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Sulphur Compounds and Their Significance

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ABSTRACT: Sulfur (or sulphur in British English) is a chemical element with the symbol S and atomic number 16. It is abundant, multivalent and nonmetallic. Under normal conditions, sulfur atoms form cyclic octatomic molecules with a chemical formula S₈. Elemental sulfur is a bright yellow, crystalline solid at room temperature.

Sulfur is the tenth most abundant element by mass in the universe and the fifth most on Earth. Though sometimes found in pure, native form, sulfur on Earth usually occurs as sulfide and sulfate minerals. Being abundant in native form, sulfur was known in ancient times, being mentioned for its uses in ancient India, ancient Greece, China, and ancient Egypt. Historically and in literature sulfur is also called brimstone,^[5] which means "burning stone".^[6] Today, almost all elemental sulfur is produced as a byproduct of removing sulfur-containing contaminants from natural gas and petroleum.^{[7][8]} The greatest commercial use of the element is the production of sulfuric acid for sulfate and phosphate fertilizers, and other chemical processes. Sulfur is used in matches, insecticides, and fungicides. Many sulfur compounds are odoriferous, and the smells of odorized natural gas, skunk scent, grapefruit, and garlic are due to organosulfur compounds. Hydrogen sulfide gives the characteristic odor to rotting eggs and other biological processes.

KEYWORDS: sulphur, octatomic, brimstone, fertilizers, organosulphur, hydrogen sulfide, burning stone

I. INTRODUCTION

Sulfur is an essential element for all life, but almost always in the form of organosulfur compounds or metal sulfides. Amino acids (two proteinogenic: cysteine and methionine, and many other non-coded: cystine, taurine, etc.) and two vitamins (biotin and thiamine) are organosulfur compounds crucial for life. Many cofactors also contain sulfur, including glutathione, and iron-sulfur proteins. Disulfides, S-S bonds, confer mechanical strength and insolubility of the (among others) protein keratin, found in outer skin, hair, and feathers. Sulfur is one of the core chemical elements needed for biochemical functioning and is an elemental macronutrient for all living organisms. Sulfur forms several polyatomic molecules. The best-known allotrope is octasulfur, cyclo-S₈. The point group of cyclo-S₈ is D_{4d} and its dipole moment is 0 D.^[9] Octasulfur is a soft, bright-yellow solid that is odorless, but impure samples have an odor similar to that of matches.^[10] It melts at 115.21 °C (239.38 °F), boils at 444.6 °C (832.3 °F)^[5] and sublimates more or less between 20 °C (68 °F) and 50 °C (122 °F).^[11] At 95.2 °C (203.4 °F), below its melting temperature, cyclo-octasulfur changes from α -octasulfur to the β -polymorph.^[12] The structure of the S₈ ring is virtually unchanged by this phase change, which affects the intermolecular interactions. Between its melting and boiling temperatures, octasulfur changes its allotrope again, turning from β -octasulfur to γ -sulfur, again accompanied by a lower density but increased viscosity due to the formation of polymers.^[12] At higher temperatures, the viscosity decreases as depolymerization occurs. Molten sulfur assumes a dark red color above 200 °C (392 °F). The density of sulfur is about 2 g/cm³, depending on the allotrope; all of the stable allotropes are excellent electrical insulators.

Sulfur is insoluble in water but soluble in carbon disulfide and, to a lesser extent, in other nonpolar organic solvents, such as benzene and toluene.

Scientists measure the sulfur isotopes of minerals in rocks and sediments to study the redox conditions in the oceans in the past. Sulfate-reducing bacteria in marine sediment fractionate sulfur isotopes as they take in sulfate and produce sulfide. Prior to 2010s, it was thought that sulfate reduction could fractionate sulfur isotopes up to 46 permil^[26] and fractionation larger than 46 permil recorded in sediments must be due to disproportionation of sulfur compounds in the sediment. This view has changed since the 2010s as experiments show that sulfate-reducing

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bacteria can fractionation to 66 permil.^[27] As substrates for disproportionation are limited by the product of sulfate reduction, the isotopic effect of disproportionation should be less than 16 permil in most sedimentary settings.^[28]

In most forest ecosystems, sulfate is derived mostly from the atmosphere; weathering of ore minerals and evaporites contribute some sulfur. Sulfur with a distinctive isotopic composition has been used to identify pollution sources, and enriched sulfur has been added as a tracer in hydrologic studies. Differences in the natural abundances can be used in systems where there is sufficient variation in the ³⁴S of ecosystem components. Rocky Mountain lakes thought to be dominated by atmospheric sources of sulfate have been found to have characteristic ³⁴S values from lakes believed to be dominated by watershed sources of sulfate.

