Sulphur – Essential to the Fertilizer Industry
As a Raw Material, Plant Nutrient and Soil Amendment

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Abstract

Sulphur and sulphuric acid continue to be critical inputs for the Arab and worldwide fertilizer industries. Strong growth in supply in the last several years, particularly from oil and gas resources, was matched by demand growth, much from a revitalized fertilizer sector. Like most other commodities, sulphur has not escaped market turmoil in 2008. An analysis of sulphur supply and demand, with likely trends for the next decade, illustrates the position of this raw material and plant nutrient. Sulphur is produced predominantly in the elemental form, mostly recovered from the oil and gas industry, especially in West Asia. World sulphur consumption in the fertilizer industry was 40 million tons in 2007, which will keep growing in the coming years, especially in Africa and West Asia with the increases of phosphate fertilizer production in these regions.

Sulphur deficiency has become widespread over the past several decades in most of the agricultural areas of the world, especially in Asia and Africa, which provides a large market (estimated at about 10 million tons of sulphur annually) for the Arab and worldwide fertilizer industry. The most popular traditional sulphur fertilizers are ammonium sulphate, single superphosphate (SSP), potassium sulphate and ammonium phosphate sulphate. New elemental sulphur-containing fertilizers are now in the market to meet the increasing demand. Various new and traditional sulphur products can also used be used as soil amendments for land reclamation of salt-affected soils and calcareous soils. The market potential and agricultural uses of sulphur as a plant nutrient and soil amendment are examined in detail.

Sulphur Consumption in Fertilizer Industry

Sulphur has been a key raw material for the fertilizer and chemical industries. It is the primary source for sulphuric acid, the world's most widely used chemical, in a host of manufacturing processes. Sulphuric acid is used by the fertilizer industry to manufacture primarily phosphates, as well as other fertilizers like ammonium sulphate. Based on present technology and economic considerations and agronomic needs, the phosphate fertilizer industry will continue to depend on sulphur and sulphuric acid as raw materials.

Global sulphur consumption in 2007 increased to a record 73.9 million tons, up 4.3% over 2006, after 14 consecutive years of growth since 1993 (Figure 1) (The Sulphur Institute, 2008). The increasing sulphur demand in fertilizer industry contributed mostly to the continuous market growth, which depends largely on the situation of the world phosphate fertilizer production, consumed about 39.7 million tons sulphur in 2007, a 5.6% increase over 2006, in response to higher demand for phosphate manufacture from Africa and China and stronger agricultural commodity markets. The non-fertilizer industrial sulphur consumption also increased to 34.3 million tons, (Figure 2), aided by improved global economic growth. The current economic slow-down had well impacted previous expectations for sulphur consumption for phosphate production, which reduced sulphur consumption in fertilizer industry to 37 million tons in 2008.

Figure 1. World sulphur consumption

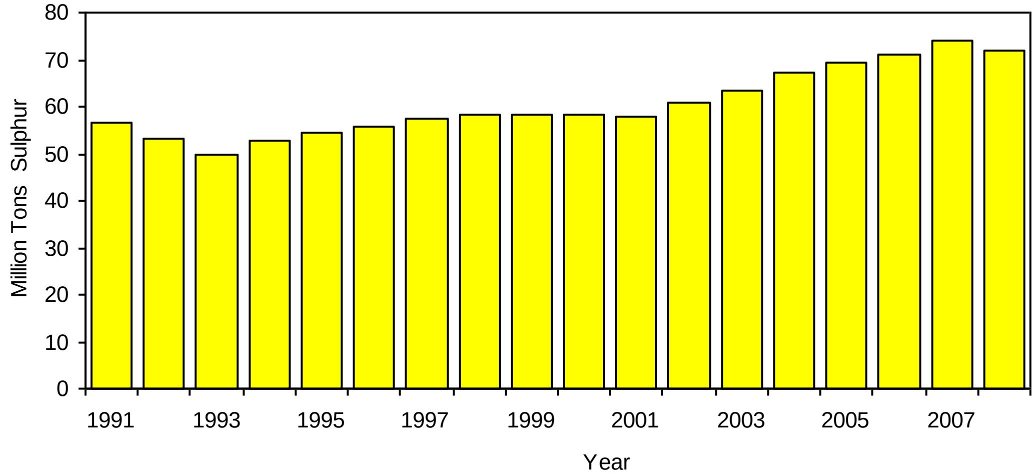
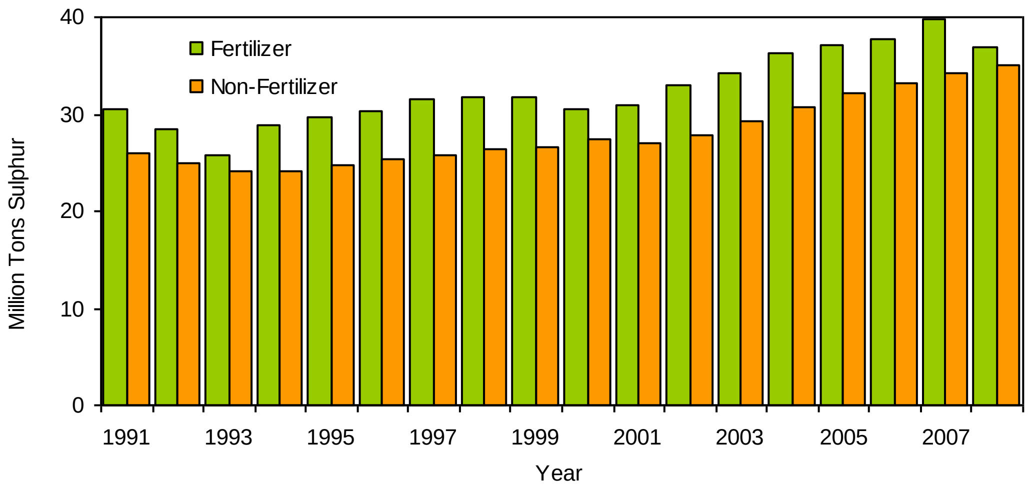


