Reprinted from *Fertilizer Technology & Use*, 2nd Edition
Copyright © 1971, Soil Science Society of America
677 South Segoe Road, Madison, Wis. 53711 USA

RP-295/11

Production, Marketing, and Use of Sulfur Products

JAMES D. BEATON
The Sulphur Institute
Washington, D.C.

ROBERT L. FOX
University of Hawaii
Honolulu, Hawaii

I. INTRODUCTION

Sulfur (S) has been recognized as one of the elements essential for plant growth for approximately 130 years. It is a macronutrient and, like N, P, K, Ca, and Mg, must be available in relatively large amounts for good crop growth. Deficiencies of S were identified as early as 1900 on certain soils in the Pacific Northwestern States (Beaton, 1969). In Canada, this deficiency was first recognized in 1927 on some soils in Alberta (Beaton, 1969).

Interest in S as a plant nutrient has increased greatly in the past few years, and reports of S deficiency throughout the world are becoming more frequent and extensive. Crop deficiencies of S occur in many nations in Asia, Oceania, Africa, Western Europe, South America, Central America, and the Caribbean. The majority of soils in tropical and subtropical regions are inherently S deficient. Sulfur deficiencies have been confirmed in field experiments in many parts of the USA and Canada.

The main reasons for greater occurrence of S deficiencies are:

1) Increased use of high-analysis, practically sulfur-free fertilizers
2) Higher crop yields which increase the withdrawal of plant nutrients including S from the soil
3) Greater consumption of low-S fuels and more emphasis on control of air pollution, thus reducing this previously important atmospheric source of plant nutrient S
4) Decreased use of S as a fungicide and insecticide
5) Increased ability to identify soils low in S
6) Decreased levels of soil organic matter

Sulfur deficiencies become more numerous and serious when heavy rates of N, P, K, and other fertilizers are applied. The need for S fertilization of agricultural crops is very closely related to the amounts of N being applied. Figure 1 demonstrates the close association between these two elements. In this figure it is obvious that crop response to S occurred only when N was applied. Equally important is that S deficiency restricted the crop response to

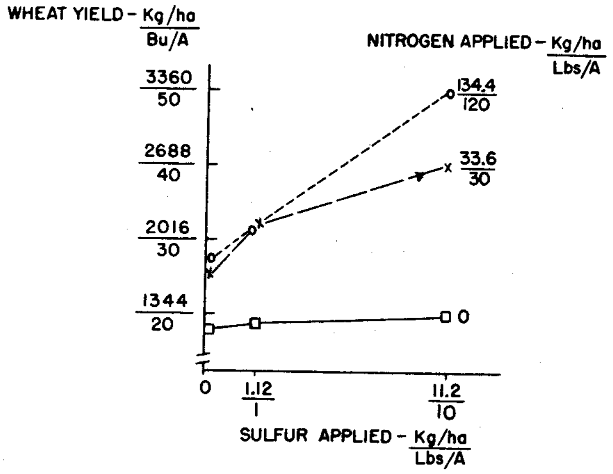

Fig. 1—Effect of S at different rates of N fertilization on yield of spring wheat (Reisenauer & Leggett, 1957).

N fertilization. Thus, the need for S should be considered in all well-balanced fertilizer programs.

Inadequate S seriously retards the growth of plants because this element is required for:

1) The synthesis of the amino acids, cystine, cysteine, and methionine which are essential components of protein. Approximately 90% of the S in plants is found in these amino acids (Martin, 1966)
2) The formation of chlorophyll, even though S does not occur in this substance
3) The activation of certain proteolytic enzymes such as the papainases
4) The synthesis of certain vitamins (biotin and thiamin or vitamin B_1), glutathione, and of coenzyme A
5) The formation of the glucoside oils found in onions, garlic, and cruciferous plants
6) The formation of certain disulfide linkages which are associated with the structural characteristics of protoplasm (the concentration of sulfhydryl (—SH) groups in plant tissues has also been shown to be related to increased cold and drought resistance in some species)
7) The formation of ferredoxin which has an important role in all photosynthetic processes (Arnon, 1965; Zaneti & Forti, 1969)
8) The formation of a ferredoxin-like compound which is involved in the fixation of N by root nodule bacteria (Koch et al., 1970) and free living N-fixing soil bacteria (W. A. Bulen, 1968. Notes on biochemistry of nitrogen fixation. Abstr. 155th Amer. Chem. Soc. Nat. Mtg., San Francisco, Calif.)
9) The activity of ATP sulfurylase, an enzyme concerned with the metabolism of S (Adams & Rinne, 1969; Ellis, 1969)

Crops differ in their requirements for S. The S, N, P, K, and Mg contents

Table 1—Approximate quantity of nutrients contained in various crops

Crop	Yield		Nitrogen (N)	Phosphorus (P)†	Potassium (K)‡	Sulfur (S)	Magnesium (Mg)
	kg/ha*	units/acre	kg/ha*				
Grains§							
Corn	12,544	200 bu	358	52	230	49	74
Grain sorghum	8,064	8,000 lb	291	54	207	43	40
Wheat	5,376	80 bu	168	34	112	25	27
Barley	5,376	100 bu	168	28	140	28	--
Oats	3,584	100 bu	112	22	112	22	22
Rice	7,280	145 bu	151	25	150	20	17
Forage Crops§							
Alfalfa	12,544	6 tons	375	35	251	34	34
Clovers	8,064	4 tons	179	20	149	20	26
Grasses (general)	8,064	4 tons	134	20	112	18	17
Coastal bermudagrass	22,328	10 tons	638	72	370	50	56
Orchardgrass	15,805	7 tons	314	48	289	56	--
Oil Crops§							
Soybeans (beans only)	3,360	50 bu	207	25	112	11	13
Peanuts	3,360	3,000 lb	246	22	112	28	31
Rapeseed	2,240	2,000 lb	101	18	123	39	--
Fiber Crops§							
Cotton	1,400	2.5 bale	140	37	84	26	18
Stimulant Crops§							
Tobacco	3,360	2,800 lb	106	12	179	24	27
Sugar Crops							
Sugarcane§	67,200	30 tons	135	19	235	90	110
Sugar beets (tops & roots)	67,200	30 tons	179	28	235	55	--
Vegetables							
Potatoes (tops & tubers)	26,880	400 bu	224	27	286	30	27
Cabbage (heads)	44,800	20 tons	146	16	118	41	11
Turnip (tops & roots)	67,200	25 tons	128	25	213	43	25
Onions (tops & bulbs)	44,800	20 tons	134	27	99	28	13

* kg/ha × 0.9 = lb/acre. † P × 2.3 = P_2O_5. ‡ K × 1.2 = K_2O.
§ All aboveground portions.

of several crops are shown in Table 1. Vegetable crops such as cabbage, turnip, and onion have long been rated as having high S requirements. However, somewhat more S is required for high yields of coastal bermudagrass, orchardgrass, corn, and sorghum. An adequate supply of readily available S is especially important for vegetable crops because they have a fairly short growing season. Legumes, particularly alfalfa, have intermediate S requirements. Rapeseed, sugarcane, cotton, and tobacco require as much S as some of the leguminous crops. Most small grains and grasses need less S. Table 1 also shows that the S requirements of some crops are quite similar to those of P and Mg.

In addition to the direct nutritional effect of S on plant growth, this element may have a number of beneficial side effects. The acidifying effect of S sources like ammonium thiosulfate, ammonium sulfate, finely divided S, etc., in fertilizer bands in calcareous or high-pH soils may increase the availability of other essential nutrients such as P, Mn, and Zn. Heavier rates of elemental S or H_2SO_4 may be applied where more general pH adjustments are needed. Sulfur and a number of its compounds are helpful in the reclamation of salt-affected soils. Several of these materials are used for water treatment to increase the rate of its penetration into soil.

II. PRODUCTION, AGRONOMIC EFFECTIVENESS, AND USE

Sulfur constitutes approximately 0.1% of the earth's crust. The forms in which it usually occurs are: elemental S (brimstone) in deposits associated with calcite, gypsum, and anhydrite; combined S in metal sulfide ores; combined S in mineral sulfates; hydrogen sulfide contaminant in natural gas; organic contaminants in crude oils; pyritic and organic compounds in coal; and organic compounds in tar sands (Comiskey et al., 1969).

The main sources of the S used in the fertilizer industry are elemental S (brimstone) from dome and volcanic deposits, recovered S from H_2S in sour natural gas and a variety of petroleum refining operations, and S recovered as SO_2 from the roasting of various metal sulfides (Tisdale, 1968). Sulfate salts of Mg, K, and Ca also provide some S to this industry. Descriptions of the production processes used to obtain S from these sources have been omitted here because of the excellent reviews on this subject in the first edition of this book (Kapusta & Wendt, 1963; Smith & Makower, 1963; Tisdale & Cunningham, 1963), in Chapters 10 and 13 of this revision, and in other publications (Anonymous, 1968a, 1968b; Boeglin & Whaley, 1967; Comiskey et al., 1969; Estep, McBride, & West, 1962; Freeport Sulphur Co., 1968; Goar, 1968; Haynes, 1959; Heck, 1968; Jacobs, 1968; and R. S. Cunliffe, 1969. Optimizing conversion of hydrogen sulphide to sulphur. Proc. 19th Can. Chem. Eng. Conf. and 3rd Symp. on Catalysis, Edmonton, Alta., Oct. 19-22).

A. Fertilizers Containing Elemental Sulfur

The use of elemental sulfur to reduce soil pH and to reclaim alkali soils is well known. Problems of dustiness, unpleasantness, and fire hazards have limited its utility as a fertilizer even though there are obvious economies in the use of practically pure S. Addition of elemental S to fertilizers devoid of this element is an excellent alternative for taking advantage of its high degree of purity and for minimizing the reduction in grade of the other plant nutrients. The most important new fertilizers containing elemental S which have been developed during the past few years are discussed below.

1. AMMONIUM PHOSPHATE-SULFUR

Elemental S has been introduced into diammonium phosphate by metering it as one of several solid feed streams to a TVA ammoniator-granulator (Bixby, Tisdale, & Rucker, 1964; Tisdale, 1968). Homogeneous products of uniform particle size usually containing 12-15% S were prepared in this manner.

Laboratory and pilot plant investigations have demonstrated that satisfactory monoammonium phosphate products containing up to 20% S can be produced by both pan granulation and a blunger process (W. F. Hastings. 1964. Pilot plant development of granular fertilizers containing elemental sulphur. Rep. prepared by Cominco Ltd., Trail, B. C., for The Sulphur Institute). Pan granulation was used by two separate groups to incorporate elemental S into diammonium phosphate. One group demonstrated that coatings of between 5-20% S could be made readily[1] while the other workers prepared a product containing 6.7% elemental S (Unpublished data, Cominco Ltd., 1962).

A pan-granulated monoammonium phosphate-sulfur material was as effective as finely divided S or gypsum for increasing alfalfa yields in a field trial in British Columbia. Sulfur-containing diammonium phosphate prepared in a similar manner was found to be a satisfactory source of S for alfalfa in growth chamber and field studies (Unpublished data, CDA, Kamloops, B. C., and Cominco Ltd., 1963). These excellent growth responses are probably related to the enhanced rate of oxidation of elemental S in the presence of water-soluble phosphate fertilizers (Beaton et al., 1968-69; Bloomfield, 1967).

Ammonium phosphate fertilizers containing elemental S should be ideal for bulk blending with other granular fertilizers or for use in direct application to the soil. They should be particularly useful for topdressing legume crops in situations where both P and S are required. In severely S-deficient soil areas, these materials should be broadcast or topdressed on established crops several months prior to planting or the beginning of the growing season. To obtain early season response from ammonium phosphate-sulfur materials in starter fertilizers it may be necessary to include about 15-20% of the total added S in sulfate form.

2. AMMONIUM POLYPHOSPHATE-SULFUR

A product containing 12% N, 23% P, and 15% S (12-52-0-15) was prepared by TVA by spraying liquid S onto a rolling bed of granular ammonium polyphosphate (Achorn & Scott, 1969). Samples of this product were shipped for evaluation in bulk blending operations in the Willamette Valley of Oregon.

The agronomic suitability and reactions of these fertilizers in soil are expected to be similar to those of ammonium orthophosphate materials. As with ammonium orthophosphate-sulfur products, the ammonium polyphosphate-sulfur fertilizers should be applied well in advance of the growing season or with added soluble sulfate when used on soils low in available S.

3. AMMONIUM PHOSPHATE-UREA PHOSPHATE-SULFUR

A fertilizer based on ammonium phosphate, urea phosphate, and elemental S is described as particularly suited for use on alkaline soils (Davis & Burns, 1967). A typical grade contains 15% N, 20% P, and 5% S (15-45-0-5).

---

[1] J. F. McCullough and M. L. Salutsky. 1963. New uses for sulfur in fertilizers. W. R. Grace & Co. final report to The Sulphur Institute.

4. CONCENTRATED SUPERPHOSPHATE-SULFUR

The TVA developed a process for adding elemental S to concentrated superphosphate, often referred to as TSP or triple superphosphate (Young, 1966). The resulting granular product has excellent physical properties and contains about 18% P (40% P_2O_5) and 15-20% S. Run-of-pile concentrated superphosphate that has been passed through a chain mill and scalping screen is fed into a granulating drum at a rate of about 7.3 metric tons (8 short tons) per hour and granulated with steam and water. The steam was fed through a drilled pipe sparger beneath the bed near the feed end of the drum at a rate of about 38 kg/metric ton (75 lb/short ton) of product to preheat the feed material and promote granulation. Molten S was sprayed on the bed at a rate of about 200 kg/metric ton (400 lb/short ton) of product. Eleven to fifteen liters (3-4 gal) of water/min and about 3 liters (.75 gal) of aqua ammonia/min were sprayed on the bed to complete granulation and to decrease the free acid content of the product. The product was dried in a gas-fired rotary drier and sized to −6+14 mesh, in conventional screening and crushing equipment.

A pan granulation technique was found to be a practical and economical method for incorporating nutrient S into concentrated superphosphate[2]. Coatings of 5, 10, 15, and 20% by weight of elemental S were applied by this method.

Samples of TVA's product containing 18% P and 20% S (0-40-0-20) have been tested and found to be excellent sources of both P and S for forage crops in California (M. B. Jones, unpublished data, Univ. of California, 1967), Oregon (Dawson, 1969), Montana (Smith, Stoltenberg, & Graham, 1968), and Nebraska (Fox et al., 1964).

One fertilizer manufacturer in the Western USA is now producing a granular concentrated superphosphate-elemental S material containing 15-17% P and 20% S (0-35-0-20 to 0-38-0-20). Most of the product marketed to date has been fall applied and plowed down for potato production the following spring.

5. SULFUR-FORTIFIED NORMAL SUPERPHOSPHATE

Sulfur-fortified normal superphosphates containing 20-30% S are produced in Australia and New Zealand (Tisdale, 1968). The S can be introduced in the molten or solid form either during or just after the addition of sulfuric acid. The purpose of the added elemental S is to increase the ratio of S to P for use on S-deficient soils and also to extend the availability of S in soils where leaching losses of sulfate are serious. Enriched normal superphosphate containing 13% P and 7% S (0-30-0-7) is now made and sold in the USA.

