al.*, 1993).

(i) Organic-Sulfur

Sulfur is a constituent of soil organic matter therefore, organic-S contents are highly correlated with organic carbon and nitrogen (Probert and Samosir, 1983). Tisdale *et al.* (1993) reported that in most well-drained, noncalcareous soils, the C:N:S ratio is about 120:10:1.4. According to Probert and Samosir (1983), the relative proportions of C:N:organic-S is about 140:10:1.3 which does not vary much on a world-wide basis. It was pointed out by Tisdale *et al.* (1993) that there exists more variability in soils in relation to C:S ratio than in C:N ratio. Neptune *et al.* (1975) reported that C:N ratios are higher in tropical soils than in temperate soils. Evans (1975) indicated that soil organic matter is enriched in S relative to N, with an N:S ratio of about 8 compared with a ratio of 15 to 17 in plant proteins.

Organic-S compounds in soils remain uncharacterized (Probert and Samosir, 1983; Tisdale *et al.*, 1993). However, three broad groups of S compounds are recognized which include the HI-reducible S, C-bonded S, and residual or inert S (Freney, 1986; Tisdale *et al.*, 1993).

HI-Reducible S: This is the fraction that is primarily made up of organic S and it is reduced to H_2S by hydriodic acid (Evans, 1975; Freney, 1986; Tisdale *et al.*, 1993). Its S is principally in the form of SO_4^{2-} esters and ethers with C—O—S linkages (Freney, 1986; Tisdale *et al.*, 1993) and these include such compounds as sulfated polysaccharides, choline sulfate and lignin bisulphites (Freney, 1961; Freney, 1986; Tisdale *et al.*, 1993). Also, this fraction is considered to represent about 30 to 70% of the organic S in soils. Moreover, HI-reducible S is found to be the most labile form of organic S.

Carbon-Bonded S: In this group, S is directly bonded to C and is reduced to S^{2-} with Raney nickel (Probert and Samosir, 1983; Tisdale *et al.*, 1993). This fraction includes the S-containing amino acids - cysteine and methionine. The carbon-bonded S accounts for 10 to 20% of the total organic S.

Residual or Inert S: This organic S fraction is not reduced by either hydriodic acid or Ni. Although still unidentified, this fraction is considered to account for 30 to 40% of the total organic S (Tisdale *et al.*, 1993).

(ii) Inorganic-Sulfur

The inorganic forms include the solution SO_4^{2-} , adsorbed SO_4^{2-} , insoluble SO_4^{2-} , and reduced inorganic S compounds. The first two forms of inorganic S represent the readily available fraction of S utilized by plants (Tisdale *et al.*, 1993).

Solution Sulfate: The S in the soil solution is in the form of SO_4^{2-} . Williams (1975), reported that in the surface horizons of most well-drained soils water-soluble sulfates are generally small, but under arid and poor drainage conditions, sulfate levels may be higher. Blair and Sale (1996), reported that generally in temperate soils solution sulfate levels are moderate to high whereas in tropical soils solution sulfate levels tend to be lower.

Adsorbed Sulfate: Adsorbed sulfate occurs when the sulfate anion is adsorbed onto positively charged sites in soil (Blair and Sale, 1996). According to Blair and Sale (1996), this process tends to occur more in kaolinitic rather than montmorillonitic clays, lower soil horizons than upper horizons, soils higher in Al and Fe oxides and increasing soil acidity or lower soil pH. Aylmore *et al.* (1967), reported that SO_4^{2-} adsorbed on kaolinite clay is weakly held, whereas that adsorbed onto Al and Fe oxides is more tightly bound and may be highly resistant to leaching. This is useful because SO_4^{2-} ion would otherwise leach from the soil profile. Highly weathered

soils such as the Ultisols and Oxisols contain appreciable amounts of adsorbed SO_4^{2-} (Tisdale *et al.*, 1993).

Insoluble Sulfate: Several forms of insoluble sulfates occur in soils such as barium and strontium sulfates, sulfate associated with CaCO_3 and basic Fe and Al oxides (Williams, 1975). However, Tisdale *et al.* (1993) indicated that S occurring as a coprecipitated or co-crystallised impurity with CaCO_3 is an important fraction of the total S in calcareous soils. They also pointed out that both the solubility and availability of SO_4^{2-} coprecipitated with CaCO_3 are influenced by such factors as particle size of CaCO_3 , moisture content of the soil, ion effects, and ionic strength.

Reduced Inorganic S (S^{2-} and S^0): In well-drained upland soils, sulfides do not exist. However, under waterlogged conditions, inorganic S occurs in reduced forms such as FeS , FeS_2 and H_2S (Mengel and Kirkby, 1987; Tisdale *et al.*, 1993). According to Konopka *et al.* (1986), reduced forms of S and S^0 are common in soils and their biological oxidation is an important part of the S cycle. Tisdale *et al.* (1993), however, established that S^0 is not a direct product of SO_4^{2-} reduction in reduced soils, but is an intermediate formed during chemical oxidation of S^{2-} . Moreover, the authors indicated that accumulation of S^0 may occur in soils where oxidation of reduced forms of S is interrupted by periodic flooding.

2.4 SULFUR TRANSFORMATIONS IN SOILS

2.4.1 Sulfur Transformations in Upland Soils

According to Freney and Swaby (1975) and Tisdale *et al.* (1993), numerous transformations of S in soil occur as it converts back and forth from inorganic to organic forms of sulfur due to the presence of microorganisms. Freney and Swaby (1975), stated that during soil formation, the sulfides of primary minerals are converted to sulfate which is changed, in turn, to many and varied organic compounds by microorganisms, plants and animals. They indicated that as a result, S can be found in soils in many forms (see section 2.3.2). Trudinger (1975), listed a number of major microbial transformations of S and these are presented in Table 2.3.

Table 2.3 Major microbial transformations of sulfur.

Organisms	Reactions		
Most microorganisms	SO_4^{2-}	$\Rightarrow$	Cysteine (+ other organic S-compounds)
Many heterotrophs	Cysteine	$\Rightarrow$	H_2S
Heterotrophs	Cysteine	$\Rightarrow$	SO_4^{2-} (via organic pathway)
<i>Beggiatoa</i>	H_2S	$\Rightarrow$	S^0
Dissimilatory sulfate reducers (<i>Desulfovibrio</i> , <i>Desulfotomaculum</i>)	SO_4^{2-}	$\Rightarrow$	H_2S
Chemosynthetic sulfur autotrophs e.g. <i>Thiobacillus</i>	H_2S	$\Rightarrow$	SO_4^{2-}
	H_2S	$\Rightarrow$	S^0
	S^0	$\Rightarrow$	SO_4^{2-}
Photosynthetic sulfur autotrophs	H_2S	$\Rightarrow$	S^0
e.g. <i>Chlorobium</i> , <i>Chromatium</i>	H_2S	$\Rightarrow$	SO_4^{2-}

(Source: Trudinger, 1975)

In the humid regions, most of the S accumulates in organic forms in the surface horizon of well-drained non-calcareous soils and in arid zones and calcareous soils, large amounts of inorganic SO_4^{2-} accumulate (Freney and Swaby, 1975). According to Tisdale *et al.* (1993), the supply of S to plants depends greatly on the SO_4^{2-} released from the organic soil fraction as well as from plant and animal residues. Furthermore, the authors claimed that about 4.5 to 14.6 kg/ha of S is mineralized each year from the organic fraction.

Mineralization of S occurs when organic S is converted to inorganic SO_4^{2-} whereas immobilization is the reverse, that is, the conversion of SO_4^{2-} to organic S. Tisdale *et al.* (1993), indicated that any factor that influences the growth of microorganisms is thus bound to change the S mineralization and immobilization processes.