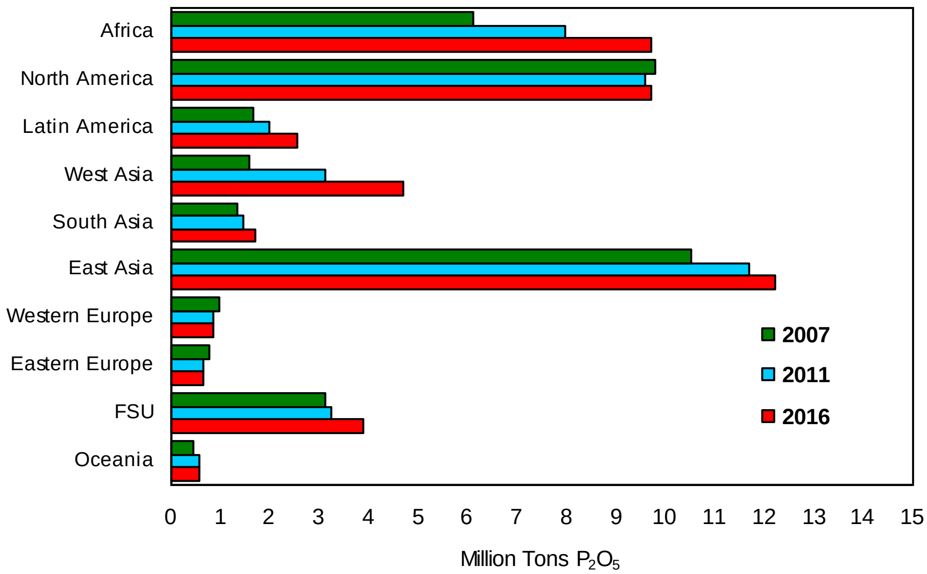
Figure 2. World sulphur consumption in non-fertilizer and fertilizer industries



Over 54% of the world sulphur consumption was for fertilizer production in 2007, totaled 39.7 million tons, with the 93% used to manufacture sulphuric acid for phosphate fertrilizers. Sulphuric acid is used by the phosphate industry to produce wet-process phosphoric acid (WPPA) and Single Superphosphate (SSP). Whereas SSP is an important fertilizer used mostly in developing countries, namely China, India, and Brazil, as well as Australia and New Zealand, WPPA is an intermediate product used to produce other fertilizers of which the most important are Monoammonium and diammonium phosphates (DAP/MAP). In 2007, WPPA and SSP production accounted for 36.2 and 6.8 million tons of phosphate, respectively, jointly accounting for 90% of total phosphate production. Productions of other fertilizers based on sulphur include synthetic ammonium sulphate, potassium sulphate (SOP), elemental sulphur-based fertilizers, ammonium thiosulphate (ATS) and some compound fertilizers (Messick, De Brey and Fan, 2002). Sulphur is an important plant nutrient, and elemental, sulphate or other forms of sulphur also sometimes are added or blended with other fertilizers to meet the increasing demand for sulphur and correct sulphur deficiency in crop production. Elemental sulphur can also be used in agriculture as a pesticide or fungicide.

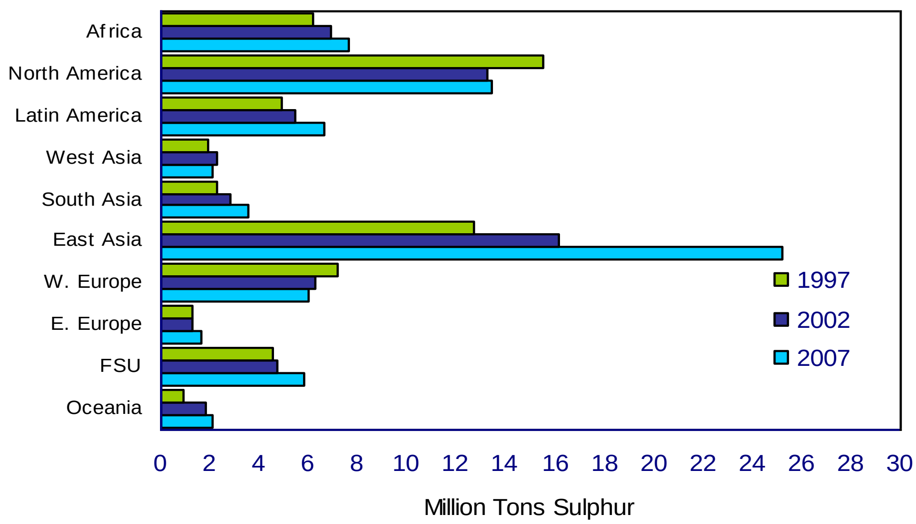
Phosphoric acid production has grown in recent years with Africa, East Asia and North America remaining the largest regions of impact. These will continue to dominate the scene, but production in West Asia, most notably in Saudi Arabia, will become apparent (Figure 3). According to recent press reports, this production will be available starting in 2011 or 2012.

Figure 3. Regional phosphoric acid production trend



Over the last decade, total sulphur consumption increases in East Asia, Latin America, Former Soviet Union (FSU), Africa, Oceania, South Asia, and West Asia more than offset declines in North America and Western Europe (Figure 4). East Asia became the world's biggest sulphur consumer, led by China, mostly driven by the fast growth of high analysis phosphate fertilizer production in recent years, surpassing North America.

