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SULPHUR FERTILIZERS - NEW PRODUCTS ADD TO CONVENTIONAL SOURCES TO OFFER A WIDE RANGE OF OPTIONS (a)

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1. Introduction

As agricultural productivity has increased, the demand for all nutrients has increased. While N fertilization, in particular, and to lesser degrees, P and K fertilization needs have been addressed, S has emerged as the fourth major nutrient for the fertilizer industry. This trend will only continue and will be exacerbated with the reduction of sulphur dioxide emissions, which have served as a significant source of S for crop production for a number of years. Furthermore, the increased trend to use high-analysis fertilizers devoid of S, combined with declining levels of soil organic matter, a significant potential source of S, have reduced soil S content to levels where S is increasingly becoming a limiting factor to higher yields and production.

Ammonium sulphate and single superphosphate (SSP) dominate the current available worldwide supply in so far as volume of fertilizers used containing S, representing 75% of the approximately 10 million tons of S applied in fertilizers annually. While these historically popular sources will be in use for a number of years to come, production is limited and future availability may diminish due to competing production processes. These materials belong to a broader group of what are termed “S fertilizers with sulphate carriers” as opposed to “elemental S-based S fertilizers.” The elemental S-based S fertilizers are newer on the scene and production technologies for a series of these types of products have gained attention in recent years. These products are gaining market share, and a growing array of S fertilizers are available to accommodate different soil, crop and application conditions and situations.

2. The Rising Demand in S Fertilizer Requirements

The Sulphur Institute (TSI) developed a model to track and forecast S fertilizer requirements. The model, based on historical data, forecasts soil S supply and demand on a country and regional basis and includes all major crops. Sulphur supply is represented by total fertilizer application and their relative efficiency in soils based on climatic and soil considerations. Sulphur fertilizer application information is based on International Fertilizer Industry Association (IFA) data and that obtained by TSI through various public sources. Sulphur demand is derived from production data for crops and specific animal products using historical and forecast data from the Food and Agriculture Organization. The S content of crops and animal products are derived from leading agricultural S research organizations. Fertilizer efficiency factors are used to account for losses by leaching and mineralization for tropical and temperate regions of the world. The difference between S requirements, fertilizer

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application, and fertilizer efficiency variables, determines S deficiencies (surpluses) for each country or region. Field trials conducted by TSI and others have delineated and confirmed the predictions by the model.

In 1999, 9.6 million tons of S were applied to soils worldwide through fertilizers. The current potential S fertilizer market is estimated to accommodate an additional 8 million tons. With increased food production raising S requirements, and assuming slower expansion rates for S application in accordance with recent history, the unfulfilled requirement for S fertilizers is projected to grow to 10.6 million tons by 2010.

A regional breakdown of world S deficits is shown in Figure 1. Asia is the region manifesting the greatest sulphur shortfalls. Intensified agricultural production, pressured by the backdrop of food self-sufficiency goals and limited land resources in the globe's two most populous nations, China and India, has created the S nutrient imbalance. Asia's annual S fertilizer deficit, currently estimated at over 4 million tons, will increase to close to 6 million tons by 2010, with over two-thirds represented by China and India. China's current deficit of about 1.8 million tons is expected to grow to 2.4 million tons. India's deficit is projected to increase from 1.3 million tons to 1.8 million tons in 2010.