Sulfur, usually as sulfide, is present in many types of meteorites. Ordinary chondrites contain on average 2.1% sulfur, and carbonaceous chondrites may contain as much as 6.6%. It is normally present as troilite (FeS), but there are exceptions, with carbonaceous chondrites containing free sulfur, sulfates and other sulfur compounds.^[32] The distinctive colors of Jupiter's volcanic moon Io are attributed to various forms of molten, solid, and gaseous sulfur.^[33]

It is the fifth most common element by mass in the Earth. Elemental sulfur can be found near hot springs and volcanic regions in many parts of the world, especially along the Pacific Ring of Fire; such volcanic deposits are currently mined in Indonesia, Chile, and Japan. These deposits are polycrystalline, with the largest documented single crystal measuring 22×16×11 cm.^[34] Historically, Sicily was a major source of sulfur in the Industrial Revolution.^[35] Lakes of molten sulfur up to ~200 m in diameter have been found on the sea floor, associated with submarine volcanoes, at depths where the boiling point of water is higher than the melting point of sulfur.^[36]

Native sulfur is synthesised by anaerobic bacteria acting on sulfate minerals such as gypsum in salt domes.^{[37][38]} Significant deposits in salt domes occur along the coast of the Gulf of Mexico, and in evaporites in eastern Europe and western Asia. Native sulfur may be produced by geological processes alone. Fossil-based sulfur deposits from salt domes were once the basis for commercial production in the United States, Russia, Turkmenistan, and Ukraine.^[39] Currently, commercial production is still carried out in the Osiek mine in Poland. Such sources are now of secondary commercial importance, and most are no longer worked.

Common naturally occurring sulfur compounds include the sulfide minerals, such as pyrite (iron sulfide), cinnabar (mercury sulfide), galena (lead sulfide), sphalerite (zinc sulfide), and stibnite (antimony sulfide); and the sulfate minerals, such as gypsum (calcium sulfate), alunite (potassium aluminium sulfate), and barite (barium sulfate). On Earth, just as upon Jupiter's moon Io, elemental sulfur occurs naturally in volcanic emissions, including emissions from hydrothermal vents.

The main industrial source of sulfur is now petroleum and natural gas.^[7]

Some of the main classes of sulfur-containing organic compounds include the following:^[47]

- Thiols or mercaptans (so called because they capture mercury as chelators) are the sulfur analogs of alcohols; treatment of thiols with base gives thiolate ions.
- Thioethers are the sulfur analogs of ethers.
- Sulfonium ions have three groups attached to a cationic sulfur center. Dimethylsulfoniopropionate (DMSP) is one such compound, important in the marine organic sulfur cycle.
- Sulfoxides and sulfones are thioethers with one and two oxygen atoms attached to the sulfur atom, respectively. The simplest sulfoxide, dimethyl sulfoxide, is a common solvent; a common sulfone is sulfolane.
- Sulfonic acids are used in many detergents.

Compounds with carbon-sulfur multiple bonds are uncommon, an exception being carbon disulfide, a volatile colorless liquid that is structurally similar to carbon dioxide. It is used as a reagent to make the polymer rayon and many organosulfur compounds. Unlike carbon monoxide, carbon monosulfide is stable only as an extremely dilute gas, found between solar systems.^[48]

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Organosulfur compounds are responsible for some of the unpleasant odors of decaying organic matter. They are widely known as the odorant in domestic natural gas, garlic odor, and skunk spray. Not all organic sulfur compounds smell unpleasant at all concentrations: the sulfur-containing monoterpene (grapefruit mercaptan) in small concentrations is the characteristic scent of grapefruit, but has a generic thiol odor at larger concentrations. Sulfur mustard, a potent vesicant, was used in World War I as a disabling agent.^[49]

Sulfur-sulfur bonds are a structural component used to stiffen rubber, similar to the disulfide bridges that rigidify proteins. In the most common type of industrial "curing" or hardening and strengthening of natural rubber, elemental sulfur is heated with the rubber to the point that chemical reactions form disulfide bridges between isoprene units of the polymer. This process, patented in 1843, made rubber a major industrial product, especially in automobile tires. Because of the heat and sulfur, the process was named vulcanization, after the Roman god of the forge and volcanism.