6. COMPLETE N-P-K SULFUR MATERIALS

Two complete fertilizers containing 10% N, 9% P, 25% K, and 3% S (10-20-30-3); and 12% N, 11% P, 20% K, and 3% S (12-24-24-3), used for

---

[2] Ibid.

the fertilization of cotton, were produced in the Southeastern USA. Molten S^{0} was introduced into a TVA-type ammoniator-granulator through two nozzles located about 25 cm (10 in.) above the rolling bed (Tisdale, 1968). Sulfur was added at the rate of 30 kg/metric ton (60 lb/short ton) of product and the production rate was 27 metric tons (30 short tons)/hour.

Production of three complete fertilizers, each containing 3% by weight of elemental S, was begun recently in one of the South Atlantic States. Details of the procedure for adding elemental S to these fertilizers made by the Norsk Hydro process have not been released. These products analyzed 21% N, 3% P, and 12% K (21-7-14-3); 15% N, 7% P, and 13% K (15-15-15-3); and 18% N, 4% P, and 15% K (18-9-18-3).

7. UREA-SULFUR

A 40-0-0-10(S) fertilizer containing urea and elemental S was marketed for a few years on a limited scale in the Western USA. Although production has been discontinued in this region, the material is of sufficient interest to note that it was made by fusing urea and elemental S, followed by prilling (Tisdale, 1968). The product has excellent storage and handling properties. It was reported to be useful for direct application, bulk blending, and in granulation processes.

Currently a urea-sulfur fertilizer with an analysis of 40-0-0-10(S) is being used on crops such as rice and coastal bermudagrass in the West South Central States and in Mississippi and New Mexico. It is made by coating urea particles with finely divided elemental sulfur.

The elemental S component of the discontinued urea-sulfur product did not oxidize rapidly enough to provide adequate available S early in the growing season (Koehler, 1965). However, it became available for subsequent plant growth. Reducing the particle size to −100 mesh greatly improved the effectiveness of urea-sulfur for early growth. For maximum effectiveness, urea-sulfur should be applied several months in advance of the growing season and, when feasible, it should be incorporated into the soil.

8. POTASSIUM CHLORIDE-SULFUR

Crystalline KCl (−7+16 mesh) was successfully coated with liquid S in a laboratory-scale pan granulator[3]. This process was found to be a practical way for incorporating nutrient S, but it was not an effective way of inhibiting dissolution.

9. POTASSIUM CHLORIDE-UREA-SULFUR

The preparation of a granular fertilizer containing at least 35% by weight of KCl and 5-40% by weight of a 1:1 mixture of urea and elemental S is described in US Pat. no. 3,501,282 (Titus, 1970). The proposed benefits of this fertilizer include agglomeration of finely divided KCl particles into hard durable

---

[3] Ibid.

granules and production of a more balanced fertilizer having low hygroscopicity and water solubility.

10. SULFUR COATINGS FOR SLOW-RELEASE UREA AND POTASSIUM CHLORIDE

In recent years there has been a considerable interest in developing slow-release N fertilizers at a reasonable cost. One promising approach to achieving controlled release is to coat water-soluble N fertilizers with relatively insoluble, inexpensive materials such as elemental S.

Sulfur-coated urea (SCU) has been produced on a pilot-plant scale at TVA (Sulphur Institute, 1968). The basic process involves the formation of a S shell around each urea particle by spraying atomized molten S on a rolling bed of urea particles and then adding a light coating of a petroleum wax (also applied in the molten state) to seal the microscopic pores and cracks in the S coatings. The wax contains a small amount of microbicide to prevent its being attacked by soil microbes. Finally, a small amount of conditioner is added to give good product handling characteristics. The analysis of a typical SCU product is 35% N, 19% S, 3% wax, 0.5% microbicide (coal tar), and 1.5% conditioner. Details of the pilot plant process follow.

The urea is fed continuously to the 0.9-m diameter (3 ft) by 1.3-m long (4 ft) coating drum, where it is preheated in the first section, coated with molten S in the second, and coated with the hard wax sealant containing microbicide in the third section. Retaining rings are used to separate the three sections and these can be adjusted to give bed depths of 15-20 cm (6-8 in.). From this drum, the product passes to the cooler and then to a drum where it is coated with a conditioning agent.

The molten S is applied with an atomizing-type spray nozzle; hot air is used for the atomizing. The nozzle is positioned about 15 cm (6 in.) above the bed to spray downward onto the rolling bed. Air pressure is adjusted to prevent excessive turbulence in the bed. The air for heating the granules and for atomizing the S is heated electrically as is the S feed tank. The S feed line is steam jacketed. The amount of S applied is controlled by adjusting the feed rate to the atomizer and by controlling the fertilizer feed rate. The S rate is controlled by adjustment of the pressure of N-displacement gas in the S weigh tank.

Controlled tumbling and uniform flow of particles under the S spray nozzle are obtained by lining the interior of the coating drum with felt, which also serves as insulation. In addition, circumferential ribs of felt about 2 cm (3/4 in.) wide and 0.5 cm (3/16 in.) high spaced 2.5 cm (1 in.) apart are provided in the coating section. The molten wax-microbicide mixture is fed through a steam-jacketed line and applied with an orifice-type nozzle.

Greenhouse and field experiments have shown that SCU reduces the toxicity of single massive doses of urea to bermudagrass turf (Allen, Mays, & Terman, 1968); minimizes the harmful effect of urea on germination and early growth of sensitive crops such as corn (Allen et al., 1968); promotes more uniform growth of grasses (Mays & Terman, 1969a) and protein in forage crops (Allen et al., 1968); reduces luxury consumption of N (Mays & Terman, 1969a); and is believed to reduce the apparent loss of ammonia from surface-applied urea (Terman & Hunt, 1964). In a year with unusually heavy spring rainfall, a SCU product was superior to several uncoated water-soluble N fertilizers for corn production in Kansas (L. S. Murphy, unpublished data, Kansas State Univ., 1969). SCU was shown to be slightly more effective than urea for paddy rice in Arkansas (R. B. Diamond, and D. A. Mays, 1970. Agro-economics of sulfur-coated urea. 67th Ann. Mtg. Assoc. Southern Agr. Workers, Memphis, Tenn., Feb. 2-4).

The economics of using SCU products were reviewed recently (Diamond & Mays, 1970) and definite savings could be realized from their use, particularly in situations where split applications of water-soluble N sources were required. Improvements in the process for making SCU have reduced costs to the point where the N it contains is only about 20-25% more expensive than that supplied as urea or ammonium nitrate. Incentives for using SCU will be even greater when credit is given for the contained S which becomes available for plant uptake (Mays & Terman, 1969b). The value of this element in crop production and turfgrass management (Beaton, 1970) is well known.

A number of other processes have been proposed for including S in coatings on slow-release fertilizers. For example, Thiokol has developed a product similar to TVA's SCU (Fleming, 1970; Thiokol Chemical Corp., 1969); Allied Chemical has used alternating layers of S, gilsonite, and fatty acid (Formaini, 1967); Bidlack and Bidlack (1967) have applied alternating layers of tung oil and S; Commerical Solvents Corp. (1968) has formed layers of salt by reacting sulfur trioxide and alkaline materials; and Standard Oil of Indiana used S plus a plasticizing agent (O'Connor, 1965).

At TVA, S coatings were also successfully applied to diammonium phosphate crystals and granules, ammonium phosphate nitrate granules, and potassium chloride granules (Rindt, Blouin, & Getsinger, 1968). Sulfur-coated KCl may be a practical way of reducing luxury consumption of K, minimizing leaching losses of K on sandy or highly weathered soils, and avoiding high concentrations of troublesome chloride. The agronomic properties of sulfur-coated KCl are presently being studied in greenhouse trials at TVA and field experiments in Wisconsin, Hawaii, and elsewhere.

11. ROCK PHOSPHATE-SULFUR AND MICRONUTRIENT-SULFUR FUSIONS

There has been periodic activity and interest, dating back to at least 1916, in the preparation of rock phosphate-S mixtures. A process involving sublimaation of elemental S and its subsequent recrystallization on the surface of finely divided rock phosphate was patented in 1930 (Bodrera, 1930). Clairborne and Peterson (1937) suspended rock phosphate in molten S and crushed the mix after it had cooled. Acidulating agents soluble in molten S such as H_2SO_4, H_3PO_4, $(NH_4)_2SO_4$, and others can be added to the rock phosphate-molten S mixture (Gilbert, 1939). The agronomic value of these molten S-rock phosphate products has not been fully evaluated.

Renewed interest in the rock phosphate-S materials in the 1960's resulted in a simple process for their preparation based on stirring finely divided rock phosphate into molten S followed by cooling and grinding to suitable size (Kittams & Attoe, 1965). Applications of −40 mesh particles of this product effectively increased plant growth and P uptake on slightly acid soil, but they were only partially available on a calcareous soil (Attoe, Allen, & Fenster, 1966-67; Kittams & Attoe, 1965).

Ball clay was used by the TVA to promote granulation of mixtures containing pulverized rock phosphate and 7-16% sulfur (Hignett & Hoffmeister, 1965). A granular rock phosphate-S product containing *Thiobacilli* has been made in Australia (CSIRO, 1967-68). Limited quantities of this material, known as "Biosuper," are being tested in field trials in the Northern Territory of that country.

Micronutrient-S fusions have been made by adding micronutrient salts to molten sulfur (Ludwick, Sharpee, & Attoe, 1968). The data obtained by Ludwick et al. (1968) and Sharpee et al. (1969) suggested that fusions of certain micronutrient salts with S will provide prolonged release of Mn, Zn, and Cu. Neither the rock phosphate-S nor the micronutrient-S fusions are being produced commercially.

12. GRANULAR SULFUR PRODUCTS CONTAINING ADDITIVES

Several types of high-analysis elemental S assemblages have been developed which eliminate the undesirable aspects of applying finely divided elemental S. In order to obtain crop response during the first growing season after fertilization, it is essential for these products to disintegrate at a reasonably rapid rate following application to soil. For early response, at least 30-40% of the S should be −80 mesh to ensure a significant conversion to the sulfate form.

High-analysis granular S assemblages have been prepared by suspending sodium bentonite in molten S and either prilling or pan-granulating the molten material (Bridger & Bixby, 1966; and G. L. Bridger, L. W. Ross, & P. H. Li, 1966. Development of a water-degradable granular sulfur product. Georgia Inst. Tech. Final Rep. to The Sulphur Institute; Hastings & McGowan, 1966). Additives such as gypsum, goulac (calcium lignosulfonate), and ammonium sulfate have been incorporated either alone or in various combinations to improve binding where needed and to assist in subsequent disintegration of the granules.

Soluble salts like sodium sulfate and ammonium sulfate have been included to supply an available source of S and in some methods of preparation to assist in the formation of hard durable granules. However, ammonium sulfate should not be used with certain assemblages because it may impair their disintegration properties. Surfactants can be added to facilitate the entrance of water into the granules. The quantities of the additives can vary widely, but it is important to maintain the S content as high as possible and still retain desirable disintegration characteristics.

A high-analysis prilled sulfur product which contains 88% S has been marketed for several years. The remaining portion is believed to be mainly bentonite. This product has good physical properties making it suitable for bulk blending or for direct application. Upon contact with water it will degrade into smaller particles which facilitate the oxidation of sulfur to sulfate. Several investigators (Matocha, 1969; H. Feilinger, 1968. Performance of new sulfur fertilizer formulations. M. S. Thesis, Univ. of Minnesota, St. Paul) have found that this commercial product did not correct S deficiency in the first year following application. However, there appears to be sufficient disintegration of prills of elemental S-bentonite (Hoeft & Walsh, 1970) and pan-granulated elemental S-bentonite (Jones, Martin, & Ruckman, 1970) during the first year after fertilization for these preparations to become effective sources of S in the second and subsequent growing seasons. Pan-granulated sulfur-gypsum (78% S) proved to be as satisfactory as either finely divided S or gypsum for alfalfa growth in field experiments in British Columbia (Beaton et al., 1968–69).

Another high-analysis (90% S) product with nonspherical granules became commercially available in 1970. Its agronomic effectiveness has not been reported to date, but on the basis of simple water degradability tests it promises to be a satisfactory source of S.

Because of the uncertainty of adequate availability of high-analysis elemental S products during the first growing season, they should be added several months before the growing season begins, especially when they are not incorporated into the soil. Also, it appears that the performance of elemental S-bentonite materials can be vastly improved by the inclusion of sulfate salts.

13. GRANULAR SULFUR PRODUCTS DEVOID OF ADDITIVES

Sulfur prills free of additives of any sort have been produced, but they are not a suitable source of plant nutrient S because of their extremely slow rate of disintegration in the soil (Beaton & Hubbard, 1969).

Flake S is used for direct application and bulk blending. Its effectiveness depends upon flake size and thickness. This source of elemental S is not expected to correct S deficiencies during the first growing season after application unless approximately 25% of the particles are less than 60 mesh. As with prilled S and S-bentonite products, the agronomic suitability of flake S could be improved by the addition of soluble sulfate salts.

Experimental quantities of porous sulfur granules have been made by at least two commercial concerns. Agronomic evaluation of these products is currently underway.

14. ANHYDROUS AMMONIA-SULFUR

Although elemental S is not soluble in aqueous media, it can be dissolved in liquid anhydrous ammonia. Solubility of S increases with a decrease in the temperature of ammonia (Phillips & Scott, 1966). Anhydrous ammonia-sulfur solutions can be made by adding weighed amounts of solid elemental S (usually −20 mesh) to a pressure reservoir, then metering in the amount of liquid ammonia necessary to achieve a specific S concentration. The rate of dissolution of S in anhydrous ammonia can be increased by agitation for a short period of time. Under conditions of continuous plant operation, molten S can be metered directly into a mixing chamber along with the desired amount of liquid anhydrous ammonia. After a retention time of about 20 minutes, the solution can be pumped from the mixing chamber into pressurized storage vessels or tank cars.

Liquid S is preferred for the production of this fertilizer because it contains no water and little or no SO_2, both of which are frequently found in ground solid S (Tisdale, 1968). Both these impurities cause serious corrosion of equipment. Water from any source should be avoided because it can lead to the troublesome precipitation of ammonium thiosulfate in supply lines and orifices (Bixby & Rucker, 1965; Tisdale, 1968). Concentrations of about 10% S in this product are preferred under conditions of high temperatures to prevent precipitation of the S in application equipment (Tisdale, 1968). Anhydrous ammonia-sulfur solutions have been offered commercially as 74-0-0-10 and 70.5-0-0-14 (Bixby and Rucker, 1965). Small quantities of this product are presently being made and marketed in eastern Oregon and southwestern Idaho. It was also made and sold in Colorado for a few years.

In spite of favorable agronomic results (Koehler, 1965; Scott & Tisdale, 1966) acceptance of the product has been slow because of concern about corrosion of pressure vessels and application equipment and plugging of screens (Scott, Wilbanks, & Burns, 1967), supply lines, and orifices (Bixby & Rucker, 1965). Furthermore, there have been objections to the minor modifications that must be made to equipment such as pumps (Scott et al., 1967) and the need to flush out all equipment after these formulations have been used. Nullification of insurance on anhydrous pressure vessels upon the introduction of foreign substances such as S has also discouraged use of this fertilizer.