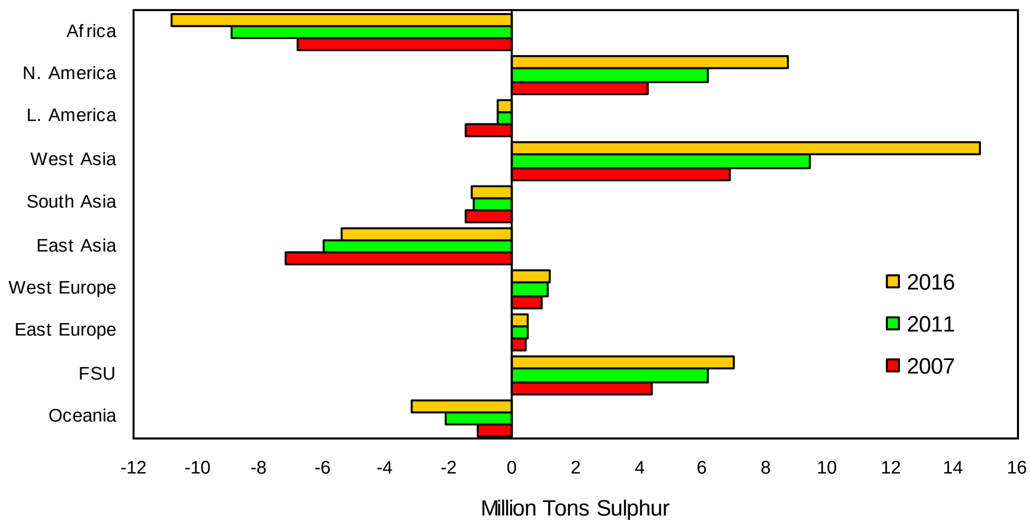
Figure 4. Regional sulphur consumption in the last decade



World total sulphur consumption is projected to increase to 91 million tons by 2016, for an average annual growth rate of 2.5%. The largest incremental growth is expected from Africa, East Asia, West Asia, Latin America, and Oceania. Sulphur consumption for fertilizer production is projected to increase to 49.3 million tons, for an average annual rate of 2.8%. Much of the increment is expected to originate from Africa, followed by East Asia and West Asia. In contrast, sulphur consumption in North America and West Europe will continue to decrease, with the further reduction of phosphate fertilizer production and export.

The world sulphur market is in a surplus mode, although it became a deficit in 2007 as global demand increases outstripped global production growth in 2007. Sulphur supply in all forms is projected to increase by 32 million tons to 102 million tons in 2016; demand climbs by 20 million tons to 91 million tons. The resulting sulphur surplus increases to 11 million tons. West Asia, North America and the FSU provide the bulk of excess supply on the basis of their large-scale production of recovered sulphur (Figure 5), whereas Africa is the major deficit region, due to its sizeable phosphate industry, followed by East Asia and South Asia, mainly based on the rapid growth and developing phosphate sector.

Figure 5. World sulphur balance by regions

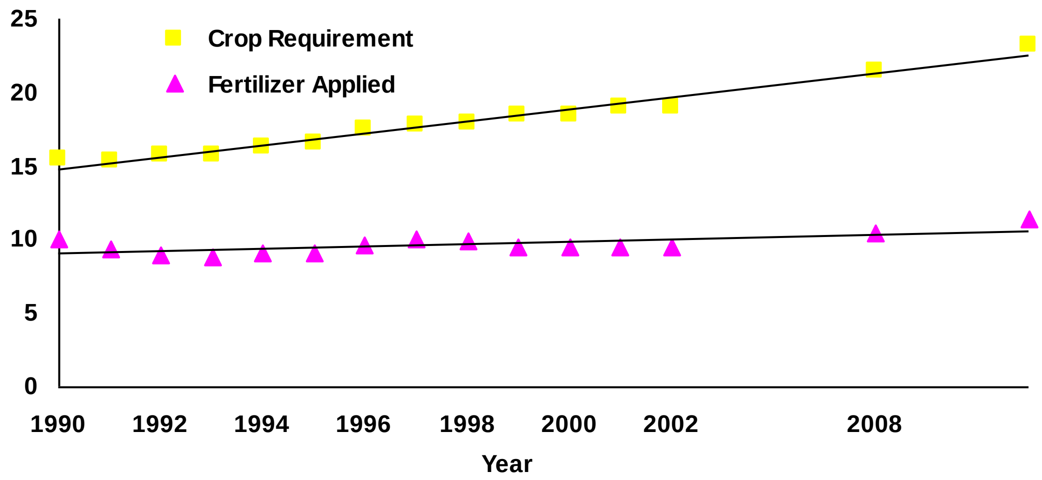


Sulphur Use as Plant Nutrient

Sulphur is one of the major essential plant nutrients, and it contributes to an increase in crop yields by providing direct nutritional value and improving the use efficiency of other essential plant nutrients, particularly nitrogen and phosphorus. As agricultural productivity has increased, the demand for all nutrients has increased. While nitrogen fertilization, in particular, and to lesser degrees, phosphorus and potassium fertilization needs have been addressed, sulphur 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 sulphur for crop production for a number of years. Furthermore, the increased trend to use high-analysis fertilizers devoid of sulphur, combined with declining levels of soil organic matter, a significant potential source of sulphur, have reduced soil sulphur content to levels where sulphur is increasingly becoming a limiting factor to higher yields and production.

