Engineering of Sulfur Production Processes

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Introduction:

Elemental Sulfur or sulphur (same spelling) is a bright yellow crystalline solid at room temperature. The chemical symbol for sulfur is S and atomic number 16. It is abundant as multivalent, and nonmetallic. Chemically, sulfur reacts with all elements except for gold, platinum, iridium, tellurium, and the noble gases. Sulfur has four oxidation states (-2, +2, +4 and +6) and four naturally occurring isotopes (^{32}S, ^{33}S, ^{34}S and ^{36}S), of which ^{32}S is most abundant at 95% of the mass.

Sulphur primarily occurs in four oxidation states in geological environments: S^{2-} (sulphides and sulphosalts), S^{0} (elemental sulphur), S^{4+} (SO_2 in volcanic gas) and S^{6+} (SO_3 in volcanic gas). Its oxidation state determines how S is incorporated into mineral phases.

The most important occurrence of S associated with igneous rocks is in metal sulphide mineralisation. Many metals exhibit chalcophilic tendencies, leading to the formation of many sulphide and sulphosalt ore minerals, such as chalcosite Cu_2S, pyrite FeS_2, sphalerite ZnS, galena PbS, cinnabar HgS, stibnite Sb_2S_3 and oldhamite CaS. Evaporite minerals generally take the form of anhydrous or hydrated sulphates, *e.g.*, barite $BaSO_4$, gypsum $CaSO_4.2H_2O$, anhydrite $CaSO_4$ and epsomite $MgSO_4.7H_2O$. Pyrite present in sediments is another source of sulphate.

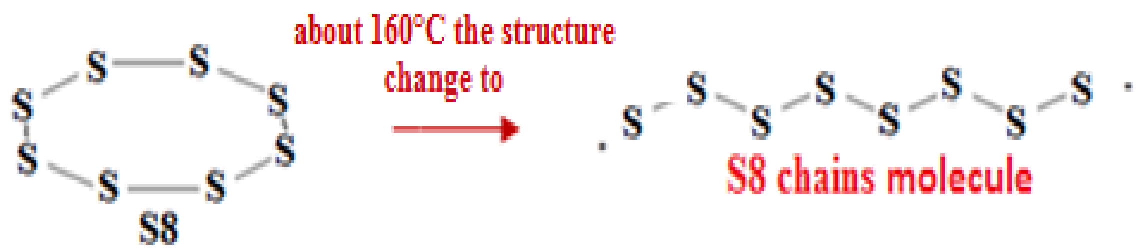
Sulfur is a by-product of large-tonnage waste from oil and gas production facilities. The forecast for the global production of sulfur makes it important to seriously consider various alternative uses of sulfur as well as its complete utilization (disposal). In recent years, China has been the biggest contributor of sulfur as a by-product, due to increase in the number of refineries and gas processing plants (17 million tons in 2018). After China, the largest producers of sulfur are the USA (9.7 million tons), Russia (7.1 million tons), Saudi Arabia (6 million tons), Canada (5.5 million tons), Japan and Kazakhstan (both = 3.5 million tons each) with total annual production of 80 million tons in 2018.

Sulfur has a large number of different allotropic modifications due to the high ability of its atoms to combine with each other to form ring or chain molecules. Allotropes of sulfur can be classified into two types of intramolecular allotrope (formed due to chemical bonding between sulfur atoms) and intermolecular allotrope (formed due to sulfur molecule's arrangement within crystals).

Sulfur atoms unite to form chains (catena/polycatena sulfur) and cyclic rings (cyclo-S_n: where n represents number of atoms) which allows millions of sulfur allotropes (intramolecular) to exist (considering all sulfur atoms' possible combinations). It should be noted that if S_n molecules have 6–12 sulfur atoms, they exist in the form of rings (very stable) while molecules with less than six or greater than twelve sulfur atoms can either exist in the form of ring or chain (unstable).

Allotropes differ in physical properties and are quite similar in most chemical properties. They can exist together in equilibrium in certain proportions, depending on temperature and pressure.

The presence and concentration of each allotrope and, consequently, the physical and chemical properties of solid sulfur depend on the thermal history. The most important allotropic modifications are rhombic (α), monoclinic (β) and plastic. Sulfur α forms **rhombic** crystal and is stable below 95.5 °C (melting point 112.8 °C); sulfur β forms **monoclinic** needles and is stable between 95.5 °C and melting point (119.3 °C). Both are made up of cyclo-S_8 molecules. Liquid sulfur above 159 °C is a solution of linear chains, without regular arrangement between them, formed by opening S_8 rings and polymerizing them.



Source of Sulfur

Sulfur can be obtained from both natural and man-made sources; although, much of the sulfur obtained worldwide from both sources is very difficult to quantify. For instance, sulfur obtained from mining and byproducts of environments (like oil refineries, processing plants of natural gas and smelters of nonferrous metals) can be reasonably quantified. However, sulfur obtained from industries and electric power plants are very difficult to define. Additionally, sulfur emissions obtained through natural sources are difficult to quantify because of the variability of sources, emissions and compounds involved.

- **Natural Sources of Sulfur**

The natural sources of sulfur production are very complex and difficult to quantify. Sulfur is available in various minerals in the crust of earth, which makes it one of the very few elements to be present in earth's crust in elemental state. It is also available in coal, oil and natural gas in the form of various compounds and quantities. Additionally, sulfur is an essential part of all living creatures, including plants and animals. Minerals of sulfide available in lithosphere are weathered to produce sulfates, out of which some is discharged into oceans by various processes like erosion and river runoff. The leftover weathered sulfate produces several compounds by reactions with bacteria, which are eventually incorporated into plant/soil systems. Animals use/eat plants containing sulfur constituents, which eventually produce sulfates after the ingestion process.

Volcanoes are the most affected but best known naturally available sources of sulfur. The sulfur compounds emitted during volcanic activities happen during non-eruptive time as well as during eruption. Moreover, seawater also contains sulfur in a way that every gram of water contains 2.56 mL of sulfate. The availability of sulfur in water bodies is due to weathered minerals and decay of underwater species. As the bubbles (molecules) of water, in particular, at sea, river, ocean or any water body break, salt particles are formed and get into atmosphere. Naturally available sources of sulfur contribution are shown is Figure 1.

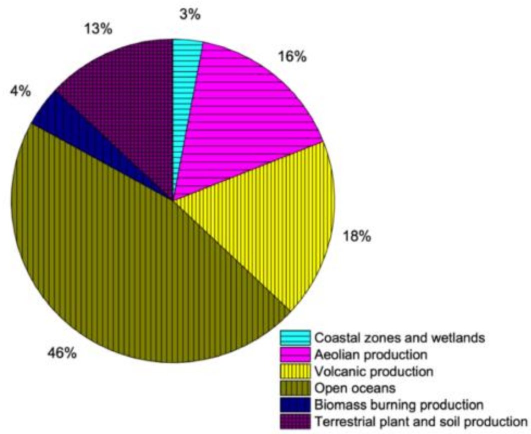


Figure 1. Contribution of sulfur through natural resources