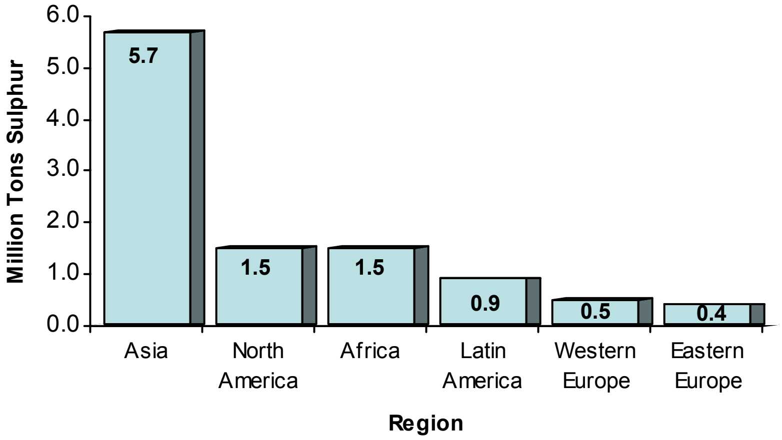

Figure 1. Regional Plant Nutrient S Deficit in 2010

The Western European S market is one of the most advanced in the world. The significant drop in sulphur dioxide emissions since the 1970s, coupled with intensive agronomic practices including the use of high-analysis, S-free fertilizers spurred the region to action to correct the deteriorating S nutrition status. Sulphur deficiency was qualified as a major nutritional problem in arable crops. Comprehensive agricultural research and extension systems facilitate farmers' response to the deficit. It is projected that the market will remain at the current level of 500,000 tons in 2010 within Western Europe, as the increased need for S, particularly in the North, is partially offset by efficiency gains in fertilizer application. Additional commercial opportunities are expected to arise in Eastern Europe, as several countries project sulphur dioxide reductions in part resulting from their proposed entry into the European Union. The current Eastern European S deficit of 300,000 tons is expected to rise by 100,000 tons by the end of the decade.

In North America, the reduction in atmospheric deposition of sulphur dioxide combined with crop intensification continues to shape sulphur deficiencies. The Environmental Protection

Agency recently estimated that sulphur dioxide emission reductions accelerated by 1 million tons between 1999 and 2000, following the 6 million ton reduction from 1981 to 1999, with further declines projected. Continued reductions in sulphur dioxide emissions and increased yields are expected to expand areas of S deficiency. Furthermore, some research institutions are evaluating the need to increase current S fertilizer recommendations in line with existing trends. The North American deficit for S fertilizers is expected to increase from the current 1.2 million tons to 1.5 million tons by 2010.

Latin America is developing as a market for S fertilizer. Agricultural production increased significantly over the last decade, which in conjunction with the rising use of high-analysis fertilizers leads to increasing instances of S deficits, particularly in Argentina. The largest fertilizer consumer, Brazil, is an important and growing user of ammonium sulphate and SSP. The current increased market opportunity in Latin America is estimated at 600,000 tons, and is projected to rise to at least 900,000 tons by the end of the decade.

3. Sulphur Fertilizers

There are two types of S fertilizers: those that are in the sulphate form and those that need to go through a chemical reaction to get into that form for plant uptake. The bulk of S fertilization comes from multi-nutrient fertilizers that are already in the sulphate form. Ammonium sulphate, SSP, and potassium sulphate (K_2SO_4) are the leading products by volume. Although these products were originally applied for their N, P, and K content, respectively, they are increasingly recognized for their S content in its own right. Sulphur is not called the fourth nutrient in vain. All major multi-nutrient S fertilizers provide S in the form of the sulphate (SO_4^{2-}) anion, readily available for uptake by plants. Adding to the array and sophistication of available S products, elemental S in various formulations and liquid fertilizers are capturing increasing shares of S fertilization, mainly in the developed world, at present.

The trend to increase the N, P, and K analyses of fertilizers over the last four decades gradually squeezed out most of the S in the major N, P and K fertilizers, urea, DAP and MOP, respectively. What was once removed because it was considered incidental, is now required.

3.1. Multi-Nutrient Sulphur Fertilizers

Ammonium sulphate is mostly produced as a co-product of other industries. An estimated 70% of global output originates from the production of caprolactam, an intermediate for the manufacture of synthetic fibers. A small amount is recovered from coke oven gas, with most of the remainder produced synthetically from sulphuric acid and ammonia. In 2000, approximately 18 million tons of ammonium sulphate fertilizers were produced, equivalent to over 4 million tons of S. Over 3 million tons of S equivalent are used directly, with the remainder used for blending with other fertilizers. Improvements in the ammonium sulphate formulation processes allow for increasing shares of larger-sized granular material, which is easy to handle and suitable for bulk blending. This has greatly increased application options and spreading performance. Ammonium sulphate is also popular in Europe in the manufacture of compound fertilizers, now deliberately being added to increase sulphur content of compound fertilizers.

New processes in caprolactam production for the fiber market, will gradually reduce production of by-product ammonium sulphate from this arena, although this result will be slow, since the value of ammonium sulphate from this source reduces overall caprolactam costs. In other developments relating to by-product ammonium sulphate production, a new nickel production process is expected to co-produce ammonium sulphate: high-pressure acid leach of nickel lateritic ores is projected to come on stream mostly in Oceania and East Asia. Moreover, in North America, ammonia-based flue-gas desulphurization technology will produce ammonium sulphate at a coal power plant and an oil sands project.