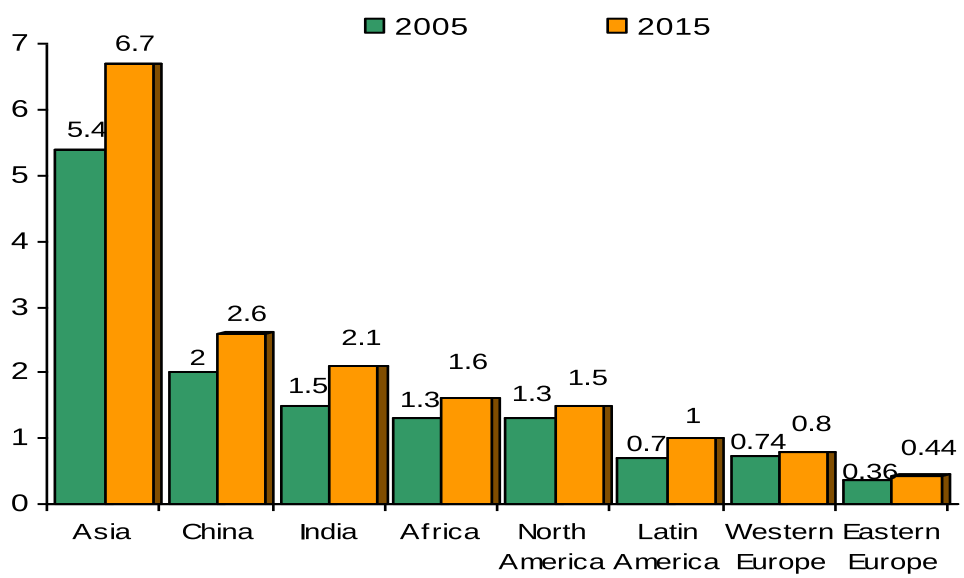
According to estimates of TSI based on crop demand, fertilizer efficiency and current inputs, the current S deficit is about 10.4 million tons annually. With increased food production raising S requirements and assuming slower expansion rates for S application, this S deficit is projected to grow to 12.5 million tons by 2015 (Figure 6) (The Sulphur Institute, 2008).

Figure 6. Plant Nutrient Sulphur Requirement and Deficit (Mt)



A regional breakdown of world S deficits is shown in Figure 7. Asia is the region manifesting the greatest sulphur shortfalls. Intensified agricultural production, pressured by the backdrop of food self-sufficiency goals, limited land resources and unbalanced fertilization, in the globe's two most populous nations, China and India, have created the sulphur nutrient deficiencies. The deficiencies are expected to grow due to the widespread gap between available production and supply and crop requirements. Asia's annual S fertilizer deficit is projected to increase from over 5.4 million tons currently to 6.7 million tons by 2015, with over 70% represented by China and India. This creates both opportunities and challenges for the agriculture and fertilizer industry to explore the huge food production and market potentials in this region**.**

Figure 7. Regional Plant Nutrient Sulphur Deficit in 2005 and 2015 (Mt S)



To develop China and India, Asia's two largest sulphur markets, The Sulphur Institute (TSI) has continuously worked on increasing public awareness and knowledge about sulphur at various levels, including governmental, agricultural research and educational institutes, fertilizer industries and local farmers by different research, extension and educational programs, such as field demonstrations, workshops, and publication and distribution of materials. These programs have made significant progress. For example, since 1993, TSI, collaborating with 15 institutions throughout China as a cooperative network has achieved significant advances in evaluation of sulphur fertilizer requirements and promotion of sulphur fertilizer use in Chinese agriculture, identified more than 30% of soils in China, equivalent to about 40 million hectares, which are sulphur deficient (Fan, 2007). Sulphur fertilizer significantly increased crop yields in 468 field trials, 87% of the total trials completed, with average yield increases from 7% to 30%. With the increased awareness of the importance of sulphur in agriculture, sulphur fertilizer production and use in China is growing. In 2000, the Chinese government recognized sulphur as a plant nutrient, encouraging production of sulphur-containing NPK compound fertilizers. In 2007, the total sulphur-based NPK compound fertilizer output reached 9.5 million tons, providing 1 million tons S.

In India, since 1990, TSI, in collaboration with various international organizations, namely International Fertilizer Industry Association (IFA), and Fertilizer Association of India(FAI), has conducted an integrated research and development program to delineate S deficiencies in Indian agriculture and to advance S fertilizer use for a more balanced fertilization. **The project results prove that the S deficiency situation in India is critical:**

- From over 49,000 soil samples that were analyzed to determine soil S fertility levels in 18 Indian states, the results showed that 75% of cropped soils were S deficient or potentially S deficient, eq. about 80 million ha of S deficient arable land which requires about 1.6 million tons S fertilizer nationwide for sustaining agricultural production.

- Sulphur fertilization significantly increased crop yields in over 90% of 193 field trials completed by an average of 29%, and ranged from 9% to 45% in the 18 states. Assuming a yield increase of a conservative15%, the total grain yield increase, for example, of rice of 48 million tons in India, would rise food production from current 200 million ton to 248 million ton and food supply level per capita by 20%.

- Sulphur fertilizer could increase soil S fertility, resulting in higher yield for the following crops. Residual effects of S fertilizer were recorded in 163 field trials completed from 1998 to 2005, with average crop yield increases of 6% to 48%.

- Sulphur fertilization also improved crop quality by increasing protein content for fodder and wheat, and oil content for mustard.

- The effect of S fertilization on crop yield and quality resulted in high fertilizer efficiency and high economic returns to farmers in all tested crops, with the average Value to Cost Ratio (VCR) ranging from 24 for Bean-Mustard cropping system, to the highest of 76 for Groundnut-Wheat cropping system.

The results have increased the awareness of Indian governmental policy makers in fertilizer and agricultural industries on the importance of S in Indian agriculture. The Indian government, recognizing the benefits of S fertilizer in agriculture from extensive S research project, officially approved S as an essential fertilizer nutrient, and added sulphur fertilizer products, including sulphur bentonite, to the Fertilizer Control Order (FCO) and included the S content of fertilizers as a part of product specifications and eligible for governmental subsidy system. Therefore, for all fertilizers containing S listed in the FCO, manufacturers can specify the minimum guaranteed S content for its inclusion and print the S content on the fertilizer bag. This changes in the FCO and fertilizer subsidy regulations have helped bring S into the mainstream of balanced nutrient application.