II. DISCUSSION

Sulfur appears in a column of fixed (non-acidic) alkali in a chemical table of 1718.^[61] Antoine Lavoisier used sulfur in combustion experiments, writing of some of these in 1777.^[62]

Sulfur deposits in Sicily were the dominant source for more than a century. By the late 18th century, about 2,000 tonnes per year of sulfur were imported into Marseille, France, for the production of sulfuric acid for use in the Leblanc process. In industrializing Britain, with the repeal of tariffs on salt in 1824, demand for sulfur from Sicily surged upward. The increasing British control and exploitation of the mining, refining, and transportation of the sulfur, coupled with the failure of this lucrative export to transform Sicily's backward and impoverished economy, led to the Sulfur Crisis of 1840, when King Ferdinand II gave a monopoly of the sulfur industry to a French firm, violating an earlier 1816 trade agreement with Britain. A peaceful solution was eventually negotiated by France.^{[63][64]}

In 1867, elemental sulfur was discovered in underground deposits in Louisiana and Texas. The highly successful Frasch process was developed to extract this resource.^[65]

In the late 18th century, furniture makers used molten sulfur to produce decorative inlays.^[66] Molten sulfur is sometimes still used for setting steel bolts into drilled concrete holes where high shock resistance is desired for floor-mounted equipment attachment points. Pure powdered sulfur was used as a medicinal tonic and laxative.^[39]

With the advent of the contact process, the majority of sulfur today is used to make sulfuric acid for a wide range of uses, particularly fertilizer.^[67]

In recent times, the main source of sulfur has become petroleum and natural gas. This is due to the requirement to remove sulfur from fuels in order to prevent acid rain, and has resulted in a surplus of sulfur.^[7]

Sulfur may be found by itself and historically was usually obtained in this form; pyrite has also been a source of sulfur.^[72] In volcanic regions in Sicily, in ancient times, it was found on the surface of the Earth, and the "Sicilian process" was used: sulfur deposits were piled and stacked in brick kilns built on sloping hillsides, with airspaces between them. Then, some sulfur was pulverized, spread over the stacked ore and ignited, causing the free sulfur to melt down the hills. Eventually the surface-borne deposits played out, and miners excavated veins that ultimately dotted the Sicilian landscape with labyrinthine mines. Mining was unmechanized and labor-intensive, with pickmen freeing the ore from the rock, and mine-boys or carusi carrying baskets of ore to the surface, often through a mile or more of tunnels. Once the ore was at the surface, it was reduced and extracted in smelting ovens. The conditions in Sicilian sulfur mines were horrific, prompting Booker T. Washington to write "I am not prepared just now to say to what extent I believe in a physical hell in the next world, but a sulfur mine in Sicily is about the nearest thing to hell that I expect to see in this life."^[73] Elemental sulfur was extracted from salt domes (in which it sometimes occurs in nearly pure form) until the late 20th century. Sulfur is now produced as a side product of other industrial processes such as in oil refining, in which sulfur is undesired. As a mineral, native sulfur under salt domes is thought to be a fossil mineral resource, produced by the action of anaerobic bacteria on sulfate deposits. It was removed from such salt-dome mines mainly by the Frasch process.^[39] In this method, superheated water was pumped into a native sulfur deposit to melt the sulfur, and then compressed air returned the 99.5% pure melted product to the surface. Throughout the 20th century this procedure produced elemental sulfur that required no further purification. Due to a limited number of such