2.4.2 Factors Influencing S Mineralization and Immobilization

Sulfur Content of Soil Organic Matter: Generally, mineralization of S depends on the S content of the decomposing material. Tisdale *et al.* (1993), pointed out that smaller amounts of SO_4^{2-} are released from low S-containing residue. Incubation studies by Barrow (1961), showed that a soil obtained from beneath the unfertilised native pasture did not result in any S mineralization. The author concluded that this was due to a low S content in the decomposing portion of the soil organic matter. Stewart *et al.* (1966b), found that in a sulfur deficient soil, the

decomposition rate of the wheat straw was dependent upon the sulfur content of the straw, and suggested that more sulfur is required for microbial decomposition of cellulose. They also found that for maximum rate of decomposition of straws to occur, the S content of the straw must exceed 0.15%. Similar results were also reported by Wu *et al.* (1993) and Chapman (1997a), who found that decomposition of barley straw was limited by S in all the soils, but this was dependent on the straw S content. Chapman (1997a), found that mineralization occurred at a straw S content of 0.15% irrespective of any S addition. At 0.11% S, a balance was reached where decomposition was not retarded in the absence of added S, but immobilization occurred if S was added. He further found that at 0.07% and 0.04% S, immobilization increased and decomposition was retarded if S was not added. Investigations on the effects of the combinations of glucose-carbon, nitrate-nitrogen and sulfate-S on S mineralization by Ghani *et al.* (1992), showed that the additions of C or S resulted in decreased S mineralization whereas addition of N slightly enhanced S mineralization. The authors also observed that the mineralized S appeared to be derived almost exclusively from C-bonded forms of soil organic S. In addition, they noted that there were substantial increases in hydriodic acid (HI)-reducible forms during the 14-week incubation period. Similar results were also reported by Saggar *et al.* (1981), who found that addition of cellulose-C and ^{35}S -sulfate resulted in net immobilization of inorganic SO_4^{2-} and a net mineralization of N. An experiment on carbon substrate mineralization and S limitation (Chapman, 1997b) showed that less S is required for glucose decomposition than for cellulose decomposition. These results are in conformity with the findings of Stewart *et al.* (1966a).

Tisdale *et al.* (1993), established that if the C/S or N/S ratio is too large, immobilization of S may occur. Furthermore, they indicated that at or below a C/S ratio of about 200/1, only mineralization of S occurs and above this ratio, immobilization or tie-up of SO_4^{2-} in various organic forms is favored, particularly at the ratio >400/1. However, Freney (1986), pointed out that C/S ratio of organic materials provides only a rough guide to their ability to release mineral S on incubation with soils. Barrow (1960), found that SO_4^{2-} accumulates in the soil when the C/S ratio is below 200 and immobilizes when the ratio is >400. Between the ratios 200 and 400, immobilization or mineralization could occur.

Soil Temperature: It was found by Williams (1967), that mineralization of S was suppressed at 10 °C and in some soils, he found that mineralization of S did not occur at all at this temperature over a 64-day incubation period. Studies on N and S mineralization of soils representing 12 major soil series (Tabatabai and Al-Khafaji, 1980) showed that more S was released during incubation at 35 °C than at 20 °C. Williams (1967), and Chaudhry and Cornfield (1967b), found that mineralization of S increased with increasing temperatures from 20 °C to 40 °C, however, at 50 °C mineralization of S was significantly less. Watkinson and Kear (1996), found that incubation of New Zealand soils at 40 °C for 2 weeks mineralized an amount of organic S approximately equal

to the sulfate initially present and similar studies in Minnesota (USA) (O'Leary and Rehm, 1991), showed that incubation of the soils at 30 °C for 12 weeks resulted in further mineralization of S.

Soil Moisture: Soil moisture influences the activity of sulfatases, the rate of S mineralization, the form of S released from organic matter, and the movement of SO_4^{2-} in soils (Tisdale *et al.*, 1993). Williams (1967), observed that at moisture levels <15% and at >40%, S mineralization was significantly slowed. Chaudhry and Cornfield (1967a), found that optimum moisture content for mineralization was 60% maximum water holding capacity. Tisdale *et al.* (1993), indicated that gradual moisture changes between field capacity and wilting point have little influence on S mineralization. They, however, pointed out that drastic differences in soil moisture conditions can result in a flush of S mineralization in some soils. It was reported by Williams (1967), that when soils were dried and then re-moistened before incubation, they tended to release more SO_4^{2-} than when they were incubated without prior drying. Hence, Freney and Swaby (1975) suggested that care should be taken in interpreting the results of work on S mineralization when soils are dried before incubation, but, indicated that such results may be more realistic to field conditions after dry summers.

Soil pH: The effect of soil pH on S mineralization is unclear (Tisdale *et al.*, 1993). Tabatabai and Al-Khafaji (1980), found that in 12 Iowa (USA) soils, S mineralization rates were negatively correlated with soil pH. Studies on factors affecting the mineralization of organic S in soils by Williams (1967), showed that application of CaCO_3 increased the amounts of S mineralized. Furthermore, he noted that in 3 of the soils, the amount of S mineralized was directly proportional to pH up to a value of 7.5. However, above pH 7.5, he found that the S mineralization increased more rapidly, suggesting that a further factor - possibly chemical hydrolysis - was affecting the mineralization process. Moreover, in the other 3 soils he observed that mineralization was proportional to the amount of CaCO_3 applied and not to the resulting pH. It is generally true, however, that at near-neutral soil pH, microbial activity is usually encouraged which can result in S mineralization.

Source of Mineralizable S: Due to the contribution of S mineralization to plant-available SO_4^{2-} , there is interest in characterizing the labile S reserve in soil organic matter. Tisdale *et al.* (1993), indicated that most of the available S removed by plants most likely comes from the ester SO_4^{2-} fraction, although other organic S compounds are also involved. Watkinson and Kear (1996), reported that the form and amount of organic S that is mineralizable is not such a well defined chemical property as sulfate. They indicated that it may include the total organic S but comprising fractions having varying rates of mineralization. Studies by Bettany *et al.* (1980), indicated that the contribution of 6 soil organic matter fractions to S mineralization during 65 years of cultivation were in decreasing order as follows; the clay-associated humic acid contributed 36%.

the conventional humic acid contributed 26%, the humin <2 μm contributed 18%, the conventional fluvic acid, clay-associated fluvic acid, and humin >2 μm contributed 14%, 4% and 3%, respectively. The authors also observed that the ester SO_4^{2-} fraction was much lower in the cultivated soil than in the pasture soil and some fractions were observed to have lost a greater percentage of this form of S (ester SO_4^{2-}) compared to the other fractions during the 65 years of cultivation.

Presence or Absence of Plants: It has been reported by Freney and Spencer (1960), that mineralization of S in the presence of plants was greater than that which occurred in unsown soil. The authors suggested that the increased S mineralization may have been the result of greater proliferation of organisms under plants. This is highly possible in that it is well documented that microbial activity in the rhizosphere can be stimulated due to the fact that root exudates, which contain amino acids and sugars, are utilized by the microorganisms.

Time and Cultivation: S content declines faster when a soil is first cultivated. With time, however, it will reach an equilibrium level that is characteristic of the climate, cultural practices, and soil type. Allison (1973), reported that when native forest, bush or grassland is brought under cultivation, appreciable amounts of soil organic matter can be lost through mineralization processes. Williams and Lipsett (1961), Bettany *et al.* (1973), and McLaren and Swift (1977), reported that such losses of soil organic matter are invariably accompanied by corresponding losses of soil organic S. For example, in Australia Williams and Lipsett (1961), found that under virgin soil there was 128 $\mu\text{g S/g}$ of soil and in the cropped soil, the S content was 92 $\mu\text{g S/g}$ of soil. Under the cropping period of 50-60 years, the estimated loss of S was 60 kg S/ha. In Canada, under the cropping period of 65 years, the estimated S loss was 345 kg S/ha (Bettany *et al.*, 1973) and in Scotland it was 460 kg S/ha (McLaren and Swift, 1977).

Sulfatase Activity: Freney (1986), stated that a large proportion of the organic S in soils seems to be present as ester SO_4^{2-} , hence, some S is expected to be mineralized by the action of the sulfatase (sulfohydrolase) enzymes. That is, sulfatase enzymes may hydrolyze the ester sulfates, thereby releasing inorganic sulfates. It is thought that the natural substrates for sulfatase enzymes in soil, are the HI-reducible ester sulfates.

2.4.3 Sulfur Transformations in Flooded Soils

The flooding of soil during rice cultivation can lead to significant changes in the physical and chemical properties, and microbial composition (Blair, 1984), due primarily to a decrease in oxygen supply and the consequent changes in reduction-oxidation (redox potential), pH, ionic strength and mineral equilibria (Blair *et al.*, 1978). Freney and Boonjawat (1983), indicated that

strength and mineral equilibria (Blair *et al.*, 1978). Freney and Boonjawat (1983), indicated that sulfur transformations in flooded soils are principally biological and the main reactions that occur include (i) mineralization, that is, decomposition of organic sulfur compounds with the release of inorganic sulfur compounds, (ii) immobilization or conversion of inorganic sulfur to organic sulfur compounds, (iii) production of sulfides by reduction of sulfate or other inorganic sulfur compounds, (iv) production of volatile sulfur compounds, and (v) oxidation of elemental S and inorganic S compounds. Figure 2.5 shows the sulfur transformations in flooded soils.