The Western European sulphur 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 sulphur 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 have a deficit level of 800,000 tons in 2015 within Western Europe, as the increased need for S becomes more prominent with the increasing oil crop production for bio-fuels. Additional commercial opportunities are expected to arise in Eastern Europe, as several countries project sulphur dioxide reductions in part resulting from their entry into the European Union. The current Eastern European sulphur deficit of over 300,000 tons is expected to rise to 400,000 tons by 2015.

In North America, the continued reductions in sulphur dioxide emissions and increased yields expanded areas of sulphur deficiency. The North American deficit for sulphur fertilizers is expected to increase from the current 1.3 million tons to 1.5 million tons by 2015. Some research institutions are evaluating the need to increase current sulphur fertilizer recommendations in line with existing trends. Currently about 1.7 million tons sulphur was applied annually in North America through fertilizers, mostly as ammonium sulphate. The level of sulphur consumption is expected to increase, as numerous fertilizer concerns are developing marketing efforts to increase new sulphate and elemental sulphur fertilizer demand.

Latin America is developing as a market for sulphur 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 sulphur 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 700,000 tons, and is projected to rise to at least 1 million tons by 2015.

Sulphur deficiencies have been reported in many African countries (FAO 1994; IFDC 1986). In West Africa, the crop responses, from 21 field trials, to P and S are high, adding S fertilizer increased groundnut yields by 15% to 25%. In Nigeria, S responses were found in 95% of the field trials (16 out of 17) in both maize and groundnut production. Elemental S oxidizes rapidly and is equivalent to sulphate-S in availability. In East Africa and Southern Africa, of 133 field trials, 71% showed yield depression of more than 20% without S. Adding 42 kg S as gypsum in a field trial in Kenya, increased sugarcane yield from 52.5 Mt/ha to 73.7 Mt/ha.

The experimental results conducted in Africa provided convincing evidence of S response and inherent S deficiencies in many soils of Africa. Most Africa soils are highly weathered soils, with coarse texture, low pH and low organic matter which accelerates loss of sulphate. Lack of industrialization, low rate of S addition from either atmosphere or fertilizers, and the high export of products containing high level of S, such as groundnuts, palm oil, coconut, tea, coffee are making S deficiency severer in Africa. About 300,000 tons sulphur has been applied to soils in Africa, mostly through ammonium sulphate, SSP and potassium sulphate. Egypt and South Africa are the largest consumers. Based on estimate of TSI, as agriculture intensifies, S deficiencies in Africa will become more apparent and increase in frequency; and annual sulphur demand in agriculture will increase to 1.3 million tons. Sulphur is also used in soil reclamation as soil amendments in African countries, like Egypt.

Clearly, the results generated from extensive research conducted around the globe have provided solid evidence that S deficiency is limiting crop production, affecting crop yield and quality as well as economic return. Sulphur fertilization is essential to the sustainable development of agriculture, with both agronomic and economic benefits.

Sulphur-Containing Fertilizers

In order to correct the increasing S deficiencies in agriculture and bridge the projected S gaps, there is a need to recognize S as a fertilizer nutrient and increase S fertilizer supply worldwide. Ammonium sulphate and single superphosphate (SSP) dominate the current available worldwide supply in so far as volume of fertilizers used containing S. Collectively, these represent 73% of the approximately 10 million tons of S applied in fertilizers annually. While these traditional sources will be in use for a number of years to come, production is not expected in increase on a large scale and in some area may diminish due to competing production of high-analysis fertilizer processes. While the economics of using high-analysis materials is unquestionably favorable, the fertilizer industry is now faced with the necessity of introducing plant nutrient S into many of these products for use on S deficient soils.

Many fertilizer materials contain significant quantities of S. It can generally divided into two groups: 1) Fertilizer containing sulphate, and 2). Fertilizer containing sulphur.

Sulphate-Containing Fertilizers

Sulphate-containing fertilizers provide most of the fertilizer S applied to soils. These materials have the advantages of supplying S primarily as a component of multi-nutrient fertilizers in a form, SO_4^{2-} that is immediately available for plant uptake. The most significant and popular sources are ammonium sulphate, SSP, potassium sulphate, potassium and magnesium sulphate and gypsum.

Ammonium Sulphate ($(NH_4)_2SO_4$)

Ammonium sulphate (21-0-0-24S) is one of the oldest of N and S-containing fertilizers and still remains popular in the world, 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 2005, approximately 17.5 million tons of ammonium sulphate fertilizers were produced, equivalent to 4.2 million tons of S. About 3 million tons of S equivalent are used directly, with the remainder used for blending with other fertilizers. Asia and Western Europe are the leading AS producers and consumers, accounting for about 1 million tons S each in 2005. 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 S content of compound fertilizers.

The main advantages of ammonium sulphate are low hygroscopicity and chemical stability. It is a good source of both N and S. The strongly acid-forming reaction of $(NH_4)_2SO_4$ in soil can be advantageous in high pH soils and for acid-requiring crops. Its use can be undesirable in acidic soils already in need of liming.

Ammonium Nitrate-Sulphate

Ammonium nitrate sulphate was produced by neutralizing nitric and sulphuric acids with NH_3. in North America, with analyses of 30-0-0-5S and 27-0-0-11S. Of the two grades, the former, which contains about 21% $(NH_4)_2SO_4$ and 79% NH_4NO_3 was the more popular.

In Europe, ammonium nitrate sulphate is mostly made by granulating ammonium sulphate in the presence of an ammonium nitrate solution or neutralizing sulphuric acid with ammonia in an ammonium nitrate solution and then granulating. A drum granulator is preferred, but it can also be produced in a blunger. An internal desiccant is frequently used to prevent caking. The major grade is 26-0-0-14S in European market. Other specialty grades with differentiated N/S ratios also exist.

Ammonium Nitrate-Sulphate has several advantages, including less hygroscopic than either constituent individually, a satisfactory N/S ratio for director application purposes, and a combination of ammonium and nitrate forms of N. In the U.S., it has been very successfully for direct application to forage, grass seed crops, and small grains.