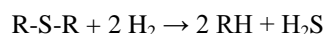
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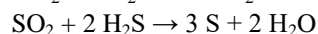
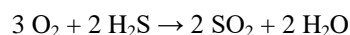
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sulfur deposits and the high cost of working them, this process for mining sulfur has not been employed in a major way anywhere in the world since 2002.^{[74][75]}

Today, sulfur is produced from petroleum, natural gas, and related fossil resources, from which it is obtained mainly as hydrogen sulfide.^[7] Organosulfur compounds, undesirable impurities in petroleum, may be upgraded by subjecting them to hydrodesulfurization, which cleaves the C-S bonds:^{[74][75]}

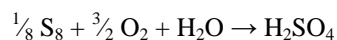


The resulting hydrogen sulfide from this process, and also as it occurs in natural gas, is converted into elemental sulfur by the Claus process. This process entails oxidation of some hydrogen sulfide to sulfur dioxide and then the comproportionation of the two:^{[74][75]}



III.RESULTS

Elemental sulfur is used mainly as a precursor to other chemicals. Approximately 85% (1989) is converted to sulfuric acid (H_2SO_4):



Sulfur reacts directly with methane to give carbon disulfide, which is used to manufacture cellophane and rayon.^[39] One of the uses of elemental sulfur is in vulcanization of rubber, where polysulfide chains crosslink organic polymers. Large quantities of sulfites are used to bleach paper and to preserve dried fruit. Many surfactants and detergents (e.g. sodium lauryl sulfate) are sulfate derivatives. Calcium sulfate, gypsum, ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is mined on the scale of 100 million tonnes each year for use in Portland cement and fertilizers.

When silver-based photography was widespread, sodium and ammonium thiosulfate were widely used as "fixing agents". Sulfur is a component of gunpowder ("black powder").

Amino acids synthesized by living organisms such as methionine and cysteine contain organosulfur groups (thioester and thiol respectively). The antioxidant glutathione protecting many living organisms against free radicals and oxidative stress also contains organic sulfur. Some crops such as onion and garlic also produce different organosulfur compounds such as syn-propanethial-S-oxide responsible of lacrymal irritation (onions), or diallyl disulfide and allicin (garlic). Sulfates, commonly found in soils and groundwaters are often a sufficient natural source of sulfur for plants and bacteria. Atmospheric deposition of sulfur dioxide (SO_2) is also a common artificial source (coal combustion) of sulfur for the soils. Under normal circumstances, in most agricultural soils, sulfur is not a limiting nutrient for plants and microorganisms (see the Liebig's law of the minimum#Liebig's barrel). However, in some circumstance, soils can be depleted in sulfate, e.g. if this later is leached by meteoric water (rain) or if the requirements in sulfur for some types of crops are high. This explains that sulfur is increasingly recognized and used as a component of fertilizers. The most important form of sulfur for fertilizer is the calcium sulfate, commonly found in nature as the mineral gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Elemental sulfur is hydrophobic (not soluble in water) and cannot be used directly by plants. Elemental sulfur (ES) is sometimes mixed with bentonite to amend depleted soils for crops with high requirement in organo-sulfur. Over time, oxidation abiotic processes with atmospheric oxygen and soil bacteria can oxidize and convert elemental sulfur to soluble derivatives, which can then be used by microorganisms and plants. Sulfur improves the efficiency of other essential plant nutrients, particularly nitrogen and phosphorus.^[81] Biologically produced sulfur particles are naturally hydrophilic due to a biopolymer coating and are easier to disperse over the land in a spray of diluted slurry, resulting in a faster uptake by plants.

The plants requirement for sulfur equals or exceeds the requirement for phosphorus. It is an essential nutrient for plant growth, root nodule formation of legumes, and immunity and defense systems. Sulfur deficiency has become widespread in many countries in Europe.^{[82][83][84]} Because atmospheric inputs of sulfur continue to decrease, the deficit

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in the sulfur input/output is likely to increase unless sulfur fertilizers are used. Atmospheric inputs of sulfur decrease because of actions taken to limit acid rains.^{[85][81]}

Elemental sulfur is one of the oldest fungicides and pesticides. "Dusting sulfur", elemental sulfur in powdered form, is a common fungicide for grapes, strawberry, many vegetables and several other crops. It has a good efficacy against a wide range of powdery mildew diseases as well as black spot. In organic production, sulfur is the most important fungicide. It is the only fungicide used in organically farmed apple production against the main disease apple scab under colder conditions. Biosulfur (biologically produced elemental sulfur with hydrophilic characteristics) can also be used for these applications.