15. SULFUR SUSPENSIONS

Finely divided elemental S has been successfully incorporated into suspensions. Suspensions containing 9% N, 8% P, 15% K, and 10% S (9-18-18-10), and 12% N, 5% P, 10% K, and 20% S (12-12-12-20) have been prepared at TVA by mixing finely ground S (< 20 mesh) with a base suspension containing 12% N and 18% P (12-40-0), urea-ammonium nitrate solution, and potassium chloride (Achorn & Myers, 1969; TVA, 1966).

Suspension fertilizers containing S and micronutrients have also been prepared (TVA, 1966). Examples are a 13-6-8 (13-13-13) containing 4% S as −35 mesh crude S, 2% Zn as zinc oxide, 1% Cu as copper sulfate, 0.2% B as sodium borate, and 0.1% Mn as manganese oxide; an 8-7-13 (8-16-16) with 8% S, 0.2% B, and 0.6% Mn; and an 11-5-9 (11-11-11) with 8% S, 4% Mg, and 2% Zn.

Stable N-S suspensions with contents of up to 50% S have been prepared from urea-ammonium nitrate solution, elemental S, and clay (Bixby, 1969). A typical grade is 24-0-0-24 containing 2% attapulgite.

There has been some activity in developing suitable sulfur-water suspensions. In the State of Washington, a commercial concern cooperating with TVA prepared a 30% S suspension in water using −150 mesh S and 3% sodium bentonite (Bixby, 1969). Sodium bentonite clay pre-gelled into a 10–12% slurry was superior to attapulgite clay. Attempts at applying the suspension by introducing it into anhydrous ammonia in a tee before passing the mixture through standard applicator knives were not entirely satisfactory. An alternative method of taking the two materials in separate tubes to common injection shanks was to be tried. Preparation of the initial suspension by spraying molten S into the clay slurry was also to be tested.

Tests conducted at TVA showed that sulfur-water suspensions containing about 60% S and 1% attapulgite could be prepared from −20 mesh crushed lump S (J. Silverberg & A. J. Dixon, unpublished data, Tennessee Valley Authority, 1969). Satisfactory suspensions containing 40% S were produced from flowers of S and 1% clay. These suspensions were cold-blended by dispersing attapulgite clay in the water of formulation for 5 min. The S was added and mixing continued for an additional 5 min.

A stable S suspension can also be prepared by passing gaseous H_2S and SO_2 into water containing a small amount of ethylene glycol (Every & Grimsley, 1968a). Its properties when mixed with other ingredients of a fertilizer suspension are unknown. Similar suspensions have been made in formulations of water containing phosphate slimes (Every & Grimsley, 1968b). The suspension is neutralized with a base, then filtered, and dried. Resuspension of the product is easy and long lasting.

There is little or no information available concerning the agronomic effectiveness of sulfur suspensions. Elemental S in the particle size ranges suitable for suspensions should oxidize rapidly enough to supply available S under most soil conditions. However, if the S suspensions are to be broadcast and left on the soil surface they should be applied several months before seeding. Incorporation of these suspensions into the soil should be encouraged. Some sulfate should be included along with the elemental S in suspensions that are used in starter fertilizers.

B. Fertilizers Containing Sulfate

A number of fertilizers containing S in the sulfate form are commonly marketed for the correction of deficiencies of this plant nutrient. These materials have the advantage of supplying S in a form that is immediately available for plant uptake.

1. AMMONIUM SULFATE

This is one of the oldest of the N- and S-containing fertilizers. For many years it has been a byproduct of the coking of coal. Large quantities of ammonium sulfate result from the manufacture of caprolactam, the raw material for nylon 6. By 1972 the average recovery of byproduct ammonium sulfate is expected to be approximately 3-4 kg/kg of caprolactam produced and will total about 3 million metric tons (Stanford Research Institute, 1967).

Ammonium sulfate is also an important byproduct of various metallurgical operations. Sulfur dioxide evolved during the smelting of sulfide ores is collected, concentrated, and converted to sulfuric acid, which is in turn neutralized with ammonia. Byproduct ammonium sulfate is also produced from the aqueous ammonia solutions used in the pressure leaching treatment of sulfide ores of nickel and cobalt.

Ammonium sulfate is also manufactured by introducing ammonia gas and CO_2 into a water slurry of gypsum. Calcium carbonate is precipitated, and the soluble ammonium sulfate recovered from the liquid. This method has not been widely adopted because the economics of the process are not always favorable. However, in the TVA sulfate recycle process for the manufacture of nitric phosphate fertilizers (TVA, 1966), this conversion is considered to be commercially feasible.

2. AMMONIUM NITRATE-SULFATES

Ammonium nitrate-sulfate with an analysis of either 30-0-0-5(S) or 27-0-0-11(S) has been produced at TVA. Of the two grades, the former has been used most widely. Both grades are homogeneous, granular products made by neutralizing nitric and sulfuric acids with ammonia, and concentrating and feeding the product onto a tumbling bed of recycled product on a pan granulator. Ammonium nitrate-sulfate has several advantages over ammonium sulfate and ammonium nitrate individually. It is less hygroscopic and does not possess the hazardous properties of ammonium nitrate. In addition, the proportions of N and S in this fertilizer correspond rather closely to actual plant nutrient requirements. The combination of 75% ammoniacal and 25% nitrate N makes the product equally useful for both autumn and spring applications.

Equimolecular mixtures of ammonium sulfate-nitrate, analyzing 26-0-0-12(S), are produced on a significant scale in Western European countries, especially West Germany (Anonymous, 1968c). The various processes used to manufacture this fertilizer in Europe have been described elsewhere (Anonymous, 1969).

A 30-0-0-5(S) is being manufactured by one commercial concern in the western USA and one in western Canada. Details of these processes are not available at the present time.

The TVA ammonium nitrate-sulfate is being used extensively in the Lower Rio Grande Valley of Texas for direct application to citrus and in bulk blends applied to vegetables, grain sorghum, and cotton. It has also been used in bulk blending operations in Nebraska. In the Pacific Northwest USA the commercial 30-0-0-5(S) fertilizers are being applied directly to forage and grass seed crops in the Willamette Valley of Oregon and to winter cereals in eastern Oregon and Washington and northern Idaho.

3. AMMONIUM PHOSPHATE-SULFATE

The processes used for manufacturing ammonium phosphate-sulfate are many and varied. Many ammonium phosphate-sulfate products are made by treating a mixture of phosphoric and sulfuric acids with NH_3. They are also prepared by introducing substantial quantities of nearly saturated ammonium sulfate solutions and concentrated sulfuric acid into the phosphoric acid reaction circuit.

The most common grade of ammonium phosphate-sulfate contains 16% N, 9% P, and 14% S (16-20-0-14). It is made up of about 40% monoammonium phosphate and 60% ammonium sulfate. Another grade sometimes offered contains 13% N, 17% P, and 20% S (13-39-0-20).

The 16-20-0-14(S) is popular in many countries for direct application to forage crops, especially legumes. It is also frequently used for formulating bulk blends. In some areas it is placed with the seed of cereal crops at rates up to 134 kg of material/ha (120 lb/acre).

4. AMMONIUM PHOSPHATE-SULFATE-GYPSUM AND AMMONIUM PHOSPHATE-SULFATE-UREA

A granular product containing 15% N, 13% P, and 8% S (15-30-0-8), based on ammonium phosphate, ammonium sulfate, and gypsum, is being manufactured in the Southeastern USA. It is claimed to be suitable for both bulk blending and direct application.

Experimental quantities of a homogeneous product containing 23% N, 10% P, and 6% S (23-23-0-6) based on ammonium phosphate, ammonium sulfate, and urea were made by a manufacturer in western Canada.

5. UREA-AMMONIUM SULFATE

Mechanical mixtures of urea and ammonium sulfate with a grade of 34-0-0-11(S) have been sold in western Canada since 1967. Handling and storage characteristics of these mixtures have not been completely satisfactory, but these difficulties can be overcome by coating the blends with paraffin wax (Roberts, 1970). Homogeneous 34-0-0-11(S) and 38-0-0-6.5(S) products made by coating ammonium sulfate fines with urea have been marketed on a trial basis in the Pacific Northwest USA.

The TVA has demonstrated that grades such as 30-0-0-13(S), 34-0-0-9 (S), and 40-0-0-4(S) can be made by oil-prilling preparations of ammonium sulfate fines in molten urea. Other processes for making such products include coating ammonium sulfate fines with urea in an ammoniator-granulator and by air-prilling. Because of the dilution effect of ammonium sulfate in these fertilizers, potential losses of NH_3 during the hydrolysis of urea should be reduced. The physical properties of urea-ammonium sulfate are apparently superior to urea alone. Granules of this material can be further improved by the addition of some gypsum, which forms a complex with urea.

6. CALCIUM SULFATE

Gypsum ($CaSO_4 \cdot 2H_2O$) is used as a source of S in areas close to where it is mined or produced as a byproduct. Its relatively low S content, 18.6% in pure form to about 13.3% in byproduct sources, limits the extent to which it can be profitably used. Although it is difficult to apply, finely divided gypsum will usually produce a quick response with most crops.

7. NORMAL SUPERPHOSPHATE

Normal superphosphate is made by reacting rock phosphate with sulfuric acid in approximately equal portions by weight. The product is composed of approximately 50% gypsum or its lower hydrate and about 50% monocalcium phosphate. Minor amounts of dicalcium phosphate, tricalcium phosphate, apatite, and other impurities may also be present. Normal superphosphates usually contain 10–12% S and are excellent sources of this plant nutrient. In fact, the occurrence of S deficiencies has been delayed in many areas of the world because of the incidental application of this nutrient in normal superphosphate.

8. POTASSIUM SULFATE AND POTASSIUM-MAGNESIUM SULFATE

Fertilizer grade potassium sulfate (K_2SO_4) contains 41.5% K (50% K_2O) and 17.6% S. Commercial potassium-magnesium sulfate usually analyzes 18% K (22% K_2O), 11% Mg (18% MgO), and 22% S. Both materials will readily correct deficiencies of plant nutrient S. They are often used to formulate bulk blends for cropping situations where chloride-free K fertilizers are preferred. In some areas these salts are applied directly as sources of K, S, or Mg individually or to remedy multiple deficiencies of two or all three elements.

A homogeneous prilled fertilizer containing 20% N, 17% K, and 7% S (20-0-20-7) was introduced recently. This material, containing all of the S as K_2SO_4, is reported to be suitable for direct application as well as for bulk blending. In addition, it can be used in the preparation of fluid fertilizers.

9. MAGNESIUM SULFATE

This salt, containing 13% S and 9.8% Mg, is occasionally used to supply Mg in clear liquid fertilizers and foliar sprays. Fertilization with this source will also provide incidental additions of immediately available S.

10. SULFATES OF MICRONUTRIENTS

The sulfate salts of micronutrients are also incidental carriers of S. Examples are: copper sulfate ($CuSO_4 \cdot 5H_2O$), 12.8% S; ferrous sulfate ($FeSO_4 \cdot H_2O$), 18.8% S; manganese sulfate ($MnSO_4$), 21.2% S; zinc sulfate ($ZnSO_4 \cdot H_2O$), 17.8% S; and zinc-manganese-ammonium sulfite, 20% S. While these compounds are rarely, if ever, used for the S values only, they nonetheless supply this element in a plant-available form when used alone, in mixed fertilizers, or as foliar sprays.

C. Fertilizers Containing Other Forms of Sulfur

There are three materials containing reduced or partially oxidized S compounds which are used in the rapidly expanding market for fluid fertilizers. These are ammonium thiosulfate, ammonium polysulfide, and ammonium bisulfite. A fourth material, SO_2, has been tested and found to be a suitable source of plant nutrient S.

1. AMMONIUM THIOSULFATE

Ammonium thiosulfate is perhaps the most widely used S-containing product in the fluid fertilizer industry. It may be prepared by reacting SO_2 and aqueous ammonia forming at first an ammonium sulfite solution, which reacts further with elemental S to form an ammonium thiosulfate solution. In two somewhat similar methods, aqueous ammonia, S, and oxygen (air) are reacted under conditions of high temperature and pressure to yield the compound directly (Eisenbraun & Ulmer, 1969; Every & Cox, 1970). Another process has been developed in which ammonium bisulfite solution is reacted with NH_3 and S, and catalytic amounts of H_2S to eventually produce a 60% thiosulfate solution (Mack, 1969).

Commercial solutions of ammonium thiosulfate have a density of 1.3 kg/liter (11 lb/gal). The N content is actually somewhat greater than indicated by the chemical formula [$(NH_4)_2S_2O_3$] because of free NH_3 which is added to ensure stability. Without a slight excess of NH_3, the material would slowly decompose, liberating free S in the process. It is usually marketed as a 60% aqueous solution containing 12% N and 26% S.

Solutions of ammonium thiosulfate are compatible in any proportion with neutral to slightly acid (not less than pH 5.8) phosphate-containing fluids including liquids, suspensions, and slurries produced from orthophosphates and polyphosphates of wet process or electric furnace manufacture. Ammonium thiosulfate can be blended with these phosphate materials in a reactor vessel or nurse tank. When blended with ammonium phosphate fluids, the supplemental N should be supplied as ammonium nitrate, urea, or urea-ammonium nitrate solutions. Anhydrous or aqua ammonia are not used except when the pH of the phosphate solutions is less than 5.8 and adjustment to this level is desired.

Ammonium thiosulfate can be readily blended with aqueous ammonia and N solutions. It is not compatible with anhydrous ammonia. Blending of a wide variety of N-S, N-P-S, and N-P-K-S formulations containing up to 10–12% S is usually possible with relative ease. However, problems of salting-out can occur when mixing ammonium thiosulfate with potassium chloride, and ammonium nitrate or urea-ammonium nitrate solutions.

Ammonium thiosulfate is essentially noncorrosive and may be stored in mild steel or aluminum containers. It should not be allowed to contact tin, copper, brass, or other copper alloys. Storage temperatures should be between −1.1 and 37.8C (30 and 100F). It can be applied directly with solution applicators or applied through open ditch and sprinkler irrigation systems.

2. AMMONIUM BISULFITE

This byproduct of smelting operations is made by absorbing SO_2 gas in aqua ammonia. It is available commercially as a 55-60% solution containing 8.5% N and 17% S. Its density is 1.3 kg/liter (10.8 lb/gal). Small amounts of ammonium sulfite and ammonium sulfate are usually present. The solution is nonpressure and has a pH of about 5.2. Crystallization temperature is 0C (32F) and freezing temperature is −28.9C (−20F).

Ammonium bisulfite (NH_4HSO_3) in combination with aqueous ammonia or N solutions can be used to obtain almost any desired N to S ratio. Like ammonium thiosulfate and polysulfide, it cannot be used in acidic solutions. With ammonium phosphate solutions such as 8-11-0 (8-24-0), however, grades such as 10-4-0-3(S) (10-10-0-3), 8-4-0-8(S) (8-8-0-8), and 15-7-0-1(S) (15-15-0-1) have been prepared. At TVA, 10-13-0-3(S) (10-30-0-3), and 10-11-0-5(S) (10-26-0-5) grades have been made using ammonium bisulfite and ammonium polyphosphate solutions.