Urea-Ammonium Sulphate

Granular urea-ammonium sulphate has been made by coating ammonium sulphate fines with urea in a granulator and by air prilling. Grades range from 40-0-0-14S to 31-0-0-13S. Urea-ammonium sulphate granules tend to be more resistant to physical breakdown and less hygroscopic than urea prills. Its physical properties can be further improved by the addition of gypsum, which forms a complex with urea. The N/S ratio may be varied from 3:1 to 7:1, resulting in considerable flexibility in the correction of N and S deficiencies in most soils. The acid-forming reaction of $(NH_4)_2SO_4$ in soil can reduce urease activity and NH_3 volatilization by reducing pH rising from urea hydrolysis.

Ammonium Phosphate-Sulphate

Ammonium phosphate sulphate (APS) is a complex of ammonium sulphate and ammonium phosphate. The most common grades of ammonium phosphate-sulphate in India are 20-20-0-13 to15S and 16-20-0-13 to 15S. It is composed of about 40% monoammonium phosphate (MAP) and 60% ammonium sulphate. Other products of this type include 13-39-0-20S, 19-9-0-20S, and 23-20-0-7S. The latter contains some urea. They are made by several processes, including reaction a mixture of phosphoric acid and sulphuric acid with ammonia, and introducing ammonium sulphate solutions and H_2SO_4 into a H_3PO_4 plant reaction circuit. Production in 2005 totalled over 2 million tons, providing over 250,000 tons sulphur and has increased in prominence as a source of sulphur, especially in India.

Direct application of 16-20-0-15S to forage crops, particularly legumes, is practiced in many countries. It is also popular for in-row applications on small grains and rapeseed/canola. This product is frequently used for formulating bulk blends.

In 1993, China developed a new technology of producing S-based NPK compound fertilizers using phosphate rock, sulphuric acid, ammonia, urea and potassium chloride as raw materials. This new technology combines all the three technical processes for producing ammonium phosphate, potassium and NPK(S) together, greatly simplifying the production process, and reducing production cost. The major product contains 14.5%N, 16% P_2O_5**,** 14.5% K_2O, and 11%S ($(NH_4)_2SO_4$ and K_2SO_4). Recently, production S-based NPK compound fertilizer in China increased to 9.5 million tons, providing over 1 million tons S.

Single Superphosphate (SSP)

Single Superphosphate was once the most important P source in the world and still is a major P fertilizer in China, India, Australia and New Zealand due to its P and S contents. It is composed of 50% by weight each of monocalcium phosphate and gypsum or its lower hydrate. SSP contains 12 to 22% P_2O_5 and 10 to 14% S and is an excellent source of S. The occurrence of S deficiencies has been delayed in many areas of the world because of the involuntary addition of S when large amount of SSP was used to supply P in the past. Its S (10 to 14%) and Ca (18 to 21%) contents can be important in soils low in these nutrients, and good for crops with high S and Ca demand, like oil and legume crops.

World production of SSP has ranged around 42 to 45 million ton product per year, providing 5.1 to 5.4 million tons S, accounts for 45% of S applied. Most of this production is concentrated in Asia, like China and India. Production of SSP worldwide is relatively stable with a tendency to decline; the majority of phosphorus capacity expansion plans include tradable compound fertilizers and ammoniated phosphates; this contributes further to S deficiencies and the need to replace the foregoing S source.

Potassium Sulphate (K_2SO_4)

Potassium sulphate is the major potash fertilizer containing S. It is a white material containing 50 to 53% K_2O and 17 to 18% S. The production of potassium sulphate has been stable in recent years worldwide, averaging around 4.5 to 5.0 million tons. The current market for K_2SO_4 is about 4.4 million tons of products, equivalent to about 0.8 million tons of S per year. Potassium sulphate is produced by different processes, depending on the original raw material. Most K_2SO_4 is recovered directly from potash salts or brines. About 40% of world K_2SO_4 capacity is based on the reaction between potassium chloride and H_2SO_4, which consumes about over 300,000 tons S as sulphuric acid. Potassium sulphate is widely used as specialty fertilizer for valuable cash crops such as potatoes and tobacco, which are sensitive to chloride, and also it has the advantage of supplying S. Most consumption and production occur in North America, East Asia, Western Europe and Latin America.

Potassium Magnesium Sulphate (K_2SO_4 , $MgSO_4$)

Potassium magnesium sulphate is a double salt and contains 18% K (22% K_2O), 11% Mg and 22% S. It has the advantage of supplying both Mg and S and is frequently included in mixed fertilizers for the purpose on soils deficient in these two elements. They are particularly useful when low levels of chloride are desired, as is often the case for crops such as tobacco, potatoes, peach, some legumes and turf grass. It is suitable for direct application, bulk blending and inclusion in suspensions.

Magnesium Sulphate and Sulphate of Micronutrient

Magnesium Sulphate containing 13% S and 9,8% Mg has been used as a source of Mg and S in clear liquid fertilizers and foliar sprays.

Micronutrient sulphate salts are also incidental carrier of S. For example, in the group consisting of Cu, Fe, Mn, and Zn, concentration of S varies between 13 and 21%.

Fertilizers Containing Elemental Sulphur

Elemental S based fertilizers are the most concentrated S carrier. Modern technologies increased their use in direct applications or as additives to N-P-K fertilizers.

Elemental S is a yellow, insert, water-insoluble crystalline solid. When S is finely ground and mixed with soil, it is oxidized to SO_4^{2-} by soil microorganisms. This oxidation process determines the effectiveness of S in supplying S to plant, and depends on several factors, including particle size, rate, method of application; S-oxidizing characteristics of the soil; and environmental conditions. S oxidation rate increase as particle size is reduced.