Standard-formulation dusting sulfur is applied to crops with a sulfur duster or from a dusting plane. Wettable sulfur is the commercial name for dusting sulfur formulated with additional ingredients to make it water miscible.^{[77][86]} It has similar applications and is used as a fungicide against mildew and other mold-related problems with plants and soil.

Elemental sulfur powder is used as an "organic" (i.e., "green") insecticide (actually an acaricide) against ticks and mites. A common method of application is dusting the clothing or limbs with sulfur powder.

A diluted solution of lime sulfur (made by combining calcium hydroxide with elemental sulfur in water) is used as a dip for pets to destroy ringworm (fungus), mange, and other dermatoses and parasites.

Sulfur candles of almost pure sulfur were burned to fumigate structures and wine barrels, but are now considered too toxic for residences.

Sulfur (specifically octasulfur, S₈) is used in pharmaceutical skin preparations for the treatment of acne and other conditions. It acts as a keratolytic agent and also kills bacteria, fungi, scabies mites, and other parasites.^[87] Precipitated sulfur and colloidal sulfur are used, in form of lotions, creams, powders, soaps, and bath additives, for the treatment of acne vulgaris, acne rosacea, and seborrhoeic dermatitis.^[88]

Many drugs contain sulfur.^[89] Early examples include antibacterial sulfonamides, known as sulfa drugs. A more recent example is mucolytic acetylcysteine. Sulfur is a part of many bacterial defense molecules. Most β -lactam antibiotics, including the penicillins, cephalosporins and monobactams contain sulfur.^[47]

IV. CONCLUSIONS

Most of the soluble sulfate salts, such as Epsom salts, are non-toxic. Soluble sulfate salts are poorly absorbed and laxative.^{[128][129]} When injected parenterally, they are freely filtered by the kidneys and eliminated with very little toxicity in multi-gram amounts.^[130] Aluminium sulfate is used in the purification of drinking water,^{[131][132]} wastewater treatment plants and papermaking.^{[133][134]}

When sulfur burns in air, it produces sulfur dioxide. In water, this gas produces sulfurous acid and sulfites; sulfites are antioxidants that inhibit growth of aerobic bacteria and a useful food additive in small amounts. At high concentrations these acids harm the lungs, eyes, or other tissues. In organisms without lungs such as insects or plants, sulfite in high concentration prevents respiration.

Sulfur trioxide (made by catalysis from sulfur dioxide) and sulfuric acid are similarly highly acidic and corrosive in the presence of water. Sulfuric acid is a strong dehydrating agent that can strip available water molecules and water components from sugar and organic tissue.^[135]

The burning of coal and/or petroleum by industry and power plants generates sulfur dioxide (SO₂) that reacts with atmospheric water and oxygen to produce sulfuric acid (H₂SO₄) and sulfurous acid (H₂SO₃). These acids are components of acid rain, lowering the pH of soil and freshwater bodies, sometimes resulting in substantial damage to the environment and chemical weathering of statues and structures. Fuel standards increasingly require that fuel producers extract sulfur from fossil fuels to prevent acid rain formation. This extracted and refined sulfur represents a large portion of sulfur production. In coal-fired power plants, flue gases are sometimes purified. More modern power plants that use synthesis gas extract the sulfur before they burn the gas.

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Hydrogen sulfide is about one-half as toxic as hydrogen cyanide, and intoxicates by the same mechanism (inhibition of the respiratory enzyme cytochrome oxidase),^[136] though hydrogen sulfide is less likely to cause sudden poisonings from small inhaled amounts (near its permissible exposure limit — PEL — of 20 ppm) because of its disagreeable odor.^[137] However, its presence in ambient air at concentration over 100-150 ppm quickly deadens the sense of smell,^[138] and a victim may breathe increasing quantities without noticing until severe symptoms cause death. Dissolved sulfide and hydrosulfide salts are toxic by the same mechanism.

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