According to Blair *et al.* (1978), the oxidized forms of iron (Fe^{3+}), manganese (Mn^{4+}), and nitrogen (NO_3^-) undergo transformation to their reduced forms of Fe^{2+} , Mn^{2+} , and NH_4^+ which lead to adverse consequences in relation to mineral equilibria and concentrations in the soil solution. In the case of S, under flooded conditions SO_4^{2-} may be reduced to S^{2-} , hence, the availability of S to rice plants may be greatly curtailed. Also, flooding of the soil can result in the immobilization of zinc and copper, and H_2S toxicity. The authors also pointed out that during decomposition of organic matter in a submerged soil, unstable organic substances can be produced with the consequent production of methane and carbon dioxide. A study by Sachdev and Chhabra (1974), indicated that under flooded soil conditions, addition of SO_4^{2-} -S resulted in only 12.7% of the added sulfate being present compared to that under aerobic conditions which was about 68%. They also found that in aerobic conditions 99% of the added SO_4^{2-} -S was accounted for in different fractions determined namely sulfate, organic, humus, amino acid and evolved hydrogen sulfide-sulfur. However, in flooded conditions, they found that only 56% was present in all these fractions, which shows that the remaining 44% could be in chemical forms between SO_4^{2-} and S^{2-} .

Blair and Lefroy (1987), indicated that within a flooded soil there are aerobic and anaerobic zones and that both oxidation and reduction reactions can occur at the same time in different parts of the flooded soil. According to Freney *et al.* (1982), rice plants occupy a large volume of the planted soil and as such, oxidized zones occur which allow for the growth and metabolism of aerobic microorganisms. As a result sulfur can exist in these soils in all of its oxidized states from +6 of sulfate to -2 of sulfide (Wainwright 1984). Freney and Boonjawat (1983), stated that mineralization of S can occur in both zones, however, the inorganic S species formed would be different in the two zones.

Flooding of soils, however, may also result in a better growth environment for rice plants. This is possible in the sense that availability of water will be non-limiting, availability of various nutrients may be increased and because of the dilution effect, salt toxicities may be reduced. Nearpass and Clark (1960), found that plant growth and S uptake were higher on soils that had been flooded for a longer period before transplanting, however, they found that when soils were flooded at the same time as the rice plants were transplanted, plant growth and S uptake were comparably lower.

Blair *et al.* (1978), however, indicated that this occurred because the rice plants could utilize only the SO_4^{2-} ion as its source of sulfur.

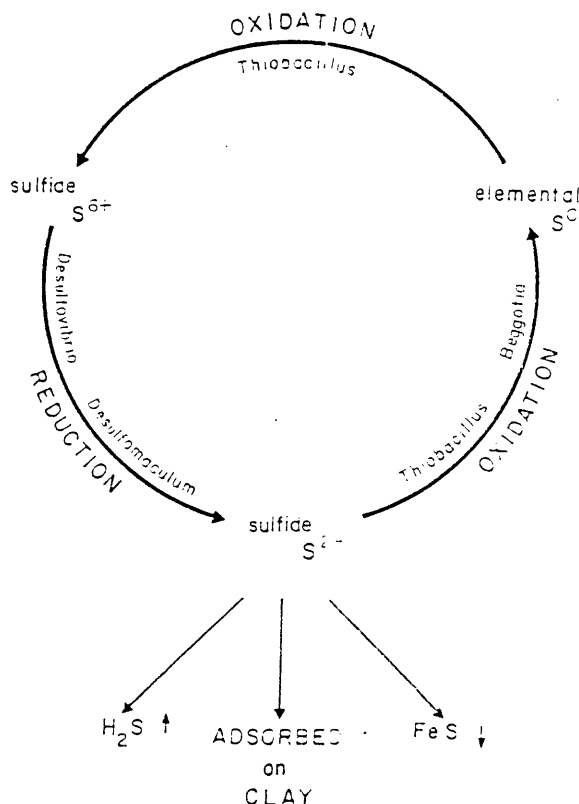


Figure 2.5 Sulfur transformations in flooded soil Source: Blair *et al.*, 1978).

2.5 ELEMENTAL SULFUR AS A SOURCE OF S FOR PLANTS

Elemental S (100% S) is an ideal slow release fertiliser. It is insoluble in water, therefore, when applied as a fertiliser it usually undergoes oxidation to water soluble sulfate before it can be taken up and utilized by plants. Weir (1975), reported that S^0 , sulfides and several other inorganic compounds can be oxidized in the soil by purely chemical processes. The author, however, stated that these processes are usually much slower which renders them less important. Oxidation by microorganisms is considered to be important and the microorganisms responsible for this are the autotrophic bacteria that belong to the genus *Thiobacillus* (Weir, 1975; Shedley, 1982). Shedley (1982), indicated that the oxidation of S^0 to SO_4 is an energy rich reaction. Vitols and Swaby (1969), reported that S^0 can be oxidized as well by heterotrophic bacteria and fungi. They further showed that the majority of S^0 oxidizing heterotrophs isolated from soil lost their ability to form SO_4^{2-} after only a few passages through inorganic media. A list of various microorganisms which are capable of oxidizing the chemical forms of reduced S is given by Konopka *et al.* (1986).

2.5.1 Factors Influencing Elemental Sulfur Oxidation in Soils

It was pointed out by Shedley (1982) that regardless of the organisms involved, the oxidation process is principally a biological process, and therefore it can be influenced by environmental factors like soil moisture, temperature, aeration soil pH, and inorganic nutrient concentrations. The size and composition of the responsible microorganisms can also affect the process of S oxidation (Weir, 1975; Shedley, 1982).

Particle Size and Form: S^0 can occur in a number of physical forms, however, these differences do not have a significant influence on oxidation rate (Weir, 1975). Simon and Schollenberger (1925), found that particle size (surface area) was more important than the surface shape. Weir (1975), reported that the initial S oxidation rate increases as particle size is reduced. Fox *et al.* (1964) found that there was a linear relationship between plant available sulfate and the approximate specific surface area of S^0 particles obtained from 2000 μm material. They showed that particles less than 0.05 mm in diameter were found to be slightly less effective than gypsum. Shedley (1982) showed that at the particle size treatment of 0.05 mm, S^0 ceased releasing sulfate 70 days after the commencement of the experiment. He also found that in the coarser particle size treatments, the release of sulfate continued throughout the experimental period.

Using different S^0 forms, Janzen and Bettany (1986) showed that the S^0 forms displayed widely differing rates of release which was attributed to the initial particle size of the product and the dispersion of the particles within the soil. Lindemann *et al.* (1991) found that the slow S^0 oxidation in some New Mexico soils was not due to S^0 source but was attributed to the buffering capacity of the calcareous soils. Li and Caldwell (1966), showed that the smaller the particle size of S, the more rapid the oxidation. The authors reported that particle size of 800-1700 μm , was found to have contributed very little to the amount of sulfate formed, regardless of the application rate and incubation period. Fenster (1965) as cited by Weir (1975), however, indicated that in spite of the fact that the finer the particle size and the quicker the initial rate of S oxidation, there is a limit and that further improvements in S recovery stops and may even decline if it goes beyond this limit. According to Germida and Janzen (1993), S oxidation is exclusively a surficial process which is limited to those atoms on the exterior of the particle directly exposed to biological activity. However, they indicated that the linear relationship between surface area and oxidation holds only up to a certain threshold level, beyond which oxidation rate diminishes. Koehler and Roberts (1982) observed in a series of experiments that the effectiveness of S^0 in increasing plant growth and S uptake, to be directly related to the total surface area of the applied sulfur. This may perhaps be due to the inhibitory effects of oxidation products (Chapman, 1989). Germida and Janzen (1993) indicated that the surface area of a fertiliser diminishes as oxidation proceeds at a rate that depends on initial particle size. Therefore, the rate of sulfate release will reduce more

rapidly in very finely divided S^0 product than in the coarse particle product. Application of a series of S^0 treatments of various particle sizes but uniform surface area (McCaskill and Blair, 1987) showed that oxidation rates were initially comparable among treatments, however, rates of sulfate production reduced faster in finely divided S^0 elements because of the rapid depletion of substrate.