Either mild steel or aluminum containers can be used for storage of ammonium bisulfite. When mixed with other solutions, such as aqua ammonia, the mixtures become corrosive to mild steel unless they have been properly inhibited. Etching at the air-liquid-metal interface takes place with these mixtures. Mild steel storage facilities must be given a special treatment before being put into service. The uninhibited solutions may be handled without difficulty in aluminum or plastic.

3. AMMONIUM POLYSULFIDE

This is a reddish-brown to black solution having a strong odor of H_2S and containing 20% N and 40-45% S. It has a density of about 1.1 kg/liter (9.5 lb/gal) and a vapor pressure of 0.70 kg/cm^2 (10 lb/in.^{2}).

Ammonium polysulfide [$(NH_4)_2S_X$] is made by reacting aqua ammonia with H_2S in the presence of heat and agitation. Small amounts of sulfates, thiosulfates, and elemental S may be present in the finished product. It is strongly alkaline, having a pH of 10.0 or greater. This product is not compatible with acidic solutions since it decomposes in an acid medium, liberating H_2S and forming colloidal S.

Ammonium polysulfide is recommended for use with anhydrous ammonia and is also compatible with aqua ammonia and urea-ammonium nitrate solutions. Generally, it is not considered to be suitable for mixing with phosphate-containing liquids, but it may be, depending on the pH and salt content of the solutions. Complete liquid fertilizers containing up to 5.8% K (7% K_2O) have been made. When contemplating using questionable materials, trial mixes are recommended before attempting full-scale mixing operations.

Mixing with NH_3 is best accomplished in a closed system at around 0.004 kg/cm^2 gauge (0.5 lb/in.^{2} gauge) in order to avoid loss of NH_3 and S precipitation. Black iron, stainless steel, or aluminum equipment should be used for handling ammonium polysulfide. Copper-containing alloys, such as brass and bronze, are subject to severe corrosion and should not be used. After use, application equipment should be cleansed with water or NH_3. Storage in open containers is possible with a layer of oil on the surface to prevent volatilization. Ideal storage temperatures are between −1.1 and 37.8C (30 and 100F). For long-term storage at temperatures below −1.1C, dilution with aqueous ammonia (25% by volume) is recommended.

Ammonium polysulfide may be applied in irrigation water in open-ditch systems. It may be injected into soil as is the practice with other liquid fertilizers. When diluted with water to 15% or lower N content, ammonium polysulfide may be applied directly to the soil surface by spray applicators. Single preplant applications have resulted in good growth responses, while several applications at lower rates may also be effective.

4. SULFUR DIOXIDE

This potential fertilizer material is prepared by burning S in air. It is also a byproduct of the mining and smelting industry. Liquid SO_2 is a high-analysis material containing 50% S. It is a pressure liquid [1.63 kg/cm^2 gauge at 15.6C (26.2 lb/in.^{2} gauge at 60F)] and must be applied using equipment similar to that used for the injection of anhydrous ammonia. Because of SO_2's incompatability with anhydrous ammonia, a separate tank and pump must be used.

In spite of favorable results with this product injected directly into soils at rates up to 72 kg of S/ha (64 lb/acre), it is not widely used as a source of plant nutrient S. The reasons for this lack of acceptance are apparently: (i) the separate tank and pump on applicator rigs referred to above; and (ii) present pumps are not capable of accurately metering the small amounts of SO_2 required for most cropping situations.

Limited amounts of this material are used for water treatment in the Imperial and San Joaquin Valleys of California. In addition, SO_2 is being used in the Imperial Valley to reclaim tile drains clogged with Fe and Mn compounds (Grass & MacKenzie, 1970). Sulfur dioxide and water are injected into tile lines at the rate of 1 kg (2.2 lb) of gas/45.4 liters (12 gal) of water. The solution is allowed to remain in the line for three to four days to ensure complete dissolution of the deposits.

D. New Ultra-High-Analysis Fertilizer Products

High-analysis fertilizers, and especially high-analysis intermediates, are receiving considerable attention, since they can reduce handling and transportation costs (Russell, 1970; Terman & Allen, 1969). About 25–34% of the cost of most fertilizers is due to transportation and handling (Russell, 1970). Several of the promising new products contain sulfur.

There is a lack of agreement on the prospects for producing ultra-high-analysis fertilizers from solutions of phosphorus sulfides in NH_3. One group of fertilizer technologists reported that P_2S_5 combines with 12 parts of NH_3 to form a clear solution which could have a grade of 48-12-0-31(S) (48-28-0-31) (Larson & Hong, 1967). However, studies conducted by TVA showed that P_2S_5 rearranges in NH_3 with the formation of insoluble crystalline compounds.

Four groups of compounds are being evaluated at TVA as potential ultra-high-analysis fertilizers. These are: vapor-phase reaction products; linear polyamides; phosphonitrilics; and cyclic metaphosphimates (Russell, 1970). Several of these compounds can be formulated to contain S.

Ultra-high-analysis products containing 42% N, 51% P (117% P_2O_5), and 3% S have been made in bench-scale equipment by gas-phase reaction of anhydrous ammonia, elemental P, and elemental S (Terman & Allen, 1969). Hydrogen sulfide was produced as a byproduct which would have to be recovered to make the processes economical. These products were essentially inert as sources of plant nutrients for crop growth. However, they could be solubilized by treatment with steam at high pressures. Other lower analysis products [7-28% N, 26-42% P (60-97% P_2O_5), and 12-56% S], higher in solubility and availability to crops, were made by reacting anhydrous ammonia with phosphorus pentasulfide.

Eight linear polyamides were made in TVA laboratories (Z. T. Wakefield, S. E. Allen, J. F. McCullough, R. C. Sheridan, and J. J. Kohler, 1969. New phosphorus nitrogen fertilizer compounds. Abstr. 158th Amer. Chem. Soc. Nat. Mtg., New York, Sept. 8-12). One of the monomers, $SP(NH_2)_3$, contains 29% S in addition to 38% N, and 29% P (64% P_2O_5) (Russell, 1970). Three other thiopolyamides, $P_2S_2(NH)(NH_2)_4$, $P_3S_3(NH)_2(NH_2)_5$, and $P_nS_n(NH)_{n-1}(NH_2)_{n+2}$, where n=10, containing 29, 31, and 32% S, respectively, have also been prepared and tested in the growth chamber at TVA (Russell, 1970). The monomer was an excellent fertilizer material. However, high application rates of the thiopolyamides resulted in slight initial toxicities believed to be caused by hydrolysis in the soil yielding H_2S. The formation of low levels of H_2S is not necessarily undesirable if favorable side effects such as disease control result.

Three derivatives of $SP(NH_2)_3$, sodium diamidothiophosphate [$NaPOS(NH_2)_2$], diammonium monoamidothiophosphate [$(NH_4)_2PSO_2NH_2$], and diammonium hydrogen thiophosphate [$(NH_4)_2HPO_3S$] were effective sources of both N and P in greenhouse tests (Sheridan, 1970; and Wakefield et al., 1969—see previous paragraph). Condensation products of the pyrolysis of $SP(NH_2)_3$ were less effective and initially toxic.

Phosphonitrilic hexaamide is another potential fertilizer material under investigation at TVA (Russell, 1970). This unsaturated ring compound contains mainly N and P, no O, and very little H. It is considered to be one of the most promising ultra-high-analysis fertilizer compounds. A related compound with the general formula $(NH_2)_4NHP_2N_2SO_2$ has also been synthesized and tested. It contains 14% S, exhibits no toxicity, and possesses acceptable agronomic properties.

The effectiveness of these ultra-high-analysis fertilizers as sources of S has not be studied. Initial availability of S for plant uptake, however, is expected to be somewhat less than with sulfate sources and to be about the same as for finely divided elemental S. Although it may be many years before these ultra-high-analysis products containing S are commercially available, fertilizer technologists should be aware of the developments that await them in the future.

It is apparent from the preceding discussion that there are numerous solid and fluid S-containing fertilizer products. Choice of a fertilizer will depend upon a number of factors including (i) cost, (ii) ease of application, (iii) local supply conditions, (iv) services of fertilizer dealers, (v) need for other nutrients present in the fertilizer, and (vi) agronomic effectiveness of product.

Methods and times of application also vary depending upon the farm operators' needs. Solid fertilizer materials can be applied either directly or be

Table 2—Recommendations for use of solid fertilizers containing sulfur

Material	Recommended use	Remarks
Ammonium phosphate-sulfur Ammonium polyphosphate-sulfur Ammonium phosphate-urea phosphate-sulfur Concentrated superphosphate-sulfur Urea-sulfur	For direct application and bulk blends apply materials several months before beginning of growing season.	If used in starter fertilizer or shortly before beginning of growing season, some readily available sulfate should be included (15-20% of the total sulfur applied).
Granular sulfur assemblages Flake sulfur	For direct application and bulk blends apply materials several months before beginning of the growing season. Fall applications should be encouraged.	Where feasible, incorporate into soil 4 or 5 months prior to planting. When applied just in advance of planting or on severely sulfur-deficient soils, some readily available sulfate should be included -- see above.
Ammonium sulfate	For direct application and to some extent for bulk blending. Should be effective at most any time.	Tends to segregate in bulk blends unless physical properties are improved by granulation. Where significant leaching losses are expected, apply shortly before planting or the beginning of the growing season.
Ammonium nitrate-sulfate Ammonium phosphate-sulfate Ammonium phosphate-sulfate-gypsum Normal superphosphate Potassium sulfate Potassium-magnesium sulfate Urea-sulfate	For direct application and bulk blends. Should be effective at most any time.	Where significant leaching losses of sulfate are expected, apply shortly bebefore planting or the beginning of the growing season.
Calcium sulfate (gypsum)	For direct application. Should be effective at most any time.	Difficulties may be encountered in application. Where serious leaching losses occur, apply shortly before planting or the beginning of the growing season.

used in bulk blending. Fertilization with solids can be done at different times including preplant in the fall, winter, or spring. Topdressing of established crops can be carried out before, during, or after the growing season. Similar alternatives exist for most fluid sources. In addition, some clear liquid fertilizers may be applied to the irrigation water, a practice commonly referred to as fertigation. The form of S, whether it is elemental S, sulfate, or a partially oxidized form, present in the fertilizer must receive serious consideration when deciding upon the time and method of application.

Although mention has been made of preferred methods and times of application for a number of S-containing materials, for purposes of convenience, recommendations for their use and other remarks related to proper application of solid and fluid fertilizers are summarized in Tables 2 and 3, respectively.

III. BENEFITS FROM AND NEEDS FOR SULFUR PRODUCTS

Successful marketing of fertilizers is dependent upon favorable marketing opportunities. The profitable marketing of sulfur products can best be done in areas where S fertilization has resulted in significant yield increases.

Soils heretofore considered adequate in S may become depleted rapidly because developments such as new high-yielding varieties, high plant populations, and improved management practices including heavier rates of fertilization, irrigation, and double cropping are all contributing to greater withdrawals of soil S. The increasing need for S in these dynamic soil cropping situations will eventually be translated into demand for fertilizers supplying this nutrient. The authors have summarized pertinent information in the following sections which they believe will be helpful in the marketing of sulfur-containing products.

A. Yield Responses and Recent Developments in the Need for Plant Nutrient Sulfur

Brief discussions of crop responses on S-deficient soils in several regions of the USA and in the four western provinces of Canada follow. It is not to be inferred that responses to S now occur on all soils in these areas. When S responses do occur they are often quite large and the increased crop production is of considerable value to the grower.

Following the discussion of crop responses, some recent developments in the need for plant nutrient S in the various areas of North America are reviewed.

1. SOUTH ATLANTIC STATES (VA., N. C., S. C., GA., FLA.)

Sulfur-containing fertilizers increased the yield of cotton, tobacco, and coastal bermudagrass in North Carolina; cotton, Ladino clover-grass swards, and carpetgrass in South Carolina; cotton, coastal bermudagrass, Ladino clover

Table 3—Recommendations for use of fluid fertilizers containing sulfur

Material	Recommended use	Remarks
Ammonium thiosulfate	For direct application and blending with fluid fertilizer products. Can be broadcast prior to planting or applied in starter fertilizers. Can be topdressed on certain growing crops. It can also be added through open ditch and sprinkler irrigation systems. Should be effective most any time.	Can be blended with all neutral fluid phosphate products now available, all nitrogen solutions except anhydrous ammonia, and most micronutrient solutions.
Ammonium bisulfite	For direct application and blending with most other N and N-P fluids. Can be sprayed or dribbled on prior to planting. It can also be added through open ditch and sprinkler irrigation systems. Should be effective most any time.	Can be blended with all neutral fluid P products now available and all N solutions except anhydrous ammonia. In many instances it is applied simultaneously with anhydrous ammonia. The two products from different tanks are taken to the ground through separate metering systems and injected into soil on common applicator knives.
Ammonium polysulfide	For direct application and blending with other N solutions. It is frequently injected into soil. However, broadcast spray applications are possible following dilution with water. Single preplant applications are effective. Repeated applications at low rates are often made to growing crops through open ditch irrigation systems. Should be effective at most any time.	Ammonium polysulfide is generally not considered suitable for mixing with fluids containing P.
Sulfuric Acid	For mixing with wet process ammonium polyphosphate and anhydrous ammonia in the preparation of clear liquid blends. Should be effective at most any time.	Sulfuric acid has been applied directly to crops such as onions and garlics for weed control purposes.
Suspensions containing elemental sulfur	For direct application and for simultaneous application with other fertilizers, the suspensions should be applied several months before beginning of the growing season.	If used in starter fertilizer or shortly before beginning of growing season, readily available sulfate should be included (15-20% of the total S applied).
Suspensions containing one or more sulfate salts such as ammonium sulfate, potassium sulfate, potassium magnesium sulfate, and ammonium phosphate-sulfate	Should be effective at most any time.	Where significant leaching losses are expected, apply shortly before planting or the beginning of the growing season.

alone and with bahiagrass in Georgia; and cotton, peanuts, legumes, grass, and legume-grass mixtures in Florida. Increases in cotton yields ranged from 10% to more than 60%. Forage yields were increased by over 300–1,100% in several instances in Florida. Coastal bermudagrass yields were raised slightly more than 60% by the application of S fertilizers in North Carolina.

Because of the increasing popularity of high-analysis solid and liquid fertilizers in Georgia, it is now necessary to deliberately apply 11 kg of S/ha (10 lb/acre) to all cotton grown in the state. Sulfur has been recommended for cotton in Alabama for 10–15 years. There are indications based on field observations and plant analyses that S must soon be included in fertilizer programs for corn in Georgia. Additions of S increased the yield of orchardgrass and alfalfa at one location in Virginia in 1970.