Single superphosphate was the main P fertilizer produced during the first half of the 20th Century. A trend to higher-analysis ammoniated phosphates started in the 1950s. In contrast with ammonium sulphate, most SSP is consumed in the country of origin. Most SSP is produced and consumed in China, India, Brazil, FSU, Australia and New Zealand, with the benefits of the S component often being recognized, particularly in the latter two countries. Total S content in SSP used in 1998 was 4.5 million tons. Production of SSP is relatively stable with a tendency to decline; the majority of P capacity expansion plans include tradable compound fertilizers and ammoniated phosphates; this contributes further to S deficiencies down the road and the need to replace the foregoing S source.

Potassium sulphate is the main S-containing potash fertilizer. For purposes of this discussion potassium-magnesium sulphate is also included. The current global market for these materials is approximately 1.6 million tons of product, equivalent to close to 300,000 tons of S per year. About half of global production is mined directly from potash and sulphate salts or brines requiring no additional S. Potassium sulphate can also be produced based on the reaction between potassium chloride and sulphuric acid, known as the Mannheim Process. Potassium sulphate is normally used for situations and crops susceptible to high chloride and salt concentrations; it is facing increased competition from potassium nitrate as a chloride-free potash fertilizer, thus signaling another potential source of S deficit. Potassium-magnesium-sulphate is used in situations similar to potassium sulphate, but when magnesium is also desired.

Gypsum (calcium sulphate) is not as widely used as a fertilizer compared to ammonium sulphate. Most gypsum is commercially available in forms that are not as easy to handle, blend, and spread. One notable exception is the use of gypsum in peanut (groundnut) production. The calcium is required for proper plant pegging.

Ammonium sulphate, SSP, and potassium sulphate materials remain important S sources; however, their stable or even declining production base against the backdrop of growing S deficiencies and the increasing sophistication and understanding of fertilizer actions has attracted new S sources that are increasing market share. Sulphur fertilizer producers are introducing new products to meet diversified and specific application requirements. These can be categorized broadly into elemental S-based fertilizers and liquid S formulations.

3.2. Elemental Sulphur Fertilizers

The use of elemental S as a fertilizer is increasing mostly in the developed world and is projected to continue. Limited, if any, expansion of sulphate-containing carriers has resulted in industry giving attention to elemental S as a means to correct S deficiencies. Two features of elemental S highlight its use as a controlled-release fertilizer for permanent pastures and crops. First, it is the most concentrated S form, which lowers transport and application costs.

Secondly, it offers reserve availability. Elemental S is converted to sulphate over time. Thus, availability is a function of this process, which depends on the specific source and environmental factors. Elemental S fertilizers are now manufactured in Oceania, North America, Western Europe and West Asia.

The effectiveness of elemental S as a fertilizer is governed by its oxidation rate, which is a biological process carried out principally by bacteria of the genus *Thiobacillus*. The bacteria feed on elemental S and oxidize it to the sulphate form, making S available to plant roots. Physical factors, including soil temperature and moisture, play an important role in determining rates of S oxidation. A third critical physical factor influencing oxidation is particle size of the applied elemental S. Finer particle size increases the oxidation rate, as the greater specific S surface area provides for greater access and action by microbes. The application of coarse elemental S historically produced low yield response in S-deficient annual crops, attributable to low oxidation rates associated with large particle size. The elemental S fertilizer industry has come a long way since those early days.

New Zealand and Australia, along with the United States and Canada, were at the forefront in elemental S fertilizer research and technology, with S deficiencies recognized and addressed since the 1950s. Most research was oriented to areas of deficiency, suitable diagnostic tests, plant S requirements, S cycle modeling, oxidation modeling of elemental S, and development of effective S fertilizers. This research developed soil S testing procedures well-correlated with plant uptake.

The development of suitable elemental S fertilizers includes intensive trial work conducted most frequently in Australia and New Zealand. Much of the work focused on methodologies to incorporate elemental S with fertilizers, either during processing or into the finished product. More recent S fertilizer research in New Zealand was directed towards the development of technology to produce fine-particle elemental S suitable for incorporation into high-analysis P fertilizers or as a degradable granulated product appropriate for dry blending. An emulsifying process was developed to overcome the spontaneous ignition problem when grinding elemental S.