It was shown by Burns (1968), that in general, the finer the particle the more rapid the initial rate of S oxidation and the author pointed out that from a practical point of view, S^0 of particle size less than 180-250 μm in diameter can be as effective as gypsum in terms of crop response during the year of application, even at low rates of application. In a number of sulfur evaluation studies, Koehler and Roberts (1982) reported that the finest S^0 (<150 μm) was as effective as gypsum in increasing plant growth. They also observed that although the 250-350 μm particle size material produced some increase in yield when applied at the higher rate, it produced very little effect at lower application rate. Simon and Schollenberger (1925), reported that the fineness of S is a factor in the rate of oxidation. Hence, the kind of S^0 having the most surface exposed to the soil is bound to be more rapidly oxidized.

Studies on the influence of S and P placement and S particle size on S^0 oxidation and maize growth response (Lefroy *et al.*, 1997) showed higher oxidation of the fine (50-150 μm) S^0 , compared with the coarse (150-250 μm) particle size.

Janzen and Bettany (1987a) conducted a field study at the 4 sites in Central Saskatchewan, Canada, to examine the oxidation rate of S^0 and its influence on soil pH. They found that on all sites, finely divided S of about 7 μm diameter and applied at 200 kg/ha to soil cores, showed significant oxidation activity. It is evident that the larger the particle size, the slower the oxidation rate and thus sulfate release. From a practical view, such a characteristic can have beneficial influence especially in terms of providing S on a short-term basis as well as maintaining a steady supply of sulfate, particularly in pasture systems (Weir *et al.*, 1963).

Temperature: As with most biologically-mediated processes, S^0 oxidation is significantly influenced by temperature (Germida and Janzen, 1993). Optimum temperatures for S^0 oxidation varies with the oxidizing microorganisms and between 27° C to 40° C (Parker and Prisk, 1953; Germida and Janzen, 1993). Using 40 diverse soils, Janzen and Bettany (1987b), found that the rate of sulfur oxidation was negligible at 3° C in all the soils. Furthermore, they found that at each subsequent temperature increase, there was a progressively greater stimulatory influence on oxidation rate. Li and Caldwell (1966), found that at 4° C, little S^0 was oxidized, but, as the temperature increased to 30° C, the oxidation rate was almost 4 times greater than at 23° C. Starkey (1925a), reported that the optimum temperature for sulfur oxidation was between 27° C -

35.5° C. He further found that in a pure culture, the initial oxidation was quickened by a temperature of 35.5° C, however, later the oxidation was reduced.

Nor and Tabatabai (1977), compared rates of S° oxidation using 5 different soils which were incubated for 74 days at different temperatures and they found that oxidation was 2.3 to 6.1 times faster at 30° C than at 5° C and 1.7 to 3.7 times faster at 30° C than at 15° C. Using four day/night temperature regimes (14° C, 20° C, 24° C and 30° C) and two particle size treatments (0.01 mm and 0.4 mm), Shedley (1982) found that the oxidation rates increased linearly with temperature over the lower three temperatures (14° C, 20° C and 24° C) of the 0.4 mm treatment. He also showed that there were no further increases in sulfur oxidation rates between 24° C and 30° C temperature treatments. Tisdale *et al.* (1993), indicated that an increase in temperature increases the S° oxidation rate in soil. They showed that at temperatures above 55° C to 60° C, the S° oxidizing organisms may be killed. Also they indicated that optimum temperatures naturally vary for the different S° oxidizing organisms, but, indicated that temperatures between 25° C and 40° C are ideal for most of them. Results from eighty field oxidation rate experiments conducted under grazing throughout New Zealand (Watkinson and Lee, 1994), showed that the mean annual soil temperature (10 cm depth) was the most important factor which affected the mean annual oxidation rate constants. Watkinson and Lee (1994) also found that rate constant versus the temperature relationship for field oxidation in the five New Zealand climate regions was consistent with the mean rate constants of soil groups from a similar set of 47 soils incubated at 25° C.

Soil Moisture and Aeration: S° oxidizing bacteria are mostly aerobic, hence, their activity will be adversely affected if O₂ is lacking as under water-logged situations (Tisdale *et al.*, 1993). Generally, S° oxidation is favored by soil moisture levels at field moisture capacity. In the case of dry soils, Tisdale *et al.* (1993) stated that dry soils retain their ability to oxidize S°, however, there can be a lag period following re-wetting before they regain full capacity. Kittams (1965) cited by Samosir (1981) indicated that slow rates of S° oxidation have been ascribed to low soil moisture. Burns (1968) showed that S° oxidation is faster in the soil moisture range that is optimum for the growth of crop plants. According to Germida and Janzen (1993) and Janzen and Bettany (1987c), the rate of S° oxidation is typically related to water potential in a parabolic manner and that the maximum rates occur near field capacity and diminish at higher or lower moisture potentials. Janzen and Bettany (1987c), found that the oxidation rates were negligible at -10 MPa, increased to a maximum as water potential was increased, and then declined as water potential was increased beyond the optimum level. They also found that at low water potentials, oxidation was limited by insufficient water for microbial activity and reduced accessibility of the sulfur particles, which are highly hydrophobic. Experiments on the influence of soil moisture and tension, and sulfur oxidation on four soil types (Moser and Olson, 1953), indicated that maximum oxidation occurred between the soil moisture tensions of 0.029 atmosphere (30 cm of water) and

0.059 atmosphere (60 cm of water) and that oxidation dropped off sharply at moisture tensions below and above these values.

Microorganisms: Great variability exists in S^0 oxidation rates among soils and this is largely due to differences in microbial populations (Weir, 1975; Tisdale *et al.*, 1993) (Table 2.4). Several microorganisms are capable of oxidizing S (Vitolins and Swaby, 1969; Konopka *et al.*, 1986; Weir, 1975), but, the most important ones are those belonging to the genus *Thiobacillus* (Weir, 1975). Shedley (1982), indicated that four species of *Thiobacillus* are capable of oxidizing S^0 to sulfate and these are viz: *T. thiooxidans*, *T. thioparus*, *T. denitrificans* and *T. ferrooxidans*, and their activity can be described in the following equation (Tisdale *et al.*, 1993);



Kittams and Attoe (1965), pointed out that the rate of S^0 oxidation is related to the species and numbers of the S^0 oxidizing organisms present. Laboratory studies showed that initial rate of S oxidation can be greatly increased by inoculation with thiobacilli but also with heterotrophs (Tisdale *et al.*, 1993).

Table 2.4 Elemental sulfur oxidation rates in soils.

Location	Number of soils	Percent S^0 oxidation in various incubation periods
Australia	51	0.0 - 0.4
	64	0.5 - 4.0
	58	4.1-12.9
	100	3.0-61.6
Nebraska	1	14.0-56.0
Oregon	1	2.0-50.0
Saskatchewan	4	20.0-44.0
Wisconsin	54	3.0-73.0

(Source: Tisdale *et al.*, 1993)

McCready and Krouse (1982), showed that when solonchic soils were inoculated with *T. thiooxidans* and *T. thioparus*, a stimulatory effect on oxidation rate of S^0 was observed. The favorable effects of inoculation are often short-lived under most conditions and that addition of S^0 will encourage the growth of S^0 oxidizing microorganisms (Tisdale *et al.*, 1993). Tisdale *et al.*

(1993) suggested that this enrichment of the S^0 oxidizing capacity and the overriding influence of environmental factors could be the reason for limited success from field-scale inoculations. According to Starkey (1966), most arable soils contain sulfur oxidizing microorganisms, however, Joffe and McLean (1922) reported that the rate of S oxidation may vary significantly between the soils. Investigation on sulfur oxidizing capacity of eight Oregon soils, Joffe and McLean (1922) found that soils of low sulfur oxidizing capacity need to receive the sulfur application in advance of the growing season which ensures the development of an active sulfur oxidizing flora that has to adjust itself to the adverse conditions of aeration. Similar results were also reported by Lee *et al.* (1987) and Lee *et al.* (1988) who found that the numbers of *Thiobacilli* were low in untreated plots, but where the plots were treated initially with S^0 , the numbers of *Thiobacilli* were higher. Moser and Olson (1953), attributed the differences in the ability of the soils to oxidize sulfur to the presence or absence of *T. thiooxidans* in the soils.