2. EAST NORTH CENTRAL STATES (OHIO, IND., ILL., MICH., WIS.)

Most of the crop responses to S fertilization in this region were reported during the last 2 years. Yields of corn, sugar beets, clover, and alfalfa have been improved by the use of S fertilizers in Ohio. Sulfur fertilization raised the yield of corn in Michigan and Wisconsin. Alfalfa yields were also increased when S fertilizers were used in Wisconsin. At several locations applications of S increased alfalfa yields from 30–60%. Sulfur fertilization of corn resulted in yield increases of 5–27%.

Field trials and plant tissue surveys have revealed that some soils in central and northwestern Wisconsin, southeastern Michigan, northwestern and west central Ohio, and southern Indiana contain inadequate amounts of S for top production of corn. Certain areas of central and northwestern Wisconsin may also be low in available S for high-yielding processing crops. A need for plant nutrient S is now occurring in alfalfa fields in Ohio, Michigan and southern Indiana. Seventy-nine percent of 300 soil samples from northwestern Ohio and southern Michigan which were analyzed in 1968 by a commercial laboratory were rated as S deficient and a further 13% were considered borderline.

3. WEST NORTH CENTRAL STATES (MINN., IOWA, MO., N. D., S. D., NEB., KAN.)

Crop responses to S have been observed in Minnesota dating back to 1923. Legume crops have responded most frequently to the use of S. However, the yields of small grains, soybeans, and corn have also been increased by S fertilization. On S-deficient soils yield increases for legumes, corn, small grains, and soybeans were 49, 32, 29, and 15%, respectively.

The benefits of S fertilization in Nebraska were first observed almost 20 years ago on alfalfa. Alfalfa yields have been increased by S fertilization in numerous field trials in this state. The yield increases at S-responsive sites averaged 46% for alfalfa, 25% for field corn, and 11% for sweet corn. An 11% increase in soybean yields also occurred in one experiment.

Although very few, if any, field experiments have been conducted recently in Iowa, crop responses to additions of S were noted in the 1920's. At S-deficient locations, legume yields were increased an average of 35%, while the average yield of small grains was raised nearly 40%.

Sulfur responses in Kansas which have been reported only during the past few years averaged 33% for corn and 18% for wheat.

In recent years S deficiencies have become rather widespread in Minnesota, occurring largely on the extensive area of grey-wooded soils in the northern and central parts of the state. Also, interest in the use of this nutrient is increasing in southwestern portions of the state where approximately 75% of the soil samples from this area tested either low or medium in available S.

Sulfur deficiencies have been rather common in Nebraska, particularly on the sandier soils in the north central, northeastern, and eastern sections of the state. Much greater S requirements are expected in northeastern Nebraska where recently installed center pivot irrigation systems have resulted in striking increases in the yields of corn and forage crops. Similar installations and other irrigation developments in south central and western Kansas and North and South Dakota are expected to increase the need for S fertilization. The amount of fertilizer S needed in these and other irrigated areas will of course depend upon both the concentration of S in the irrigation water and the quantity of water used. Sandy soils in south central Kansas do not contain sufficient S for maximum yields of dryland wheat. A few soil samples from North and South Dakota have been tested for available S and most of them were in the low and medium categories.

In Iowa, some greenhouse studies have shown that several soils became deficient in S after one or more crops were removed from the test pots. Some growers in western Iowa are following soil test recommendations for S in their fertilizer programs which have been designed for high corn yields.

Deficiencies of S are now suspected in the sandy soils of southeastern Missouri. In addition, there are undocumented accounts of S being needed for top yields of corn and pastures in the northwest section of this state.

4. EAST SOUTH CENTRAL STATES (KY., TENN., ALA., MISS.)

The effect of S on cotton production has been studied intensively in Alabama and Mississippi. The average yield increase was 24% for this crop grown on soils low in available S. Forage crops on S-deficient soils in these two states also responded to S fertilization with the yield increases averaging nearly 29%. Modest increases in the yield of turnip greens occurred in Mississippi when S was included in the fertilizer program.

Sulfur deficiencies have not been reported in Kentucky. Greater use of S-containing fertilizers is expected in this region in the future, especially on the well-drained, sandy soils in the higher rainfall areas.

5. WEST SOUTH CENTRAL STATES (ARK., LA., OKLA., TEXAS)

Yield increases of approximately 17% occurred when cotton received S in Arkansas and west Texas. Small increases averaging 5% for cane and 6% for sugar resulted from the use of S fertilizers on sugarcane in Louisiana. The yield of sugar from sugar beets in west Texas was increased over 17% by S fertilization. Sulfur increased coastal bermudagrass yields in east Texas by an average of 34%. Additions of S to wheat and sorghum in west Texas increased yields of these crops by an average of 16 and 11%, respectively. It has also been shown that S fertilization of soils deficient in this nutrient increased the yields of cotton and forages in Louisiana, and peas and corn in Texas.

During recent years, heavy applications of S have been beneficial for rice production on alkaline and calcareous soils in Arkansas, Louisiana, and Texas. Current evidence suggests that the acidifying effect of S is responsible for the improved yields rather than a direct nutritional response. This may also be true for some of the responses observed in the Texas High Plains and the Lower Rio Grande Valley.

Intensive production of coastal bermudagrass and other forages on sandy soils in the humid areas of east Texas and Oklahoma has resulted in S deficiencies. Occurrences of inadequate soil S are anticipated in this portion of Texas and Oklahoma when other crops are grown under conditions favorable for top yields.

Soils in Louisiana that have been cropped for about 300 years are now becoming deficient in S for high yields of sugarcane. Replacement of low-analysis fertilizers containing normal superphosphate with materials which are essentially S-free has been partly responsible for this new need for S.

New and expanded irrigation developments in the West South Central States, espeically in western Texas and Oklahoma, will accentuate the need for plant nutrient S.

6. MOUNTAIN STATES (MONT., IDAHO, COLO., N. M., ARIZ., UTAH, NEV., WYO.)

Crop responses to S fertilization have been recorded in the states of Montana, Idaho, Colorado, New Mexico, Arizona, and Wyoming. Average yield increases of 78, 60, 25, and 22% were found at S-deficient sites for alfalfa, wheat, potatoes, and lettuce, respectively. The responses obtained with vegetable crops in Colorado and Arizona are believed to be related to soil acidification and improved water relations rather than direct nutritional effects of S.

Much of the Mountain States Region is arid or semiarid and the soils usually contain large quantities of salts including sulfates. In addition, where irrigation is practiced, substantial amounts of sulfate frequently are added through the water. Under such conditions adequate plant nutrient S is available. Consequently, deficiencies of this element are not widespread in the region except in the more humid areas of Idaho and western Montana.

Sulfur deficiencies have been found in many locations in Idaho and western Montana and at a few sites in Wyoming and Colorado. High quality irrigation water devoid of sulfate was used at the S-deficient location in Colorado.

Other instances have been reported where S-containing fertilizers increased crop yields in Colorado, New Mexico, and Arizona. Because there is no shortage of available S in soils at these locations, the favorable effects are believed to be the result of soil acidification and/or improvements in soil structure and water penetration.

7. PACIFIC STATES (WASH., ORE., CALIF.)

Deficiencies of S were identified as early as 1900 on certain soils in the Pacific Northwest. Next to N, a shortage of available S is the most frequent soil fertility problem in eastern Washington and Oregon. The occurrence of S deficiency in California soils ranks a close third after N and P.

Legume yields at locations low in available S in Washington and Oregon were increased an average of 51% by the application of S. Fertilization with S resulted in an average increase of 35% in the yield of cereals in these two states. An increase of about 200% was obtained from S treatments in orchardgrass in western Washington. Studies conducted during the past few years on subterranean clover hill pastures in western Oregon showed that yields were increased by an average of 26% with the use of S.

Large yield increases of the order of 100% occurred in California when applications of S were made to range areas composed of native clovers, introduced clovers, native grasses, and mixtures of clovers and grasses. Cultivated legume yields were raised approximately 97% by S dressings. Forage yields from irrigated pastures on S-deficient soils were increased an average of 143% by the use of S fertilizers. Substantial yield increases of 66 and 13%, respectively, resulted from applications of S-containing fertilizers to cereals and sugar beets.

Sulfur is intentionally added to fertilizers for most cropping situations in Oregon and eastern Washington. There are indications that S deficiencies are likely to become more common in western Washington, particularly when repeated heavy rates of nonsulfur-bearing N fertilizers are used.

Sulfur deficiency is recognized as an important nutritional problem in increasingly large areas of central and northern California where both primary and secondary deficiencies of this nutrient occur. If S is a primary deficiency it must be supplied before other fertilizer nutrients can be effective. Secondary S deficiencies occur only after some other nutrient deficiency has been corrected. Deficiencies of S in several corn and sorghum fields in the Sacramento Valley were reported in 1968 and greater attention to the use of S-containing fertilizers on these crops is expected in the future.

8. ALASKA AND HAWAII

Additions of S increased the yields of grass forage crops on S-deficient soil by an average of nearly 49% in Alaska and Hawaii. At several locations in Hawaii, S was responsible for increasing the yield of sugarcane by about 14%.

The need for S fertilization in Hawaii is likely to become significant in areas blanketed with relatively unweathered volcanic ash or where irrigation water contains low amounts of sulfate. High transportation costs leading to greater use of high-analysis fertilizer goods and the heavy rates of N fertilization on crops such as sugarcane and pineapple are other factors which will influence the need for S-containing materials.

9. CANADA

Crop deficiencies of S in Canada have thus far been confined to the western provinces of British Columbia, Alberta, Saskatchewan, and Manitoba. In British Columbia S-deficient soils are found in the Peace River region, Central Interior, Cariboo, North Okanagan, Okanagan-Boundary, and East Kootenay districts. Sulfur deficiency is found in one-third to two-thirds of the main area of Grey-Wooded soils in Alberta. Isolated areas of these soils within the Black soil zone are also low in available S. Grey-Wooded soils of the Peace River region of Alberta may also be deficient. Approximately 1,012,500 hectares (2,500,000 acres) of S-deficient soils occur in the northern agricultural areas of Saskatchewan. Most of these soils are located in the Grey-Wooded soil zone. Although S deficiency in northeastern Saskatchewan is usually associated with sandy soils, loam and clay loam soils may also contain inadequate levels of available S. About 20% of the S-deficient Grey-Wooded soils in Saskatchewan occur in the northwestern part of the province. Sulfur is currently considered to be potentially deficient in Manitoba on only Grey-Wooded soils and other coarse-textured and well-drained soils.

The benefits of S fertilization on the yield of legume and cereal crops in the four western provinces of Canada were reviewed in 1966 (Beaton, Harapiak, & Tisdale, 1966). In some cases yield increases of 400–500% were obtained, and responses of 75–100% were common.

Subsequent reports of crop responses to S in western Canada and other accounts of yield increases which were inadvertently omitted from the 1966 survey are summarized below. The favorable effect of S fertilization of alfalfa and other forage crops was both substantial and widespread in the province of British Columbia. Yield increases averaged 134% for this type of crop. Oat and rapeseed yields in the Peace River region of B. C. were also markedly improved by S fertilization.

Application of S fertilizers raised cereal yields in the Peace River region of Alberta by an average of 45%. Yields of alfalfa were increased an average of 93% by the use of S fertilizers. Important increases in growth of legumes also occurred in west central Alberta and large increases in rapeseed yields resulted from S fertilization in the Peace River region.

Average yield increases of approximately 144% were obtained when alfalfa received S in west central Saskatchewan. Yield responses by cereals to S fertilization averaged 24% in this area. Oilseed crops such as rapeseed and mustard also responded to dressings of S-containing fertilizers.

Applications of S increased the yield of grass forage crops and rapeseed at S-deficient locations in southern Manitoba by averages of 28 and 26%, respectively.

The small amounts of S present in fertilizers such as 11-21-0 (11-48-0) which are commonly placed with the seed of cereal crops has probably prevented serious deficiencies of this plant nutrient in many of the shallower, coarser, and drier Chernozemic soils of the Canadian Prairies. However, with increasing use of N-P goods compounded from S-free materials, including urea and 11-24-0 (11-55-0), the need for plant nutrient S will become more obvious. Expanding acreages of rapeseed will also increase the need for S, since this crop responds to S fertilization in all four provinces. Increased hay and pasture production in the grey-wooded and parkland areas, needed to support greater livestock numbers, will accelerate the removal of soil S.

10. OTHER AREAS OF THE WORLD

The benefits of S fertilization on crop production in the USA and Canada have been emphasized because of the occurrence of S deficiency in many sections of the two countries. Also, the considerable effort given to development and marketing of S-containing fertilizers in the USA and Canada has created a need for a better understanding of where and how this nutrient affects crops. It should be noted, however, that S has a favorable effect on crop growth in many other areas of the world. A brief review of some of these other responsive areas follows.

a. Australasia—Forage production is an essential feature of agriculture in Australia and New Zealand. Crop responses to S fertilization, especially on legume pasture species, are widespread and of economic significance in Western Australia, South Australia, and New South Wales. Sulfur deficiencies have also been observed in Queensland and at a number of sites in Victoria and Tasmania. Small grains and sugarcane have responded to applications of fertilizer S at various locations in Australia.

Legumes and other pasture species have responded to S fertilization on both the North and South Island of New Zealand. Deficiencies of S are extensive on the South Island, with the main responsive areas found in the Nelson, Marlborough, Canterbury, Otago, and Southland regions. On the North Island, S-deficient soils are known to occur in the Northland Peninsula and in an area east of Lake Taupo.

Elsewhere in Australasia, S deficiency is responsible for poor growth of coconut palms and low production of copra in the Territory of Papua and New Guinea. Coffee, tea, tobacco, and legumes have been affected too by inadequate levels of S in lowland and highland areas throughout Papua and New Guinea.

b. Africa—Crop deficiencies of S occur widely in the West and Equatorial African countries of Cameroon, Central African Republic, Chad, Dahomey, Ghana, Ivory Coast, Mali, Niger, Nigeria, Senegal, Togo, and Upper Volta. Peanuts and cotton and to a lesser extent cereals are the crops which most frequently benefit from the application of S-containing fertilizers in this region.

In Central Africa, cotton, peanuts, alfalfa, legume and grass pastures, corn, tea, coffee, pyrethrum, sugarcane, oilpalm, black wattle, and gumtrees have responded to applications of fertilizer S. These crop responses occur in the Congo (Brazzaville), Congo (Kinshasa), Kenya, Malawi, Rhodesia, Tanzania, Uganda, and Zambia.

c. Asia—Yields of rice, peanuts, tea, jute, berseem, moth, sugarcane, and onions are increased by S fertilization in Asia. Sulfur-deficient soils are located in Ceylon, India, Japan, and Thailand. Pineapples deficient in S have been observed in the Philippines.

d. Europe—Sulfur deficiencies have been observed in Western Europe in Finland, France, Germany, Iceland, Netherlands, Norway, Spain, Sweden, and Yugoslavia. The crops responding to additions of fertilizer S are cruciferous root crops, marrow-stem kale, forage rape, forage beets, rapeseed, small grains, legume-grass swards, and alfalfa.

e. Caribbean—Banana production has been limited by S deficiency in the Windward Islands, especially in Dominica and St. Vincent. Sulfur fertilization has resulted in increased yields of sugarcane in Puerto Rico.

f. Latin America—A need for S-containing fertilizers has been demonstrated in Argentina, Bolivia, Brazil, Chile, Colombia, Costa Rica, El Salvador, Guatemala, Honduras, Peru, and Venezuela. Sulfur deficiencies have been observed in corn, sorghum, wheat, cotton, potatoes, banana, pineapple, coffee, sugarcane, native grasses, and other forages in these areas of Latin America.