Sulphur bentonite products are manufactured by a number of processes, with molten S blended with swelling bentonite clays and solidified into useable forms, usually granules or pastilles. This material gained popularity in North America and Western Europe. Commercial S bentonite mixtures were originally marketed on a limited basis in the United States in the late 1960s, with some early products not successful mainly due to large particle size. Generally, research results indicate that particle sizes of 150 microns to 200 microns or smaller are required if elemental S is to be fully effective during the growing season in which it is applied. Recent innovations in production technology and anti-dusting agents resulted in the marketing of more effective products. The modern concept behind S bentonite fertilizers is that after application the bentonite or other binding agent absorbs moisture from the soil, causing it to expand and subsequently dissolving the pastille into minuscule elemental S particles that oxidize rapidly. A product with a range of particle sizes is preferable in many circumstances, allowing for short-term and long-term release. In North America, a water-degradable product containing 90% S granulated with bentonite clay is being produced. Produced in pastille and granular forms, these products can be used in bulk blends, direct soil applications, and suspensions. Sulphur bentonite is also produced via a drop-forming technology to produce a pastille.

Alternative formulations of elemental S, particularly tried in Oceania, included mixtures with phosphate rock, SSP, either molten or in dry form, in some cases inoculated with S-oxidizing bacteria, and with partially-acidulated phosphate rock. Adhesion of elemental S to finished products, such as triple superphosphate (TSP), DAP, and urea, offered new opportunities. This approach is an alternative to the methodology to form elemental S into granules or prills using bentonite or other binders. A new process was developed, which solved some problems regarding S fertilizer application in flooded and non-flooded crops and pastures, including improved S dispersion from the granule and better spatial distribution characteristics. A product, with micronized S bonded onto granules of high-analysis TSP is also available. The process establishes an elemental S coating on the surface of the TSP's granules. The S is non-leachable, but in a form that is readily oxidized by soil microorganisms. The special coating process involves the creation of an adhesive film on the surface of the granules by spraying minute quantities of water into a tumbling bed. The S-based dry coating material is applied after the adhesive film is established. This product offers a valid combination for situations requiring high-analysis fertilizers and the need to apply S. An expanded product line is available using other granular fertilizers, including DAP, MAP, and urea.

In Italy, a firm developed a product line of pelleted dust-free S material (fertilizer/amendment) made by extruding and drying a mixture of fine-particle S in a binder, optionally with other organic and inorganic components. The binder breaks down in the presence of moisture, releasing the fine S particles (90% to 95%<100 microns). This proprietary technology provides the flexibility to create a wide range of formulations adapted to most soils and cropping needs. The firm later launched a product containing 50% elemental S and a 50% mix of selected organic manures, recommended for fruit, beets, vegetables, legumes, and cereals. Due to its unique characteristics, it is marketed as a fertilizer and soil amendment and is included in the list of products permitted for organic farming in the European Union.

3.3. Liquid Sulphur Fertilizers

Low water solubility hampers the use of mainstream sulphate fertilizers such as ammonium sulphate and K_2SO_4, in liquid or suspension fertilizer formulations, which have gained importance. Ammonium thiosulphate solution (ATS) is a popular source of S for use in liquid fertilizers because of its solubility and compatibility with various ions. Fertilizer-grade ATS in its commercial form is in a 60% aqueous solution with a (12-0-0-26S) analysis. It is compatible in any proportion with neutral to slightly acidic phosphate-containing solutions or suspensions, as well as with aqueous ammonia (NH_3) and N solutions. It is not compatible with anhydrous NH_3 or strong acids; thus, a wide variety of N-S, N-P-S, and N-P-K-S formulations are possible utilizing this material. Ammonium thiosulphate can be applied directly by drip, sprinkler or flood irrigation. It does not corrode metal piping nor clog spray nozzles. Thiosulphate S is unique in that it exists in two oxidation states, making it more suited to the S uptake patterns of most plants; it decomposes in the soil to form approximately equal amounts of sulphate and elemental S. The sulphate is available immediately whereas the elemental S is gradually converted to sulphate by bacterial oxidation. Ammonium thiosulphate may be synthesized by reacting SO_2 and NH_3 in aqueous solution forming at first ammonium sulphite, which reacts further with elemental S to form ammonium thiosulphate solution. Alternatively, NH_3 may be absorbed in an ammonium thiosulphate solution, reacted with SO_2, then further reacted with hydrogen sulphide to form ammonium thiosulphate solution and S.

Ammonium thiosulphate has gained prominence in North America and is growing in use and importance in Europe, because of its versatility and high S concentration in fluid formulations. The largest producer of ATS has developed other liquid S fertilizers: ammonium polysulphide solution (20-0-0-40S), potassium thiosulphate (0-0-25-17S, particularly suited as a starter fertilizer) and calcium thiosulphate solution, for crops and situations requiring these other nutrients besides S. Thiosulphates ($S_2O_3^{2-}$) are noncorrosive and nonhazardous to handle; they also are well adapted to the methods used to apply fertilizer solutions. They are clear, liquid fertilizers that are suitable for direct applications or blending, offering versatility to farmers and fertilizer retailers. Manufacturers produce thiosulphates in North America and Western Europe. New liquid formulations include (26-0-0-3.1S), for early season use and suitable for all crops, particularly cereals, oilseed rape, and grass. For foliar applications, (35-0-0-1.7S) and (20-0-0-1.7S) are marketed, as are other fertilizers with S, based on ammonium thiosulphate tailored to individual requirements.