Soil pH: Microbial oxidation of S^0 occurs over a wide range in soil pH, but, for some species optimum pH can be 4.0 or lower (Tisdale *et al.*, 1993). For example, McCready and Krouse (1982) found that in soils inoculated with the acidophilic *T. thiooxidans*, which grows best in the pH range 4.0-1.0 (Konishi *et al.*, 1995), the rate of S oxidation was very slow for the first 10 weeks, however, as the soil surface pH decreased in the last 2 weeks, the rate of S oxidation increased, enhancing increased SO_4^{2-} (Figure 2.6b). They also found that S oxidation was most rapid when the soils were inoculated with *T. thioparus* which grows very well in the pH range of 7.2-4.5 and again as the soil surface pH decreased to 3.5, the rate of S oxidation was observed to be linear and 84% of the available S was oxidized in 12 weeks (Figure 2.6c).

Using six acid soils (pH range 5.1-6.0) and four alkaline soils (pH range 7.0-7.8), Nor and Tabatabai (1977) found that in general, the rates of oxidation of elemental S in acid soils were lower than those in the alkaline soils. Waksman and Starkey (1923) reported that oxidation proceeds faster between pH 2.5 and 3.5 but indicated that sulfur oxidation is very rapid over a very much wider range. The authors also showed that above pH 6.0 there was practically no oxidation of sulfur in the culture medium by *T. thiooxidans*. However, in a study of 54 Wisconsin soils, Kittam and Attoe (1965) reported no consistent relationship between the amounts of sulfur oxidized and soil type or soil pH. The authors attributed the variability in S^0 oxidation rates to differences in the number and kinds of S^0 oxidizing microorganisms present in the soils studied.

Nutrient Availability: Microorganisms generally need the same nutrients which are essential to higher plants. Burns (1968), reported that the nutrient needs of S^0 oxidizing microorganisms seem to be met from soils considered suitable for growing crops. Shedley (1982), pointed out that *Thiobacillus* being autotrophs, use energy gained from the oxidation of reduced forms of S for assimilation of atmospheric CO_2 and need enough supplies of inorganic nutrients for the synthesis

of metabolic products. In a number of experiments with *T. thiooxidans*, Starkey (1925b) reported that in the absence of ammonium nitrogen, oxidation rate was very low and the lack of the turbidity, which is the characteristic of normal growth, was found to be very evident. Furthermore, he observed oxidation was faster where no nitrogen was added, but, where KNO_3 was present even at 0.05% concentration, the oxidation was slow and was completely inhibited when 1.25% KNO_3 was present. The author pointed out that the source of nitrogen for oxidation was the ammonium compounds contained as impurity in the compounds incorporated in the sulfur medium or ammonia absorbed from the air during the period of incubation. Rapid oxidation was also found at 2.5% NH_4Cl and some oxidation occurred at 5% $(\text{NH}_4)_2\text{SO}_4$. Starkey (1925b), indicated that sulfur oxidizing organisms are much more tolerant to ammonium salts than are nitrifying bacteria. From the above findings, Starkey (1925b) concluded that nitrate was not used by *T. thiooxidans* and that ammonium ion was used and the source of nitrogen.

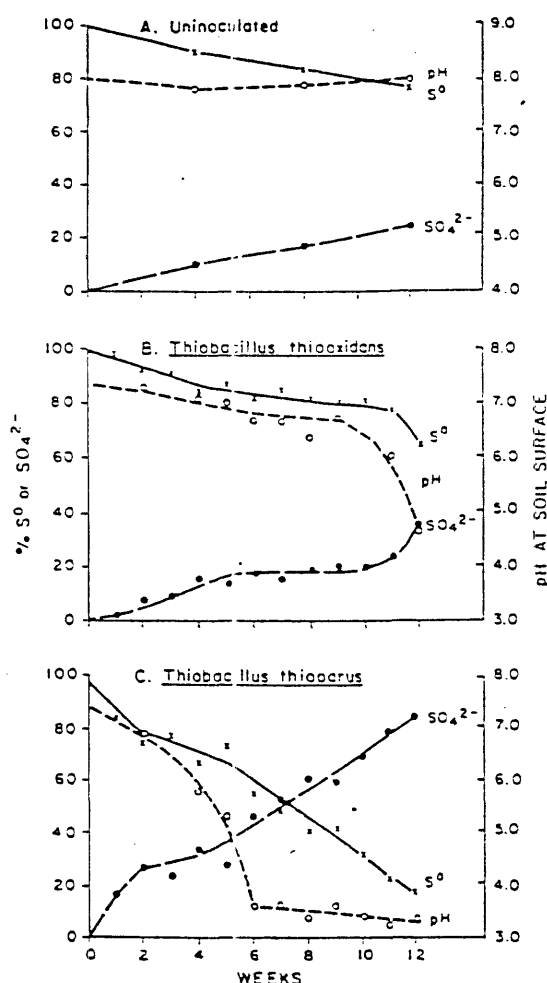


Figure 2.6 Changes in S° and SO_4^{2-} content and pH during oxidation of S° in solonchetsic soils: (a) uninoculated; (b) inoculated with *T. thiooxidans*; (c) inoculated with *T. thioarvus* (Source: McCready and Krouse, 1982).

In an experiment where eight different soils were used with differing P status, Barrow (1971), found that there was an increase in sulfate production from S^0 when P was added to the soil and that suppression of S^0 oxidation occurred when soil phosphate was in short supply. Similar results were also reported by Janzen and Bettany (1987a) and Lawrence and Germida (1988) who found stimulatory effects of available P concentrations on oxidation rate. Studies by Dana (1992), Chinoim (1994), Sholeh (1995) and Sholeh *et al.* (1997) also showed that the oxidation rate of S^0 was enhanced in the presence of phosphate. Using a high S sorbing basaltic soil (Haplohumult), Sholeh *et al.* (1997) and Lefroy *et al.* (1997) found increased S uptake by maize and higher S^0 oxidation in the presence of P. The authors ascribed these to an increase in the population of S oxidizing organisms (*Thiobacillus*) and to root proliferation in the fertiliser application zone. Friesen (1996), also found similar results where he found that fertiliser S uptake by the test crops (maize, wheat, and upland rice) was greatly enhanced in the presence of P fertiliser (TSP). He also found that in all the experiments, P mixed with S^0 increased plant growth and S recovery above treatments in which P and S^0 were physically separated. The author concluded that these results demonstrate that S^0 -oxidizing microorganisms require P for the enhancement of S^0 oxidation. Experiments by Bloomfield (1967) showed similar results where he found that oxidation of S^0 contained in granulated TSP and diammonium phosphate (DAP) mixtures was promoted. However, he found that TSP was more effective in promoting S^0 oxidation than DAP (Figure 2.7a and b).

Experiments with glucose (Starkey, 1925b), showed that small quantities of glucose may enter into the metabolism of the cells in the presence of sulfur and may be utilized either as a source of energy or as carbon for growth, or both. He also found that citric acid inhibited the growth of *Thiobacillus thiooxidans* at a concentration of 5%. but, at the concentration of 2.5%, oxidation was active. The presence of 2.5% pepton inhibited oxidation and at 1.25%, injury to the bacterium was observed which indicated that neither pepton nor amino acids were available as sources of N or C (Starkey, 1925b). Cifuentes and Lindemann (1993), reported that addition of organic matter stimulates S^0 oxidation and, in calcareous soils low in organic matter, addition of organic matter with S^0 stimulates S^0 oxidation which resulted in increased SO_4^{2-} in the soil. It has been reported by Grayston *et al.* (1986) and Germida and Janzen (1993) that fungi can use plant residues such as cereal straws as carbon sources to support S^0 oxidation. In a study where 40 different soils were examined, Janzen and Bettany (1987b) found a highly significant positive correlation between oxidation rate and indigenous soil organic matter. Similar findings were also reported by Skiba and Wainwright (1984), and Lawrence and Germida (1988) who found beneficial effects of soil organic matter on S^0 oxidation.