Granular Sulphur-Bentonite

A variety of S-bentonite fertilizers have been produced to improve the effectiveness of granular elemental S products by incorporating 5 to 10% by weight of a swelling clay such as bentonite. Particles of S-bentonite are sized for blending with solid N, P and K fertilizers. When it is applied to soil, this bentonite component imbibes soil moisture, causing fertilizer granules to disintegrate into finely divided S, which is more rapidly converted to SO_4^{2-}. This material has gained wide acceptance as a source of plant nutrient S for high analysis, bulk blend formulations because it provide elemental S in an acceptable physical form that can be converted easily in to SO_4^{2-} form in soil.

Because of uncertain effectiveness of these S sources to plants during the first growing season after application, it should be incorporated into soil prior to planting. When it is applied just before seeding and on severely S deficient soils, some SO_4^{2-} should also be provided. Repeated use of elemental S containing fertilizers tends to gradually enlarge the population of S-oxidizing microorganisms, resulting in a corresponding increase in the rate of SO_4^{2-} formation.

Elemental Sulphur fertilizers are manufactured mostly in North America, Western Europe, West Asia, Oceania, and soon Africa. The demand for micronized elemental sulphur also is established and rising in Oceania, Western Europe and Asia.

Elemental S Modified N/P Fertilizers

Elemental S can be readily incorporated into N/P fertilizer materials to provide 5 to 20% S. Monoammonium and diammonium phosphates containing from about 5 to 20% S can be made by applying a hydraulic spray of molten elemental S during drum or pan granulation. Recently, a new sulphate and elemental S-enriched MAP fertilizer was developed in North America, containing 15% S, 13% ammonium-N and 33 to 35% of phosphate. This granular fertilizer containing 50% elemental S and 50% sulphate-S provides readily available S for early plant uptake and residual S for later in the growing season. They are excellent sources of N, P and S, and satisfactory for bulk blending with other granular fertilizers or direct application, particularly for topdressing legumes when both P and S are required. Production capacity is 400,000 tons, equivalent to 60,000 tons sulphur.

The complete miscibility of urea and liquid S facilitates production of a homogeneous granular product with excellent storage and handling properties. A 40-0-0-10S prilled product was manufactured and marketed. Sulphur in this product becomes available sufficiently fast to meet crop needs.

Elemental S as an integral part of N-P fertilizer materials may be oxidized more rapidly than when it is added separately. Sulphur in granulated TSP and DAP fertilizers oxidize faster than S alone in both acid and calcareous soils. There are several possible reasons for this enhancement, including the effect of N, P, or Ca on S oxidizing microorganisms and the existence of more favourable moisture conditions around the fertilizer granule.

Sulphur enriched SSP, containing 18 to 35% S are popular in some countries, such as Australia and New Zealand. The added S is superior in its residual effect to the $CaSO_4$ already in the SSP. This S-enriched SSP has received attention in the area with high leaching losses of plant nutrients because of its potential for reducing SO_4^{2-} leaching loss and also providing available SO_4^{2-} to meet crop needs during the whole growing season.

Sulphur Coatings

One way of achieving controlled release of soluble forms of plant nutrients is to coat them with relatively insoluble and affordable material such as elemental S. S coated urea (SCU) is a controlled release N fertilizer consisting of an S shell around each urea particle. It contains 77 to 82% of urea (36 to 38% N) and 14 to 20% S coating. SCU has the greatest potential for use in situations where multiple applications of soluble N sources are needed during a whole growing season, particularly on sandy soil under high rainfall or irrigation.

Another advantage of SCU is its S content. Although S in the coating may not be sufficiently available to correct deficiencies during the early season of the first year after application, it will become an important source of plant available S in the latter growing season and succeeding year.

Sulphur coated fertilizers are manufactured mostly in North America and, Western Europe before with a production capacity of 200,000 tons per year. Recently, several SCU or S-Coated compound fertilizer plants were completed in China with a total production capacity of 400,000 tons per year under the campaign of increasing fertilizer efficiency. The production of SCU also is established and rising in West Asia.

Sulphur coating may also be used to intentionally supply plant nutrient S. For example, a product analyzing 40-0-0-10S made by coating urea with finely divided S using oil and calcium lignosulfonate as a binder is being used on rice and coastal bermudagrass in USA and Mexico.

Liquid Sulphur Fertilizers

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 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 NH_3 and N solutions. A wide variety of N-S, N-P-S, and N-P-K-S formulations are possible utilizing this material. 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.

Thiosulphate S 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. ATS 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 ATS solution. Alternatively, NH_3 may be absorbed in an ATS solution, reacted with SO_2, then further reacted with hydrogen sulphide to form ATS solution and S.

Ammonium thiosulphate has gained prominence in North America and is growing in use in Europe, because of its versatility and high S concentration in fluid formulations. Future demand for ATS is expected to continue to grow due to overall increasing recognition of the S benefits and higher recommendation rates. 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.

Sulphur Use in Soil Reclamation

Various new and traditional sulphur products, some used as fertilizers can also have applications to improve soil conditions, enhancing land utilization and crop production. When conditions such as salt and/or the presence of large concentrations of undesired elements limit land use, an opportunity for additional sulphur consumption is present.

Market Potential of Sulphur and Sulphuric Acid in Sodic Soil Reclamation

Worldwide, the total area of sodic soils is about 434 million ha, mostly distributed in Asia, Australia, Europe, and North America. If 10% of the area is irrigated land, which is suitable for soil reclamation by soil amendments, including sulphuric acid, the total potential area for soil reclamation is 43.4 million ha. This market potential to amend soils equates to a demand for sulphuric acid of at least 130 million tons (3 tons per ha), equivalent to 42 million tons sulphur. If 10% of this market potential is captured, it will increase consumption by 4.3 million tons annually.