B. Benefits From Sulfur Products Used As Soil Amendments

Productivity is reduced by saline and alkali soil conditions on about 25% of the 12 million ha (29 million acres) of irrigated land in the USA (Bower & Fireman, 1957). Also, substantial areas of nonirrigated crop and pasture lands in 14 of the western states are similarly affected by excessive accumulations of salts. The status and extent of saline and sodic areas in the 17 western states and Hawaii are shown in Table 4. In western Canada, between 6 and 8 million ha (15 and 20 million acres) of soils in the grasslands and parklands exhibit a strong influence of Na (Cairns & Bowser, 1969).

1. RECLAMATION OF ALKALI SOILS

The addition of chemicals where needed to supply Ca or to make available insoluble forms of soil Ca to replace Na adsorbed by soil colloids is often one of the remedial treatments for reclaiming salt-affected soils. Sulfur and a number of its compounds listed in Table 5 are used in soil reclamation and water treatment. The use of these materials in irrigated arid-land agriculture was reviewed recently by Tisdale (1970).

Soil structure improvement is important in the reclamation of Na-affected soils since structure influences the rate of water infiltration into the soil and also movement of water in the soil profile. Sulfur-containing soil amendments improved infiltration rates in a field study in Arizona. These amendments have also had a beneficial effect on percolation rates as found in many laboratory investigations conducted in Arizona, California, and Texas.

In the treatment of poor soil structure and slow infiltration rates, a number of S-containing soil amendments such as SO_2, H_2SO_4, $CaSO_4 \cdot 2H_2O$,

Table 4—Status and extent of saline and sodic areas in the seventeen western states and Hawaii*

State	Area reported	Total area of sodic and saline soils†	Salt-free sodic soils		Saline soils	
		ha§	ha§	%	ha§	%
Arizona	Statewide	633,825	472,299	74.5	161,526	25.5
California	Statewide	4,657,500	3,140,795	67.4	1,516,705	32.6
Colorado	Statewide	1,138,671	741,030	65.1	397,640	34.9
Hawaii	7 areas	47,554	29,107	61.2	18,448	3[illegible]
Idaho	All but 3 counties	761,426	658,983	86.5	102,443	13.5
Kansas	Statewide	170,726	129,282	75.7	41,444	24.3
Montana	4 areas	503,305‡	423,248	84.1	80,057	15.9
Nebraska	Statewide	493,446	375,996	76.2	117,450	23.8
Nevada	Statewide	454,376	261,758	57.6	192,618	42.4
New Mexico	Statewide	344,250	266,895	77.5	77,355	22.5
North Dakota	6 areas	1,067,783‡	737,047	69.0	330,735	31.0
Oklahoma	Statewide	334,793	256,325	76.6	78,469	23.4
Oregon	Statewide	603,610	561,748	93.1	41,861	6.9
South Dakota	Statewide	687,679	203,192	29.5	484,488	70.5
Texas	4 areas	890,575	778,854	87.5	111,721	12.5
Utah	7 areas	563,040	355,363	61.1	207,677	36.9
Washington	23 counties and the Columbia Basin	899,701	791,868	88.0	107,833	12.0
Wyoming	Statewide	510,758	397,479	77.8	113,280	22.2
Total		14,763,017	10,581,268	71.6	4,181,749	28.4

* Unpublished data, U.S. Salinity Laboratory, courtesy of C. A. Bower (1970).
† Irrigable. ‡ Arable. § Hectares × 2.471 = acres.

Table 5—The composition of sulfur-containing materials used in soil reclamation and water treatment

Material	Formula	Composition - %	
		S	Other
Aluminum sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$	14.4	11.4 (Al)
Ammonium polysulfide	$(NH_4)_2\,S_{(x)}$	45.0	20.5 (N)
Ammonium thiosulfate soln.	$(NH_4)_2S_2O_3 + H_2O$	26.0	12.0 (N)
Calcium polysulfide soln.	$CaS_{(x)} + H_2O$	24.0	9.0 (Ca)
Ferrous sulfate	$FeSO_4 \cdot H_2O$	18.8	32.8 (Fe)
Gypsum	$CaSO_4 \cdot 2H_2O$	18.6	32.6 (CaO)
Sulfur	S	100.0	--
Sulfuric acid (100%)	H_2SO_4	32.7	--
Sulfur dioxide	SO_2	50.0	--

* D. W. Bixby, S. L. Tisdale, and D. L. Rucker (1964).

$(NH_4)_2S_X$, and CaS_X can be successfully added to the irrigation water. Gypsum applied in irrigation water has been shown to be more effective than that applied broadcast as a dry powder. Calcium polysulfide and ammonium polysulfide when applied in the irrigation water can penetrate rather deeply into the soil, and the readily oxidizable colloidal S carried in solutions of these two sources will acidify lower soil depths. Calcium polysulfide is applied in this manner to correct problems of irrigation or plow pans.

Application of elemental S, H_2SO_4, and $(NH_4)_2S_X$ to sodic soils in California, Nevada, North Dakota, and Wyoming raised crop yields between 8.5 and 349% and by an average of 88%. These amendments are expected to have favorable effects upon crop growth on most problem sodic soils in the Mountain States and in other parts of the USA and Canada.

2. WATER TREATMENT

Substances such as the polysulfides were heretofore believed to function as soil amendments only, like elemental S which after oxidation to H_2SO_4 reacts with alkaline earth carbonates to produce a soluble form of Ca. However, McGeorge et al. (1956) and Howard (1968) suggested that calcium polysulfide applied in the irrigation water produces an immediate increase in water penetration. Robinson et al. (1968) showed that additions of ammonium polysulfide to irrigation water greatly increased the rate of water penetration. Similar effects have been observed for SO_2, $(NH_4)_2S_2O_3$, and NH_4HSO_3, but these observations have not been documented.

It is not known if the action of S-containing compounds such as $(NH_4)_2S_X$, $NH_4S_2O_3$, and NH_4HSO_3 on improving the rate of entry of water into soil is similar to wetting agents or surfactants. Ammonium polysulfide is reported to affect the water-soil contact angle and increase water penetration (Lengyel, 1963). An understanding of the action of $(NH_4)_2S_X$ is further complicated by the fact that a substantial amount of colloidal S and a sulfide is formed following dilution of this material in irrigation water (Fuller, 1962; Tisdale & Nelson, 1966). When colloidal S is formed, a corresponding amount of NH_4^+ ion must be released into solution. It is conceivable that the ammonium ion may contribute to the water treatment effect, since Cairns and Bowser (1969) found that additions of NH_4NO_3 greatly increased the rate of penetration of water into a Solonetzic soil. On the other hand, Robinson et al. (1968) concluded that the ammonium ion was not associated with an improvement in rate of entry of water. Benefits from added electrolytes such as ammonium are probably dependent upon the quality of the irrigation waters being applied. Additions of CaS_X are reported to improve penetration of waters, containing small amounts of Ca, into soils in the San Joaquin Valley of California.

3. ADJUSTMENTS IN SOIL pH

Land leveling for irrigation purposes will often expose calcareous subsoils which are too alkaline in reaction for optimum plant growth. As illustrated by the yield of grain sorghum obtained in Rush County, Kansas (see Table 6), applications of acids or acid-forming amendments will increase the productivity of these high-pH calcareous soils.

Problems of high soil pH are not restricted to only arid and semiarid areas of North America. Applications of relatively high rates of granular S and elemental S have resulted in striking increases in rice yields in Arkansas and Louisiana (Table 6). There are indications that yields of rice from certain soils in Texas can also be increased by applications of relatively high rates of S. The

Table 6—Effect of soil acidification on yield of rice and irrigated sorghum

Location	Cropping situation	Sulfur source	Application rate	S	Yield increase due to sulfur		Reference
			kg of S/ha*	kg/ha*	kg/ha*	%	
Arkansas Stuttgart	Rice (1969)	Granular S	1,120	4,501 (soil pH = 6.9)	1,827 (soil pH = 6.1)	40.6	Wells (1969)
Kansas Rush County	Irrigated sorghum (1966)	Elemental S	1,120	941	2,383	253.3	Thompson (1966)†
	Irrigated sorghum (1966)	Elemental S	4,480	941	3,951	420.0	Thompson (1966)†
	Irrigated sorghum (1967)	Elemental S	1,120	2,258	941	41.7	Thompson (1967)‡
	Irrigated sorghum (1967)	Elemental S	4,480	2,258	1,254	55.6	Thompson (1967)‡
Louisiana Acadia Parish	Rice (1966)	Elemental S (1966)	1,120	2,150	683	31.8	Wilson et al. (1968)
	Rice (1967)	Elemental S (1966)	1,120	3,774	1,019	27.0	Wilson et al. (1968)
	Rice (1968)	Elemental S (1966)	1,120	3,688	665	18.0	Wilson et al. (1968)

* kg/ha × 0.9 = lb/acre.

† Thompson, C. A. 1966. Grain sorghum fertilizer experiments. Fort Hays Branch Exp. Sta., Kansas State Univ.

‡ Thompson, C. A. 1967. Grain sorghum fertilizer experiments. Fort Hays Branch Exp. Sta., Kansas State Univ.

benefit from these heavy dressings of S in Louisiana appears to be related to increased availability of micronutrients, particularly Zn.

Soil pH has a pronounced effect on growth of many conifers as it alters availability of nutrients and greatly influences the constitution of the soil microflora and fauna (van den Driessche, 1969). In many conifer nurseries it is necessary to increase soil acidity. The effect of varying amounts of either elemental S or H_2SO_4 on lowering the pH of conifer nursery soils has been recorded in Ontario and British Columbia. Mullin (1969) found that the weight of red pine seedlings was increased an average of 28% by applications of 1,680 kg of elemental S/ha (1,499 lb/acre) and 51% by additions of 2,520 kg of elemental S/ha (2,248 lb/acre).

Acid-forming soil amendments are also used to improve the soil environment for specialty crops such as blueberries, cranberries, roses, azaleas, and rhododendrons.

4. SOIL ACIDIFICATION IN FERTILIZER BANDS

In many calcareous soils it is not economically feasible to use the amount of acidifying material that would be required to neutralize the total alkalinity of the soil mass. McGeorge (1945) suggested that it is not necessary to neutralize the alkalinity of the entire soil mass because soil zones favorable for root growth and nutrient uptake can be created by confining the S treatments to bands, furrows, auger holes, etc. The observed benefits from banding acid-forming materials for lettuce and other vegetable crops in Arizona, lettuce and potatoes in the San Luis Valley of Colorado, and corn and winter wheat in

Kansas are probably the result of more favorable conditions in the zone of fertilizer placement rather than a direct nutritional benefit from S. The acidifying effect of S sources such as $(NH_4)_2S_2O_3$ and $(NH_4)_2SO_4$ in fertilizer bands probably favored increased uptake of Mn and P by corn in Kansas (F. J. Wooding, 1969. Growth chamber and field experiments with plant-nutrient-sulfur. Ph. D. Thesis, Kansas State Univ., Manhattan.).

C. Effects of Sulfur Fertilization on Crop Quality

Yield response is the most apparent and convenient measure of the benefits from S fertilization. However, there are a number of less obvious effects of S on crop quality and crop management which are often equally important. A brief discussion of some of these important effects on crop quality follows.

1. CRUDE PROTEIN CONTENT OF CROPS

Many investigators have shown that S fertilization will increase the amount of crude protein (total N X 6.25). Although the crude protein calculation has serious limitations, it is nevertheless used rather widely as an indicator of forage quality. A large number of analyses have been made which show that S fertilization frequently increases crude protein content of forage by about 2%. The effect of S fertilization on raising crude protein levels has been reported for other crops such as corn, rapeseed, and small grains.

2. NITROGEN TO SULFUR RATIO IN FORAGES

An N/S ratio of 15:1 has in the past been considered adequate for the nutritional requirements of ruminants. However, recent work indicates that a ratio of not more than 10:1 will lead to substantial improvements in the utilization of N by ruminants. The average N/S ratio in a number of alfalfa and red clover trials was reduced from 17.8 to 13.2 by S fertilization. Additions of S-containing fertilizers have also decreased the N/S ratio in other crops including corn, sugar beets, and wheat.

3. VITAMIN A CONTENT OF FORAGE

Studies on a S-deficient soil in Nebraska have shown that the vitamin A content of alfalfa was increased an average of 13% by the application of S alone. Sulfur in combination with P resulted in an average increase of 24%.

4. NITRATE AND NONPROTEIN NITROGEN CONTENT OF PLANTS

There is often an increase in nitrate and nonprotein nitrogen (NPN) concentration in the tissue of S-deficient plants. Sulfur should be included in sound fertilizer programs to ensure that deficiencies of this element are not the cause of toxic levels of nitrate in crops, especially where heavy annual applications of high-analysis nitrogenous fertilizers are made.

Grass tetany, or hypomagnesaemia, a mineral imbalance observed in both cattle and sheep, is characterized by low blood serum Mg. Adequate S fertilization of forage crops is recommended because the availability of Mg from the gut is reduced by high amounts of NPN in the ration.

5. QUALITY OF CEREALS

Under conditions of S deficiency the methionine and cystine content of cereals will decrease. Levels of these and other amino acids and the nutritive value of cereal grain have been increased by S fertilization.

The proportion of gluten N and the cystine and methionine content of gluten from spring wheat were raised by the application of S fertilizer. In baking tests, the largest loaves of the best quality bread were obtained from spring wheat grown after legumes on plots in Alberta which had received S fertilizers.

In Idaho, S deficiency has had adverse effects upon the quality of soft winter wheat and the diameter of cookies made from this wheat. The malting properties of spring barley were improved by S fertilization.

6. COMPOSITION OF OILSEED CROPS

The oil content of rapeseed grown in western Canada was reduced by inadequate S nutrition. Seed from S-deficient rapeseed crops contained less erucic acid, slightly less linolenic acid, and much more oleic acid.

7. QUALITY OF VEGETABLES

Added S markedly improved the quality and color of turnip greens in Mississippi. Heavier heads of lettuce and greater amounts of superior-grade potatoes were obtained in the San Luis Valley of Colorado by using ammonium sulfate rather than calcium nitrate or anhydrous ammonia. There have been a number of unverified reports that the carrying quality and the storageability of vegetable crops are improved through use of acid-forming S fertilizers. In addition, there are indications that acid-forming S fertilizers also improve the uniformity of potato size and the suitability of tubers for chipping.

Substantially less caking of soil on crops such as garlic bulbs and potatoes has resulted from the use of $(NH_4)_2S_2O_3$. This has increased growers' profits by reducing deductions for dockage.