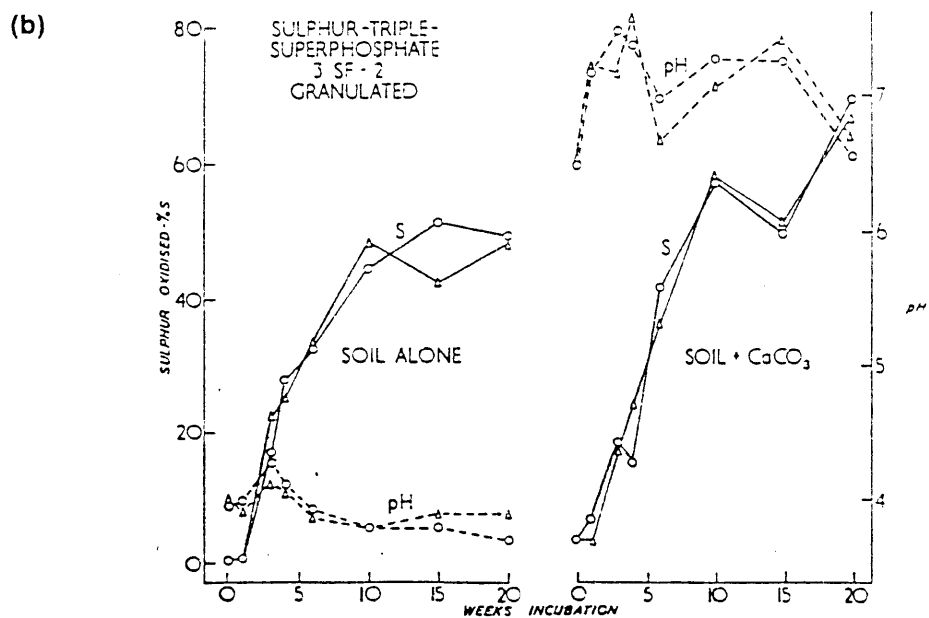
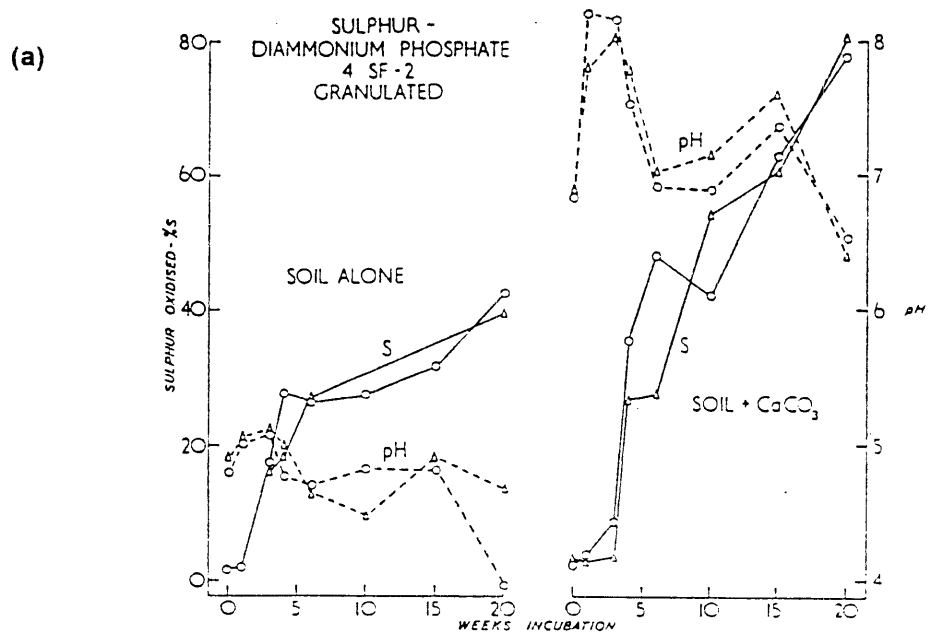


Figure 2.7 Oxidation of S^0 in granulated (a) DAP and (b) TSP (Source: Bloomfield, 1967). Δ and $\circ$ represent duplicate samples

Soil Management Practices: Various management practices employed on a soil may have significant indirect effects on oxidation of sulfur. Germida and Janzen (1993), pointed out that crop rotations, tillage practices, and methods of residue management influence soil temperature which plays a predominant role in governing oxidation. Pesticide application may suppress S^0 oxidation, though effects at normal application rates are often small (Germida and Janzen, 1993). For example, it was observed by Wainwright (1979) that application of two fungicides (dichloran and verdasan) resulted in reduced S^0 oxidation rates. Controlled environment studies conducted to characterize the effects of cropping treatment on S oxidation rate (Janzen, 1990), showed that S oxidation rates were not greatly affected by the cropping treatment (barley, beans, canola, or fallow). Hence, the author suggested that oxidation rates determined in uncropped soils may be extrapolated with little error to various cropped conditions.

2.6 SULFUR CONTAINING FERTILISERS AND THEIR EFFECTIVENESS AS SULFUR SOURCES FOR CROPS AND PASTURES

2.6.1 The Range of Sulfur Containing Fertilisers

There is a wide range of S-containing products available to the fertiliser industry. Hagstrom (1986), indicated that there is probably a wider range of S-containing fertiliser materials available to the industry than any other major or secondary plant nutrient and attributed the increasing frequency of S deficiencies to a lack of S particularly in high analysis fertilisers.

A survey of S-containing fertilisers conducted by Beaton and Fox (1971), shows sixteen dry and five fluid sources of S products. Bixby and Kilmer (1975), placed the various S-containing fertilisers under three groups based upon the chemical form of S, and these include; those containing elemental S, sulfate S, and other forms. Other forms include; thiosulfates, bisulfites, sulfides and sulfur dioxide. Some of the important S-containing fertiliser materials are presented in Table 2.5.

2.6.2 Sulfate Fertiliser Materials

It is apparent that ammonium sulfate is the S source in most of the compounds listed in Table 2.5. Tandon (1987), indicated that fertilisers containing SO_4^{2-} -S carry 5 to 24% S in them. He further pointed out that very little transformations are required in the soil for their S to be available to plants. These fertilisers are also multi-nutrient carriers, hence, their use as S fertilisers cannot be separated from their use for other nutrients which they contain (Tandon, 1987). Tisdale *et al.*

(1993), indicated that sulfate materials applied to the soil surface and moved into the soil profile with rainfall or irrigation are immediately plant available unless immobilized by microbes degrading high C/S or N/S residues. Jones (1984), mentioned that fertilisers that contain soluble sulfate compounds are readily available to plants so long as the sulfate stays in the root zone. Tisdale *et al.* (1993), stated that studies conducted to compare the effectiveness of different SO_4^{2-} sources, showed that one source of SO_4^{2-} is generally equal to any other. Hence, the authors suggested that the determining factor with respect to the selection of sulfate source, should be the cost per unit of S applied. They, however, pointed out that this can be true as long as the concomitant cation is not Zn, Cu or Mn which must be used sparingly.

Gypsum is the least soluble of the fertiliser sulfates. It is available as a mineral or can be produced as a byproduct of concentrated phosphate fertiliser manufacture (Hagstrom, 1986; Beaton, 1987; and Tandon, 1987). It is widely used for reclamation of sodic soils, particularly in arid climates where the Ca^{2+} replaces Na^+ on the exchange complex, and is leached out. However, experiments have shown that gypsum has great potential as an S source for crops and pastures. For example, work on gypsum as a fertiliser on annual grassland (Jones and Ruckman, 1966), indicated that forage production, S uptake and concentration in the forage and percentage of clover were significantly higher in the first year of gypsum application. Using free-draining lysimeters to study the behavior of sulfate-S and S° , Jones *et al.* (1968) found that concentrations of S in the leachate were highest in the gypsum treatment in the first year after application. A study on sulfur-coated triple superphosphates and gypsum conducted on an S deficient Aquic Haplustalf soil, Blair *et al.* (1994) showed that yields, S content, and recovery of fertiliser S in the tops of pastures were highest with gypsum at weeks 4 and 8. They also observed that the total yields and total recovery of fertiliser S were highest in the gypsum treatment (Table 2.6).

Gupta and MacLeod (1984), investigated the effect of various sources of S on yield and S concentration of cereal and forages, and found that gypsum was effective in increasing the S concentration in plant tissues. In rice, Samosir and Blair (1983) found that tops and root yields of rice, as well as S uptake were highest in the gypsum treatments. Dana *et al.* (1994a) found similar results where highest rice grain yields in the first rice crop were obtained with gypsum under both flooded and non-flooded conditions. A greenhouse experiment on flooded rice (Chien *et al.*, 1987), showed that gypsum was an effective S fertiliser source for flooded rice, irrespective of whether it was broadcasted on the soil surface, incorporated or deeply placed in the soil.

Table 2.5 Sources and potential sources of fertiliser sulfur.