Potassium sulphate tends to react with ammoniacal N, phosphates, and metal ion impurities to form insoluble deposits. The largest producer of K_2SO_4 in North America developed a grade twice as soluble as ordinary K_2SO_4, produced as a dry, fine crystalline material with a (0-0-49-17S-1Mg) analysis. This breakthrough increased the use of K_2SO_4 in liquid formulations and fertigation. The product also has a low salt index, reducing the impact on salt-sensitive soils and crops. It is more stable in solution at low temperature than potassium nitrate, thus reducing problems of salting out during storage, transport, and application.

4. Conclusion

The S fertilizer industry has developed materials adapted and suited to particular crop and management situations. Traditional sources, ammonium sulphate and single superphosphate will continue to lead in consumption for sulphur fertilizers in the near-term. However, elemental S-based materials will become more readily available for dry fertilizer applications and thiosulphates will continue to gain in popularity for fluid fertilizer applications. Sulphur is not like N, P, and K fertilizers; there is a much wider range of products, which offer versatility for a variety of applications. With this though, farmers, fertilizer dealers, agronomists, and others in the agricultural community need to understand how these products work for optimal performance. Appendix I provides an offering of the long list of sulphur-containing materials available.

APPENDIX I: Compilation of Various Sulphur Containing Fertilizers Available Worldwide (Taken from The Sulphur Institute Fertilizer Producers Directories)

PRODUCT NUTRIENT ANALYSIS TABLE				
	CONTENT (%)			
SULPHUR FERTILIZERS	S	N	P_2O_5	K_2O
Ammonium Nitrate with Sulphur	5 to 16	30	0	0
Ammonium Phosphate Sulphate	6 to17	Variable	Variable	0
Ammonium Polysulphide	40 to 45	20 to 21	0	0
Ammonium Sulphate	24	21	0	0
Ammonium Sulphate Liquid	9	8	0	0
Ammonium Sulphate Nitrate	14 to 15	26	0	0
Ammonium Thiosulphate Solid	43	19.5	0	0
Ammonium Thiosulphate Solution	26	12	0	0
Calcium Ammonium Nitrate with Sulphur	6	24	0	0
Calcium Nitrate with Sulphur	1 to 5	15	0	0
Calcium Sulphate (Gypsum)	17 to 18	0	0	0
Calcium Sulphate with Ammonium Nitrate	3 to 5	27	0	0
Magnesium Sulphate (Epsom Salt)	13	0	0	0
Magnesium Sulphate (Kieserite)	10 to 23	0	0	0
Micronized Sulphur*	50 to 99	0	0	0
Mixed-Grade NKs with Sulphur	5.2 to 10	Variable	0	Variable
Mixed-Grade NPs with Sulphur	2 to 21	Variable	Variable	0
Mixed-Grade NPKs with Sulphur	2 to 17	Variable	Variable	Variable
Mixed-Grade PKs with Sulphur	2 to 15	0	Variable	Variable
Nitrogen-Sulphur Solutions	2 to 6	7 to 35	0	0
Potassium Magnesium Sulphate	22	0	0	22

SULPHUR FERTILIZERS	CONTENT (%)			
	S	N	P_2O_5	K_2O
Potassium Sulphate	17 to 18	0	0	48 to 52
Potassium Thiosulphate	17	0	0	25
Single Superphosphate - SSP	11 to 14	0	16 to 20	0
Soil Sulphur	50 to100	0	0	0
Sulphur Bentonite	90	0	0	0
Sulphur-Coated DAP	12	12 to15	40	0
Sulphur-Coated TSP	10 to 20	0	38 to 43	0
Sulphur-Coated Urea	10 to14	38 to 40	0	0
Sulphur with Micronutrients	2 to 80	0	0	0
Urea with Sulphur	5 to 6	40	0	0
Urea Sulphuric Acid	9 to 18	10 to 28	0	0
Zinc Sulphate	11	0	0	0
*Includes wettable/dusting powders (dry powder) and flowable sulphur (liquid suspension)				