Scientific literature indicates that approximately 1 to 4 tons of sulphur or 3 to 11 tons sulphuric acid per hectare is required to drop soil pH from 8.0 to a more productive 6.0, which could also remove most of the exchangeable sodium and reduce its induced soil problems. Commercial application rates are usually several tons/ha for a one time application of sulphuric acid for conditioning moderately sodic soils (Miyamoto 1997) and translating into large volumes to the sulphur industry either as sulphuric acid or sulphur.

Saline or Sodic Soils

Saline soils contain sufficient levels of soluble salts to limit plant growth. Sodic soils contain high levels of sodium salts and characteristically are very high in soil reaction measured with a pH greater than 8.5. Soils in these classifications typically have low water penetration, low nutrient availability and toxic levels of some elements. If salt levels are high, poor soil structure will limit water penetration and limit plant growth. High soil pH, otherwise known as, alkaline conditions, deter availability of important nutrients like phosphorus, iron, copper, manganese and zinc, essential for plant growth. Without these, plants will grow poorly, if at all. Other elements, such as molybdenum, become more readily available and can be toxic to plants.

Most saline-sodic soils are found in areas of limited rainfall, i.e. arid and semi-arid climate regions, where irrigation would also be necessary to sustain appreciable crop production. The regions most associated with these problem soils are Asia, Australia, Europe and North America. Approximately one-third of the land being irrigated in many regions present unique cultivation problems due to poor soil fertility, soil structure, and low water permeability induced by salinity and high pH. According to estimates by the United Nations (UN) and affiliated agencies (FAO, UNESCO, etc.) more than 50% of all irrigated lands of the world have been damaged by secondary salinization, alkalization and water logging. Many millions of productive hectares in irrigation systems have to be abandoned yearly owing to these causes.

Role of Sulphur in Management of Affected Soils

Historically, gypsum has been used to improve sodic soils. The calcium replaces the sodium, which is leached; thus, improving conditions in the root zone. Sulphuric acid and sulphur, proper, are now being examined as having a role in improving affected soils. Sulphuric acid and elemental sulphur make the relatively insoluble calcium carbonate commonly, found in sodic soils, available for replacement of sodium. Sulphuric acid and sulphur lower soil pH, improve water penetration, and increase the availability of phosphorus and many other nutrients.

Sulphuric acid brings about these effects most rapidly. Because sulphur must first be oxidized to sulphuric acid by soil microorganisms, its reaction with the soil is slower than that of gypsum and sulphuric acid, but its residual effect, particularly on nutrient availability, is generally longer lasting. Also, elemental sulphur is more concentrated than gypsum and sulphuric acid, lowering transport costs. Plus, elemental sulphur is easier to handle in field conditions than sulphuric acid. Elemental sulphur is in ample supply in many parts of the world, especially North America, the Former Soviet Union, and the Middle East, which stands to make it a suitable soil amendment.

Ground agricultural sulphur has been used in studies to determine the effectiveness of sulphur for improving soil conditions. However, other available sulphur-containing materials that would offer much more convenient application have not been widely studied. The quantities of different amendments that will cause equivalent improvement by replacing adsorbed sodium are given in Table 1, relative to 1 ton gypsum. The figures in Table 1 assume 100 percent oxidation of materials like elemental sulphur or pyrites in order to be as effective as soluble calcium compounds.

Table 1. Equivalent Quantities of Some Common Amendments for Sodic Soil Reclamation

Amendment	Relative quantity [1/]
Gypsum ($CaSO_4$ $2H_2O$)	1.00
Sulphuric acid (H_2SO_4)	0.57
Sulphur (S)	0.19
Pyrite (FeS_2) - 30% sulphur	0.63
Calcium polysulphide (CaS_5) - 24% sulphur	0.77

[1]/ These quantities are based on 100 percent pure materials. If the material is not 100 percent pure necessary correction must be made. Thus if gypsum is only 80 percent pure the quantity to be added will be 1.00 x 100/80= 1.25 tons instead of 1.00 ton.

Conclusion

Sulphur and sulphuric acid are important raw materials for the fertilizer and chemical industries. Over 54% of the world sulphur consumption was for fertilizer production in 2007, totaled 39.7 million tons, with the 93% used to manufacture sulphuric acid for phosphate fertrilizers. Sulphuric acid is used by the fertilizer industry to manufacture phosphates, as well as nitrogen, potassium, and sulphur fertilizers. Over the last decade, total sulphur consumption increased in East Asia, Latin America, Africa, South Asia and West Asia, mostly driven by the fast growth of high analysis phosphate fertilizer production in recent years. The increasing sulphur demand in fertilizer industry will continue to contribute to the continuous market growth.

Sulphur is the fourth major plant nutrient which the crop demands in large amounts for their high production. About 10 million tons sulphur was applied as a fertilizer in 2005, but the additional global requirement for sulphur is potentially rising to 11 million tons per year by 2015, primarily due to the growing problem of sulphur deficiency within Asia and the Americas. This provides a tremendous market potential for both sulphur and fertilizer industries. The fertilizer industry has developed materials adapted and suited to particular crop and soil management situations. Traditional sources, ammonium sulphate and single superphosphate will continue to lead in consumption for sulphur fertilizers in the near-term. However, sulphate-containing compound fertilizers and 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 and sulphur-based products, including gypsum, sulphuric acid, and elemental-sulphur containing materials have considerable potential for use in the reclamation of sodic soils and saline soils, which account for about 434 million hectares of land worldwide. It is estimated that 10% of the area is irrigated land, which is suitable for soil reclamation by soil amendments. If just 10% of this estimated potential market is captured, sulphur consumption for land reclamation could be expanded by 4.3 million tons annually. Capturing this market potential would make a large impact on supply surpluses.

Sulphur offers a wide range of products, which provide versatility for a variety of applications. The fertilizer industry needs to invest more on education and promotion programs to accelerate commercialization of sulphur products as both fertilizers and soil amendments, which will provide significant benefits to fertilizer manufacturers, farmers, and agriculture in general.

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