Source	% S
<i>Sulfate Containing</i>	
Ammonium sulfate	24
Potassium sulfate	16-22
Calcium sulfate (gypsum)	18
Single superphosphate	12
Triple superphosphate	1.5
Ammonium nitrate-sulfate	5-11
Ammonium phosphate-sulfate	14-20
Ammonium sulfate-nitrate	15
Ammoniated superphosphate	11-13
Diammonium phosphate-sulfate	10-15
Magnesium sulfate (Kaiserite)	23
Potassium-magnesium sulfate	22
Ammonium phosphate-sulfate-gypsum	8
Ammonium phosphate-sulfate-urea	6
Urea-ammonium sulfate	4-13
<i>Elemental Sulfur Containing</i>	
Diammonium phosphate sulfur	12-15
Elemental sulfur	100
Diammonium polyphosphate sulfur	15
Diammonium polyphosphate-urea phosphate-S	5-20
Urea-sulfur	10
KCl-Urea-S	Varies
Sulfur-coated urea	Varies
Rock-P	7-16
Sulfur-bentonite	90
Sulfur fortified superphosphate	27
Ammonia-sulfur solution	10
Sulfur-anhydrite	43
<i>Other Inorganic Forms</i>	
Ammonium thiosulfate solution	26
Sulfur dioxide	50
Ammonium bisulfite	8-17
Ammonium bisulfite polyphosphate	3-5
Ammonium polysulphide	40-45
Pyrite and pyrrhorite	40-80

(Source: Germida and Janzen, 1993)

Table 2.6 Effect of S source on dry weight (g/pot), S content (mg/pot) of plant tops, and recovery of fertiliser S (%) at different harvest times and total over 96 weeks.

Treatment	Harvest Times (weeks)				Total
	4+8	12+17	24+28	36+44	
Yield (g pot)					
Gypsum	13.5 a ^A	9.2 a	4.8 b	2.5 c	30.0 a
UNE1	8.0 b	9.2 a	7.5 a	4.2 b	28.9 ab
UNE3	8.6 b	9.2 a	7.6 a	3.6 b	29.0 ab
UNE2	5.2 c	8.1 b	8.6 a	5.5 a	27.4 b
HF	5.5 c	7.8 b	8.4 a	5.6 a	27.3 b
Control	2.9 d	2.3 c	1.7 c	1.4 d	8.3 c
S content (mg pot)					
Gypsum	18.8 a	11.1 b	5.6 b	3.6 c	39.1 a-c
UNE1	8.6 b	14.2 a	10.9 a	6.5 b	40.2 ab
UNE3	9.8 b	14.1 a	11.0 a	5.8 b	40.7 a
UNE2	5.8 c	10.7 b	12.2 a	8.1 a	36.8 c
HF	6.1 c	10.7 b	12.2 a	8.3 a	37.3 bc
Control	2.8 d	2.0 c	1.5 c	1.9 d	8.3 d
Fertiliser S recovery (%)					
Gypsum	35.7 a	17.8 b	3.0 c	2.9 c	62.4 a
UNE1	8.8 b	21.8 a	14.6 b	7.0 b	52.3 b
UNE2	10.0 b	22.0 a	14.7 b	6.1 b	52.9 b
UNE3	3.9 c	12.1 c	17.6 a	9.9 a	43.5 c
HF	4.1 c	12.7 c	17.8 a	10.1 a	44.7 c

^A Data in each component followed by the same letter in the same column are not significantly different ($P < 0.05$) (Duncan's multiple range test). (Source: Blair *et al.*, 1994).

2.6.3 Elemental S Fertiliser Materials

(a) Elemental Sulfur Coated Urea (SCU)

SCU is widely used as a controlled-release N fertiliser. It consists of a S⁰ shell around each urea particle. In relation to its effectiveness as an S source, a number of authors observed that it is a poor source of S. For instance, Samosir and Blair (1983) reported that S from SCU is not available to flooded rice in the first crop after application. Moreover, they found that the total S content of straw harvested from the control and SCU treatments was in the deficiency range. The

release rate of S from SCU was found to be insignificant. Similar results were also reported for rice by Dana (1992) and Dana *et al.* (1994a), who found that in the first crop under flooded conditions, SCU resulted in significantly lower total dry matter and grain yields. Janzen and Bettany (1986) also found similar results where SCU was found to be an ineffective S source for rapeseed.

A long term study by Vaughn *et al.* (1979) on Californian grassland, showed that S uptake from SCU treatments applied at 140 kg S/ha did not differ from the control in the first year, however, a residual effect of S was measured 5 to 6 years after application. Boswell and Friesen (1993) indicated that SCU has little practical value as an S fertiliser source.

(b) Prilled Elemental Sulfur (Prilled S⁰)

Prilled elemental sulfur is made up of molten S⁰ and it contains about 95.5% S (Swanney *et al.*, 1988). Also, only about 10% of the prills are <1000 µm. A field evaluation of some of the potential S fertiliser materials (Swanney *et al.*, 1988) showed that S⁰ prills were ineffective as S fertiliser materials. Similar results were also reported by Rhue and Kamprath (1973) who found that when prilled S⁰ was broadcasted on the soil, no movement of sulfate into the lower depths was observed. They also found that oxidation of prilled S⁰ was very slow and the authors attributed this poor performance to the slow disintegration of the prills.

A study on the sources of sulfur for rapeseed (Noellemeyer *et al.*, 1981) indicated that application of prilled S⁰ resulted in lower yields and lower concentration of S in the plant. This demonstrated that oxidation rate was very slow, hence, there was insufficient S available to meet the requirements of the crop (Noellemeyer *et al.*, 1981).

(c) Mixtures of S⁰ with Superphosphate

Elemental S is added to superphosphate either by a dry-mix or wet-mix process (Boswell and Friesen, 1993). In the dry-mix process, the dry screened agricultural S is added to superphosphate after its manufacture and curing. Generally, the particle size of the S⁰ is the same as in agricultural S (Boswell and Friesen, 1993). According to Weir (1970), two techniques are involved in the wet-mix process. In one, solid S⁰ is added to the superphosphate as it is being acidulated (wet-mix fusion process). The second technique involves the application of molten S⁰ as a spray onto the acidulating phosphate rock (wet-mix molten product). In the recent past, triple superphosphate -S mixtures have been evaluated. For example, in New Zealand TSP-S⁰ mixtures were examined (Boswell, 1987) and showed that the rate of release of SO₄²⁻ was dependent on the size of the S⁰ particles incorporated in the mixtures. In West Africa, Friesen (1991) observed

that both a granulated TSP-S⁰ mixture and dry S⁰ <250 µm were as effective as the sulfate-S and in some trials more effective.

According to Boswell and Friesen (1993), in Australia TSP-S⁰ products consist mainly of TSP granules coated with S⁰; 10% and 20% S mixtures involve different thicknesses of S. Using 3 adhesive materials (UNE1 = polyvinyl alcohol UNE2 = slack wax and UNE3 = calcium lignosulfonate) to bind S⁰ (particle size <0.01 mm) to the surface of 2-4 mm diameter TSP granules, Dana *et al.* (1994a) and Blair *et al.* (1994), found that apart from gypsum, TSPS-UNE1 (UNE1) and TSPS-UNE3 (UNE3) gave the highest rice grain yields under flooded and non-flooded conditions in the first crop (Table 2.6). The authors further noted that fertiliser S uptake was highest in treatment UNE1 followed by UNE3 and elemental S. In the second crop, yield and fertiliser S uptake were found to be inversely related to that of the first crop. Differences between the TSP-S products were attributed to the method of bonding of the S coat to the TSP granules.

Boswell *et al.* (1996), conducted experiments on a coastal and an inland site where they investigated the effects of different manufacturing techniques on the availability of SO₄²⁻ to pasture from 6 mixtures of S⁰ with triple superphosphate (S⁰+TSP1, S⁰+TSP2,..... S⁰+TSP6). They showed that the rates of release of SO₄²⁻ from oxidation of S⁰ was controlled by the fineness of S⁰ particles and that the mixture prepared by sintering S⁰ with TSP was found to be the most effective in terms of rapid release of SO₄²⁻ by oxidation. This particular mixture contained sulfur particles of <75 µm in diameter. In addition, the authors observed that mixtures which comprised synthetic blends of S⁰ of particle size <150 µm or 150 - 250 µm, each mixed with mature TSP, released SO₄²⁻ at a much slower rate than with particle size <75 µm. Also, they found no response to S⁰ fertilisers at the first soil sampling days (16 or 23 days after application), but, at the second soil sampling (91 and 100 days after application, for the two sites respectively), the authors observed that most mixtures had raised topsoil sulfate concentrations at the two sites (Figure 2.8).