8. QUALITY OF TURFGRASS

Growth, color, and density of cool-season turfgrass in the Pacific Northwest USA are enhanced by applications of elemental S and $(NH_4)_2SO_4$. Warm-season grasses in Arizona and Florida have also benefited from additions of S-

Table 7—Effect of sulfur fertilization on winter hardiness of forage crops

Location	Cropping situation	Sulfur source	Application rate	Plants per m^2†	Increased survival with sulfur	Reference
			kg of S/ha*		%	
Minnesota						
Park Rapids	Alfalfa (June 1963)		0‡	75		Caldwell, Seim, & Rehm (1967); Seim, Caldwell, & Rehm (1969)
	Alfalfa (June 1963)	Elemental S	28‡	161	121.3	
	Alfalfa (June 1963)	Elemental S	56‡	161	121.3	
	Alfalfa (June 1963)	Elemental S	112‡	194	158.7	
	Alfalfa (June 1963)	Gypsum	56‡	204	172.0	
	Alfalfa (June 1963)	Gypsum	1,120‡	151	101.3	
Alaska	Bromegrass (May 1969)		0		43.1§	Laughlin (1970)¶
	Bromegrass (May 1969)	Ammonium phosphate-sulfate	78.0		3.5	Laughlin (1970)¶

* kg/ha × 0.9 = lb/acre.
† m^2 × 4,051 = acres.
‡ Applied in spring of 1962.
§ Winter mortality, %.
¶ W. M. Laughlin, unpublished data, Univ. of Alaska, 1970.

thiosulfate and ammonium bisulfite fertilizers appear to be responsible for reducing the incidence of foot rot on winter wheat in eastern Washington.

The incidence of *Fusarium* patch, the most serious disease problem of turfgrass in the State of Washington, was reduced by about 86% by application of elemental S. Significant reductions in *Ophiobolus* patch, another major turfgrass disease in the Pacific Northwest USA, resulted from applications of either $(NH_4)_2SO_4$ or elemental S. Sulfur deficiency of Merion bluegrass enhances its susceptibility to powdery mildew. Sulfate-containing fertilizers reduced the incidence of dollarspot fungus in warm-season grasses in Florida.

Addition of S to the soil creates a pH that is unfavorable to the growth of some plant pathogens. Two diseases that are regularly controlled by this method are pox of sweet potatoes and scab of white potatoes. Practical control of the two diseases can be achieved at a pH of about 5.0. In calcareous soils where it may be impractical to acidify the entire soil volume, band applications of elemental S or acid-forming S fertilizers have successfully reduced the incidence of scab and increased yields of white potatoes.

Other aspects of the desirable action of S fertilization on reduced incidence of plant diseases are less clearly understood. Besides contributing to the development of healthier plants better able to grow under adverse conditions, applications of S-containing fertilizers might also improve plant growth by destroying or controlling harmful fungi and other pathogenic microorganisms. Sulfur and its compounds are known to possess remarkable fungicidal properties. In preliminary laboratory experiments ammonium polysulfide, ammonium thiosulfate, and ammonium bisulfite partially reduced the activity of *Phytophthora cactorum*, the fungus causing crown rot of apple trees.

5. DECOMPOSITION OF CROP RESIDUES

The limited information available indicates that S plays an important role in the management of crop residues. Growth of winter wheat in the greenhouse was depressed by the addition of straw containing less than 0.15% S (Stewart, Porter, & Viets, 1966). Farm operators in the Harrington area of eastern Washington have observed that applications of ammonium bisulfite to wheat stubble resulted in more rapid decomposition of stubble and better soil tilth.

6. CROP MATURITY

Maturity of crops is very important since delays in harvesting operations of even a few days may subject crops to unfavorable weather resulting in serious reductions in both yield and quality. Fox and Hoover (1961) found in Nebraska that S-fertilized corn matured earlier than S-deficient corn. If moisture content is considered as a criterion for the stage of maturity, the maturity of canning corn was advanced by S fertilization. Moisture content of corn from S-fertilized plots in Minnesota was consistently lower than corn not receiving S.

The amount of cotton ready for the first picking was reduced by inadequate S nutrition in Arkansas. Indeterminate flowering and poor seed set occurred when N-P-K fertilizer without S was applied to rape in British Columbia. The total number of lettuce heads removed during the first harvest in the San Luis Valley of Colorado was increased by applying ammonium sulfate rather than calcium nitrate.

Crusting can be a serious problem with the emergence of small-seeded vegetable crops. Mechanical harvesting of vegetable crops, especially once-over type operations, requires uniform emergence and development of crops. Several of the S-containing liquid fertilizers are used to reduce crusting and improve soil tilth.

7. CROP DEFOLIATION

Studies at the Shafter Experiment Station in California showed that ammonium thiosulfate was an excellent desiccant for cotton. The amount of crop oil required for desiccating milo can be reduced by using this S-containing fertilizer. A mixture of ammonium bisulfite and N solution has been used with some success for the defoliation of potatoes and alfalfa, and clover grown for seed. Sulfuric acid can be used as a desiccant on pea crops. The main objection to the use of S-containing liquid fertilizers for crop desiccation is the relatively large volumes required in comparison to the common desiccating treatments.

8. PEST CONTROL

Both ammonium polysulfide and sulfuric acid have been used for weed control in onions. However, the use of these materials for this purpose has been largely discontinued because of corrosion problems. There are unconfirmed reports of the use of ammonium thiosulfate to control volunteer corn in soybeans. Wild oat seeds are destroyed by sulfuric acid. Trials are underway in the grass seed production areas of the Pacific Northwest USA to determine if concentrated sulfuric acid is a suitable alternative to burning for control of plant diseases and management of crop residues.

IV. FACTORS INFLUENCING THE EFFECTIVENESS OF SULFUR PRODUCTS

A number of soil and environmental factors influence the fertilizer value of S products. Properties of the S products also have important effects upon their reaction in soil and availability to crops.

A. Factors Influencing Oxidation of Elemental Sulfur

Because sulfate is the form in which S is taken up by plants, S in lower oxidation states must be oxidized to this state before it becomes available to plants. Elemental S is converted to sulfate by biological oxidation. Although autotrophic and heterotrophic bacteria, fungi, and actinomycetes are capable of oxidizing elemental S, activity of the autotrophic *Thiobacilli* is considered to be most important. However, the rate of oxidation of elemental S is sometimes limited by small populations of S-oxidizing organisms. The oxidation of elemental S is affected by its particle size, with particles smaller than 60 mesh oxidizing quite rapidly. Temperatures of between 30 and 40C (86 and 104F) favor the oxidation of elemental S. Oxidation proceeds rapidly over the range of soil moisture contents best suited for plant growth and is most rapid at soil moisture contents higher than field capacity. Mixing elemental S with soil usually results in the most rapid conversion to sulfate. In calcareous soils, or when some lime is added with the S, band placement is also effective.

B. Behavior of Products Containing Other Forms of Sulfur

Thiosulfate, polysulfide, sulfite, bisulfite, and sulfur dioxide are converted chemically and biologically to sulfate. Since these materials are usually applied to the soil in fluid form, a high degree of contact with the soil is expected. Several of these substances undergo transformations resulting in the formation of colloidal S when they are added to soil. Thiosulfates may be transformed initially to sulfates and tetrathionates or to sulfates and elemental S. Thiosulfates also are chemically unstable in acid solution, yielding SO_2 and elemental S. The polysulfides are chemically unstable and form colloidal S and sulfides when added to soil. These soluble sulfides are subject to rapid chemical oxidation to elemental S. Oxidation of elemental S formed from these fluid S products most likely proceeds by biological means and it will probably be affected by the same factors summarized above. Particle size of the elemental S formed during these transformations is believed to be ideal for subsequent oxidation.

Sulfur dioxide reacts with water in the soil to form sulfurous acid which in turn reacts with certain soil constituents to form sulfite salts. The sulfite salts are oxidized to sulfates either chemically or biologically.

C. Reactions of Sulfate in Soils

Sulfate is the end product of the reactions in the soil of all the S products previously mentioned. It will form sparingly soluble salts with some cations present in arid region soils. Sulfate coprecipitated with natural calcium carbonate in soils is thought to be relatively unavailable to plants. In humid regions sulfate is often leached from the upper part of soil profiles followed by an accumulation in subsurface horizons. However, under conditions of intense leaching, soluble sulfate salts can be completely lost from some medium-to-coarse textured soils.

Many highly weathered soils in regions of high rainfall in the Southeastern USA, Pacific Northwest USA, Central America, and South America contain appreciable amounts of adsorbed sulfate in their subsoils or have the ability to adsorb this form of S. The most important conditions favoring adsorption of sulfate are: large amounts of clay, especially kaolin; presence of hydrous iron and aluminum oxides; low soil pH; high sulfate concentration; impeded movement of soil solution to increase period of contact; presence of weakly held anions such as nitrate and chloride; and occurrence of cations which enhance sulfate adsorption. Liming and phosphate fertilization both reduce the ability of soils to adsorb sulfate. Although adsorbed sulfate may not be quite as available as soluble sulfate, it is nevertheless an important source of S for some plants with deep root systems and long growing seasons. Adsorption of sulfate should help to conserve S fertilizers and native soil S by reducing leaching losses in regions of high rainfall.

Sulfate present in poorly drained and submerged soils is usually reduced by bacteria to form hydrogen sulfide. This, in turn, reacts with active metallic elements such as iron to produce ferrous sulfide and ferrous disulfide. When aerobic conditions are restored, these sulfides are rapidly oxidized to elemental S. The elemental S is converted to sulfate by a process of biological oxidation which was referred to earlier.

V. PREDICTING AND DIAGNOSING THE NEED FOR SULFUR PRODUCTS

Predictions about immediate and recurring requirements for S products can be made by the balance sheet approach. Crop removal and leaching losses are deducted from the sum of all additions of this nutrient in precipitation, atmosphere, irrigation water, fertilizers, and other agricultural chemicals. The S requirements of a number of important crops were set forth in Table 1. Leaching losses will vary depending upon soil, precipitation distribution patterns, ground cover, etc. In the Northeastern USA leaching losses of S were three to six times crop removal, while in the Ohio River basin leaching losses were estimated to be 39 kg of S/ha per year (35 lb/acre per year). In industrial areas as much as 112 kg of S/ha per year (100 lb/acre per year) is deposited from precipitation, whereas this source of S may amount to only 1.1 kg of S/ha per year (1 lb/acre per year) or less in sparsely populated areas. Ten kilograms of S/ha (9 lb/acre) in precipitation has been used as a rough guide for separating areas of potential S deficiency.

Plants can obtain about 30% of their S requirement from SO_2 in the atmosphere. In most rural farming areas this source of S is unimportant. Pollution abatement is expected to reduce its importance for crops adjacent to centers of industrial activity.

Sulfur contents of irrigation waters have been used to predict the need for plant nutrient S. Waters carrying about 4 ppm of S will supply enough S for most crops.

Soil properties can give helpful clues about the need for S products. Sulfur-deficient soils are usually low in organic matter, sandy in texture, and well drained. However, deficiencies are not necessarily limited to such soils. Total soil N and organic matter are very closely related to total S in soils. In most cropping situations an adequate supply of S would be available when crops depend solely on soil organic matter for their N supply. When large amounts of N are supplied by legumes or by fertilizer, however, the supply of S from soil organic matter will probably be insufficient.

Visual symptoms may be used to detect S deficiency, but there are serious limitations in the usefulness of this approach. By the time S-deficiency symptoms are evident the yield and quality of crops may be seriously affected. In addition, it is difficult to distinguish between S and various other deficiencies such as N, Fe, and Zn.

Plant composition can be used to assess the need for plant nutrient S in some crops. This method will become more reliable and popular when additional information is obtained on critical levels and the effects of plant part, stage of growth, etc., on concentration of S. Consideration of the S content in relation to total concentration of other nutrients may also be helpful. For example, the N/S ratio shows promise of having predictive value for wheat and alfalfa.

Available sulfur soil tests are useful for identifying soils deficient in this element and for making recommendations for fertilizer S. Soil tests are offered on either a request or routine basis at several state and provincial laboratories. Many commercial and private laboratories also provide available sulfur soil tests. It is important that the extractants used in these tests remove the predominant form(s) of S in the soils being analyzed. Also, results of the soil tests should correlate closely with crop response to applications of S products.

LITERATURE CITED

Achorn, F. P., and F. J. Myers. 1969. Suspension fertilizers their production and use. Agr. Chem. 24(3):18-25.

Achorn, F. P., and W. C. Scott, Jr. 1969. Polyphosphates are revolutionizing fertilizers. Part III–Polyphosphates in mixtures. Farm Chem. 132(12):46, 48, 50, 52, 102, 104.

Adams, C. A., and R. W. Rinne. 1969. Influence of age and sulfur metabolism on ATP sulfurylase activity in the soybean and survey of selected species. Plant Physiol. 44:1241-1246.

Allen, S. E., D. A. Mays, and G. L. Terman. 1968. Low cost slow-release fertilizer developed. Crops Soils 21(3):13-15.

Anonymous. 1968a. Sulphur: the economics of new recovery systems. Part IV. Sulphur: a hidden asset in smelter gases. Eng. Mining J. 169(8):59-66.

Anonymous. 1968b. Sulphur: the economics of new recovery systems. Part V. Harvesting sulphur from sour gas and oil. Eng. Mining J. 169(10):85-92.

Anonymous. 1968c. Ammonium sulphate nitrate. Nitrogen. no. 53. p. 26, 30.

Anonymous. 1969. Prilled ammonium sulphate nitrate process from Kaltenbach. Nitrogen. no. 59. p. 39, 40, 44.

Arnon, D. I. 1965. Ferredoxin and photosynthesis. Science 149:1460-1470.

Attoe, O. J., O. N. Allen, and W. E. Fenster. 1966-67. Rock phosphate sulphur fusions as nutrient sources for crops. Sulphur Inst. J. 2(4):10-13.

Beaton, J. D. 1969. The importance of sulphur in plant nutrition. Agrichem. West 12(1): 4-6, 27.

Beaton, J. D. 1970. Sulphur in turfgrass fertilization. Sulphur Inst. J. 6(2):5-9.

Beaton, J. D., J. T. Harapiak, and S. L. Tisdale. 1966. Crop responses to sulphur in Western Canada. Sulphur Inst. J. 2(3):9-16.

Beaton, J. D., and W. A. Hubbard. 1969. High-analysis granular sulphur assemblages as sources of sulphur for lucerne. Plant Soil 30(3):373-390.

Beaton, J. D., W. A. Hubbard, R. C. Speer, and R. T. Gardiner. 1968-69. Ammonium phosphate-sulphur and sulphur gypsum: new granular sulphur sources for alfalfa. Sulphur Inst. J. 4(4):4-8.

Bidlack, V. C., Sr., and V. C. Bidlack, Jr. 1967. Tung oil encapsulated controlled release water-soluble fertilizer. U. S. Pat. no. 3,321,298.

Bixby, D. W. 1969. A look from inside the tank–sulphur in fluid fertilizers. NFSA '69 Round-Up. National Fertilizer Solutions Association, Peoria, Ill., p. 34-39.

Bixby, D. W., and D. L. Rucker. 1965. Adding plant nutrient sulphur to fluid fertilizers. Tech. Bull. 11, The Sulphur Institute, Washington, D. C.

Bixby, D. W., S. L. Tisdale, and D. L. Rucker. 1964. Adding plant nutrient sulphur to fertilizer. Tech. Bull. 10, The Sulphur Institute, Washington, D. C.

Bloomfield, C. 1967. Effect of some phosphate fertilizers on the oxidation of elemental sulfur in soil. Soil Sci. 103(3):219-223.

Bodrera, B. 1930. Fertilizer with a base of phosphate and sulphur. U. S. Pat. no. 1,777,908.

Boeglin, A. F., and T. P. Whaley. 1967. Magnesium compounds. p. 708-736. *In* A. Standen (ed.) Kirk-Othmer encyclopedia of chemical technology. 2nd ed. Vol. 12. Interscience Publishers, New York.

Bower, C. A., and M. Fireman. 1957. Saline and alkali soils. p. 282-290. *In* A. Stefferud (ed.) Soil: The yearbook of agriculture 1957. USDA, Washington, D. C.

Bridger, G. L., and D. W. Bixby. 1966. Introduction of solid and molten sulfur into liquid, granular and bulk-blended complete fertilizers. Commer. Fert. 112(2):28-31.

Cairns, R. R., and W. E. Bowser. 1969. Solonetzic soils and their management. Canada Dept. Agr. Publ. no. 1391. p. 5, 8, 19-20.

Caldwell, A. C., E. C. Seim, and G. W. Rehm. 1967. Sulfur deficiency in some Minnesota soils. Minnesota Sci. 24(1):4-6.

Clairborne, J. T., Jr., and P. D. Peterson. 1937. Phosphate-sulphur fertilizer and process of making same. U. S. Pat. no. 2,097,446. Freeport Sulphur Company.

Comiskey, P. T., L. B. Gittinger, Jr., L. F. Good, F. L. Jackson, L. A. Nelson, Jr., and T. K. Wiewiorowski. 1969. Sulfur. p. 337-364. *In* A. Standen (ed.) Kirk-Othmer encyclopedia of chemical technology. 2nd ed. Vol. 19. Interscience Publishers, New York.

Commercial Solvents Corp. 1968. Process for coating fertilizer particles with magnesium and calcium phosphates and sulphates and the resulting product. U. S. Pat. no. 3,419,379.

Commonwealth Sci. Ind. Res. Organ. 1968. Biosuper. CSIRO 20th Ann. Rep. 1967-68. p. 27-28.

Davis, C. G., and W. L. Burns. 1967. Discreet fertilizer granule containing a urea compound, sulphur, and a phosphate plant food. U. S. Pat. no. 3,333,939. Arizona Agricultural Corp.

Dawson, M. D. 1969. Sulphur on pasture legumes in Oregon. Sulphur Inst. J. 5(3):16-18.

Eisenbraun, A. A., and H. E. Ulmer. 1969. Ammonium thiosulfate. Can. Pat. no. 812,159. Allied Chemical Corp.

Ellis, R. J. 1969. Sulfate activation in higher plants. Planta 88(1):34-42.

Estep, J. W., G. T. McBride, Jr., and J. R. West. 1962. The recovery of sulfur from sour natural and refinery gases. p. 314-466. *In* J. J. McKetta (ed.) Advances in petroleum chemistry and refining. Interscience Publishers, New York.

Every, R. L., and P. F. Cox. 1970. Manufacture of ammonium thiosulfate and ammonium sulfate. U. S. Pat. no. 3,493,337. Continental Oil Co.

Every, R. L., and R. L. Grimsley. 1968a. Some unusual properties of sulphur. Sulphur Inst. J. 4(4):2-3.

Every, R. L., and R. L. Grimsley. 1968b. Method for preparation of wettable sulfur. U. S. Pat. no. 3,398,227. Continental Oil Co.

Fleming, P. S. 1970. Sulfur encapsulation of fertilizers to provide controlled dissolution rates. Can. Pat. no. 834,662. Thiokol Chemical Corp.

Formaini, R. E. 1967. Coated fertilizers. U. S. Pat. no. 3,313,615. Allied Chemical Corp.

Fox, R. L., A. D. Flowerday, F. W. Hosterman, H. F. Rhoades, and R. A. Olson. 1964. Sulphur fertilizers for alfalfa production in Nebraska. Nebraska Agr. Exp. Sta. Research Bull. no. 214.

Fox, R. L., and C. Hoover. 1961. Sulfur fertilizers aid corn and soybean production. Nebraska Exp. Sta. Quart. (Winter).

Freeport Sulphur Company. 1968. Sulphur ally of agriculture and industry. Freeport Sulphur Co., New Orleans, La.

Fuller, W. H. 1962. Reclamation of saline and alkali soils. Plant Food Rev. 8:7-9.

Gilbert, H. W. 1939. Method of making phosphate sulfur fertilizer. U. S. Pat. no. 2,161,035. Freeport Sulphur Co.

Goar, B. G. 1968. Today's sulphur recovery processes. Hydrocarbon Process. 47(9):248-252.

Grass, L. B., and A. J. MacKenzie. 1970. Reclamation of tile drains by sulphur dioxide treatment. Sulphur Inst. J. 6(1):8-13.

Hastings, W. F., and J. McGowan. 1966. Granulation of sulphur and soluble compounds. Croplife (March 1966) p. 50-54.

Haynes, W. 1959. Brimstone the stone that burns. D. Van Nostrand Co., Inc., Princeton, N. J.

Heck, R. R. 1968. Sources of Potash. NFSA '68 Round-Up, National Fertilizer Solutions Association, Peoria, Ill., p. 32-33.

Hignett, T. P., and G. Hoffmeister, Jr. 1965. Process of making a granulated, homogeneous phosphate rock sulfur fertilizer. U. S. Pat. no. 3,177,062.

Hoeft, R. G., and L. M. Walsh. 1970. Sulphur fertilization on alfalfa and corn in Wisconsin. p. 11-15. *In* 1970 Wisconsin Fertilizer and Aglime Conf., Madison, Wis. College of Agr. and Life Sci., Univ. of Wisconsin, Madison.

Howard, F. K. 1968. Liquid fertilizer in the Imperial Valley. Fertilizer Solutions. 12(3): 32-33, 35.

Jacobs, J. J. 1968. Potassium compounds. p. 369-400. *In* A. Standen (ed.) Kirk-Othmer encyclopedia of chemical technology. 2nd ed. Vol. 16. Interscience Publishers, New York.

Jones, M. B., W. E. Martin, and J. E. Ruckman. 1970. Sulphur fertilizers evaluated on California grasslands. Sulphur Inst. J. 6(2):2-4.

Kapusta, E. C., and N. E. Wendt. 1963. Advances in fertilizer potash production. p. 219-225. *In* M. H. McVickar, G. L. Bridger, and L. B. Nelson (ed.) Fertilizer technology and usage. Soil Science Society of America, Inc., Madison, Wis.

Kittams, H. A., and O. J. Attoe. 1965. Availability of phosphorus in rock phosphate-sulfur fusions. Agron. J. 57(4):331-334.

Koch, B., P. Wong, S. A. Russell, R. Howard and H. J. Evans. 1970. Purification and some properties of a non-haem iron protein from the bacteroids of soya-bean (*Glycine max* Merr) nodules. Biochem J. 118:773-781.

Koehler, F. E. 1965. Sulphur fertilization in eastern Washington. p. 27-29. *In* Proc. 16th Ann. Fertilizer Conf. Pacific Northwest, Salt Lake City, Utah, July 13-15. Pacific Northwest Plant Food Ass., Portland, Ore.

Larson, M. A., and K. C. Hong. 1967. Method comprising the application of a phosphorus sulfide-ammonia solution to the soil. U. S. Pat. no. 3,343,939. Iowa State University Research Foundation, Inc.

Lengyel, A. D. 1963. Nitro Sul. The fertilizer-soil conditioner combo. Crop Comments (June 1963) p. 2-3.

Ludwick, A. E., K. W. Sharpee, and O. J. Attoe. 1960. Manganese-sulfur fusions as a source of manganese for crops. Agron. J. 60(2):232-234.

Mack, E. 1969. Process for the continuous production of aqueous ammonium thiosulfate solutions. U. S. Pat. no. 3,473,891. Th. Goldschmidt A. G.

Martin, W. G. 1966. The neglected nutrient. p. 8-10. *In* J. Luchoh (ed.) Science. West Virginia Agr. Exp. Sta. Bull. 537.

Matocha, J. E. 1969. Response of coastal bermudagrass to various sources of sulphur on a sandy soil of east Texas. Texas A & M Univ. Prog. Rep. PR-2696.

Mays, D. A., and G. L. Terman. 1969a. Sulfur-coated urea and uncoated soluble nitrogen fertilizers for fescue forage. Agron. J. 61(4):489-492.

Mays, D. A., and G. L. Terman. 1969b. Response of coastal bermudagrass to nitrogen in sulphur-coated urea, urea and ammonium nitrate. Sulphur Inst. J. 5(3):7-10.

McGeorge, W. T. 1945. Sulphur: a soil corrective and soil builder. Arizona Agr. Exp. Sta. Tech. Bull. 201.

McGeorge, W. T., E. L. Breazeale, and J. L. Abbott. 1956. Polysulfides as soil conditioners. Arizona Agr. Exp. Sta. Tech. Bull. 131. p. 29.

Mullin, R. E. 1969. Soil acidification with sulphur in a forest tree nursery. Sulphur Inst. J. 5(1):2-3.

O'Connor, B. 1965. Slow release fertilizers. U. S. Pat. no. 3,206,297. Standard Oil Co.

Phillips, A. B., and W. C. Scott. 1966. Preparation and properties of ammonia-sulfur solutions. Agr. Ammonia News 16(3):40, 42, 44, 46.

Reisenauer, H. M., and G. E. Leggett. 1957. Eastern Washington soils need sulfur. Washington Agr. Exp. Sta. Circ. 317. 11 p.

Rindt, D. W., G. M. Blouin, and J. G. Getsinger. 1968. Sulfur coating on nitrogen fertilizer to reduce dissolution rate. J. Agr. Food Chem. 16(5):773-778.

Roberts, V. E. 1970. Caking resistant nitrogenous fertilizers. Can. Pat. no. 850,015.

Robinson, F. E., D. W. Cudney, and J. P. Jones. 1968. Evaluation of soil amendments in Imperial Valley. California Agr. 22(12):10-11.

Russell, D. A. 1970. Future trends, developments in the fertilizer industry. Agr. Chem. 25(5):17, 19, 20, 22, 49.

Scott, W. C., Jr., and S. L. Tisdale. 1966. Ammonia-sulphur solutions for agriculture. p. 273-283. *In* M. H. McVickar et al. (ed.) Agricultural anhydrous ammonia, technology and use. American Society of Agronomy, Inc., Madison, Wis.

Scott, W. C., J. A. Wilbanks, and M. R. Burns. 1967. Application of anhydrous ammonia-sulfur solutions. Agr. Nitrogen News 17(3):70-74.

Seim, E. C., A. C. Caldwell, and G. W. Rehm. 1969. Sulfur response by alfalfa (*Medicago sativa* L.) on a sulfur-deficient soil. Agron. J. 61(3):368-371.

Sharpee, K. W., A. E. Ludwick, and O. J. Attoe. 1969. Availability of zinc, copper and iron in fusions with sulfur. Agron. J. 61(5):746-749.

Sheridan, R. C. 1970. Chemistry of thiophosphoryl triamide. Sulphur Inst. J. 6(3):11-13.

Smith, C. M., L. E. Stoltenberg, and D. R. Graham. 1968. Sulphur response of alfalfa in western Montana. p. 76-83. *In* Proc. 19th Ann. Fertilizer Conf. Pacific Northwest, Salem, Ore., July 16-18. Pacific Northwest Plant Food Ass., Portland, Ore.

Smith, R. C., and B. Makower. 1963. Advances in manufacture of mixed fertilizers. p. 341-378. *In* M. H. McVickar, G. L. Bridger, and L. B. Nelson (ed.) Fertilizer technology and usage. Soil Science Society of America, Inc., Madison, Wis.

Stanford Research Institute. 1967. Chemical economics handbook. Stanford Research Inst., Menlo Park, Calif.

Stewart, B. A., L. K. Porter, and F. G. Viets, Jr. 1966. Effect of sulfur content of straws on rates of decomposition of plant growth. Soil Sci. Soc. Amer. Proc. 30:355-358.

Sulphur Institute. 1968. TVA shows sulphur coated urea. Sulphur Inst. J. 4(3):2-6.

Tennessee Valley Authority. 1966. Ammonium phosphate nitrate via nitric phosphate route calcium removal by ammonium sulfate recycle. p. 6–9. *In* New developments in fertilize technology. 6th Demonstration, Tennessee Valley Authority, Muscle Shoals, Ala., Oct. 4–5

Terman, G. L., and S. E. Allen. 1969. Ultra-high-analysis NH_3-P–S and NH_3-P–O reactio products development and agronomic evaluation. J. Agr. Food Chem. 17(4):823–826

Terman, G. L., and C. M. Hunt. 1964. Volatilization losses of nitrogen from surface-applie fertilizers as measured by crop response. Soil Sci. Soc. Amer. Proc. 28(5):667–672.

Thiokol Chemical Corp. 1969. Sulfur encapsulated fertilizer pellets. Brit. Pat. no. 1,171,255

Tisdale, S. L. 1968. Sulphur as a fertilizer. p. 285–319. *In* Y. Araten (ed.) New fertilize materials. Centre International Engrais Chimiques. Noyes Development Corp., Park Ridge, N. J.

Tisdale, S. L. 1970. The use of sulphur compounds in irrigated arid-land agriculture. Sulphu Inst. J. 6(1):2–7.

Tisdale, S. L., and H. G. Cunningham. 1963. Advances in manufacturing of secondary and micronutrient fertilizers. p. 269–286. *In* M. H. McVickar, G. L. Bridger, and L. B. Nelson (ed.) Fertilizer technology and usage. Soil Science Society of America, Inc. Madison, Wis.

Tisdale, S. L., and W. L. Nelson. 1966. Soil fertility and fertilizers. 2nd ed. The Macmilla Co., New York. p. 306.

Titus, P. E. 1970. Preparation of pelletized potassium chloride-urea-sulphur fertilizer. U. S. Pat. no. 3,501,282. Shell Oil Co.

van den Driessche, R. 1969. Fertilization. Research Notes, British Columbia Forest Service (48):6–13.

Wells, B. R. 1969. How climate, water quality, and problem soils modify the rice fertilization recommendations. Proc. 19th Ann. Arkansas Plant Food Lime Conf. p. 33–37.

Wilson, F. E., F. J. Peterson, R. M. Engler, W. P. Bonner, and J. E. Sedberry. 1968. The effect of certain micronutrients, sulphur and phosphorus on the yield of rice. Rep. Projects, Dept. Agronomy, Louisiana State University, Agr. Exp. Sta. p. 177–179.

Young, R. D. 1966. Incorporation of sulphur in granular fertilizers. Agr. Chem. 21(4). 4 p.

Zaneti, G., and G. Forti. 1969. Reactivity of the sulfhydryl groups of ferrodoxin nicotinamide adenine dinucleotide phosphate reductase. J. Biol. Chem. 244(17):4757–4760; Chem. Abstr. 71(9):40.