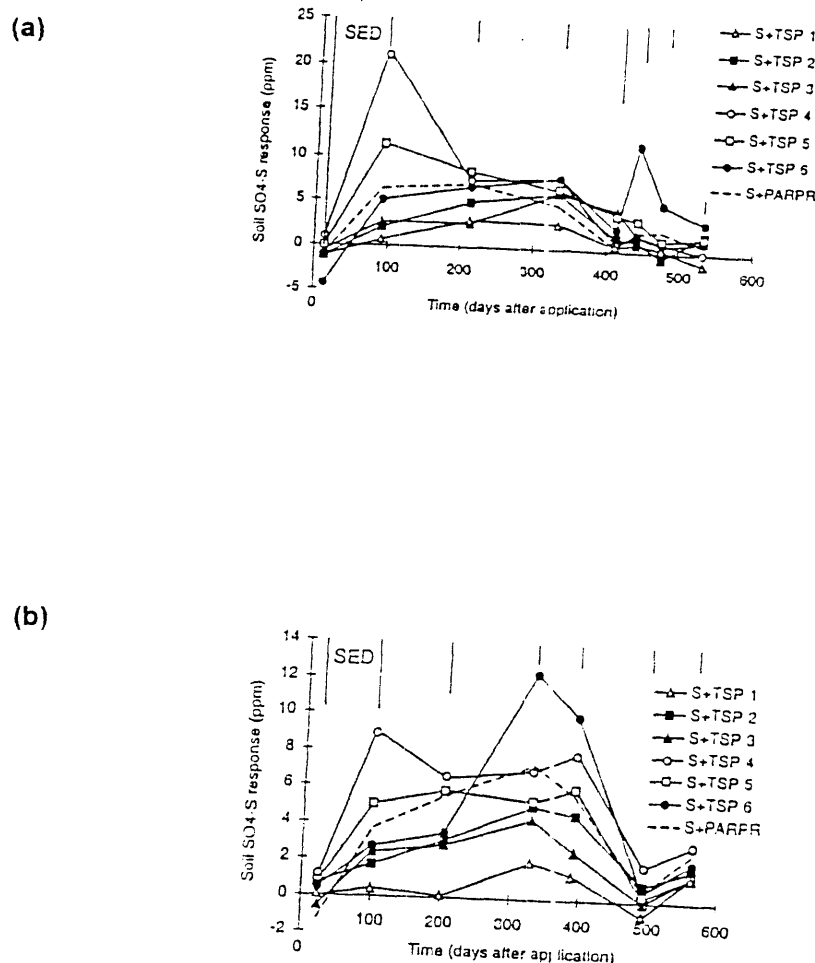


Figure 2.8 Soil sulfate-S (0-75 mm) responses (ppm) to S° fertilisers at 8 & 7 sampling occasions for a) coastal and b) inland sites, respectively. (Source: Boswell *et al.*, 1996).

(d) S° -Bentonite Mixtures

S° -bentonite mixtures can be prepared as dry mixes of ground S° and clay which are then granulated, or as wet mixes of molten S° and bentonite clay (Boswell and Friesen, 1993). Various S° -bentonite fertilisers have been produced containing 90% S° and 10% bentonite. Commercially available S° -bentonites are prepared as wet mixes (Boswell and Friesen, 1993) under various

to the soil, it takes up moisture causing granules to disintegrate thus forming more finely divided elemental S which is rapidly converted to SO_4^{2-} (Tisdale *et al.*, 1993 ; Boswell and Friesen, 1993).

Experiments on S° /sodium bentonite prills as fertilisers (Boswell *et al.*, 1988), indicated that when the proportion of bentonite in the prills was increased from 5 to 40%, the rate at which S became available for plant uptake was greatly increased. Boswell *et al.* (1988) also found that plant sulfate concentrations were increased by the S° /bentonite treatments for the whole experimental period (467 days). Swanney *et al.* (1988) showed that application of S° /Na bentonite on pastures resulted in higher plant SO_4 -S as well as soil SO_4 -S levels. However, Boswell and Friesen (1993) indicated that in pastures, commercial (90% S) S-bentonite prills have always shown a lag period before measurable release of sulfate is observed. Several authors indicated that S-bentonites had greater residual effects than sulfate fertilisers (Matocha, 1971; Hoeft and Walsh, 1975; Dear and Spencer, 1982) which implies that S-bentonites may be suitable as a maintenance fertiliser for pastures (Boswell and Friesen, 1993).

(e) Sulfur Urea (Urea- S°)

Sulfur urea, also known as sulfur impregnated urea is made by injecting molten S° into liquid urea and prilling the melt. It has 36% N and 20% S. According to Kowalenko and Baptie (1984) and Beaton and Soper (1986), Urea- S° is a homogeneous fertiliser material with finely divided elemental S (particle size $<100\text{ }\mu\text{m}$ or $<0.10\text{ mm}$) dispersed throughout each granule. This is an important factor in so far as conversion of S° to SO_4^{2-} is concerned. Using Urea- S° mixtures, which contained 10.4% or 22.4% S of finely divided S° dispersed in pellets of urea 1-3 mm in diameter, Solberg and Nyborg (1983), found that Urea- S° was oxidized as quickly as the fine powdery sublimed S° (100% particles in the range 50-100 μm in diameter). They also found that when the fertilisers were worked into a fallow soil to a depth of 10-15 cm, the S recovery from the Urea- S° as SO_4^{2-} 1-2 months after application to be 33% that from sodium sulfate. Boswell and Friesen (1993), indicated that this could mean that the fine S° in Urea- S° would overcome S-deficiency in crops, particularly in cereal grains or rapeseed. Similar results were also reported by Beaton and Soper (1986), where Urea- S° was observed to be an effective source of fertiliser S for small grain and oilseed crops in Canada. In the Philippines, Mamaril and Gonzalez (1987), reported that Urea- S° was as effective as $(\text{NH}_4)_2\text{SO}_4$ or gypsum in increasing rice yields.

(f) S/Anhydrite

According to Rothbaum *et al.* (1980), and Boswell and Friesen (1993), S/anhydrite pellets are prepared by mixing molten S^o with calcium sulfate anhydrite. Anhydrite is produced by heating gypsum to 450 °C. The molten S^o + calcium sulfate anhydrite is then pelletized in a pan granulator with water as an atomized spray. S/anhydrite contains 43% total S and 28% S^o in a finely divided form. Swanney *et al.* (1988), found that application of S/anhydrite resulted in higher plant sulfate levels which were similar to that of molten mixed sulfur superphosphate, granulated ground S^o and S^o/Na-bentonite. Soil sulfate levels were found to be higher in the first sampling 65 days after sowing the pastures. The response, however, declined faster than the other fertiliser materials (S^o/Na-bentonite or granulated ground S^o). Rothbaum *et al.* (1980), established that pellets made with 30% molten sulfur and 70% anhydrite are promising as suppliers of S to pastures and suggested that the pellets could be used additionally to superphosphate in S-deficient areas, or together with direct-application rock phosphate fertilisers in most areas. The pellets can also store well, are very strong and have satisfactory abrasion-resistance and low dust explosion hazards. Moreover, they tend to disintegrate readily in water to leave colloidal S. However, Swanney *et al.* (1988), pointed out that the likelihood of S/anhydrite to be manufactured on a commercial scale is remote because of the cost involved in heating the gypsum to 450 °C during the manufacturing process.

2.7 SUMMARY

The literature review presented in this chapter indicated that granule and particle sizes of fertiliser materials are important factors (among others) which determine the effectiveness of any fertiliser material. The review also showed that in the recent past, the increasing use of high analysis fertilisers such as urea, TSP, mono- and di-ammonium phosphates has resulted in widespread S deficiencies. Therefore, to counter this problem, various attempts have been made at using S^o to supply the crops S demand. S^o, however, must undergo oxidation before plants can utilize it. Moreover, oxidation of S^o is influenced by a number of factors and one of them is the particle size of the S^o material. Attempts such as employing finely divided S to coat granular products like TSP have been investigated and as a result a number of S^o-containing materials are now being evaluated for their effectiveness as S sources for crops. The results showed that some are effective whilst others are not as S fertiliser sources for crops. The experiment reported in Chapter 3, can be described as one of those attempts to examine the effectiveness of the coated TSP using different S^o particle sizes along with the others which have been investigated previously.