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THE EXTRAORDINARY WORLD OF SULPHUR PART 2[*]

Abstract: Sulphur is a highly reactive element, and is therefore able to enter into a wide variety of chemical combinations, resulting in the formation of compounds of widely differing properties. Reactions involving sulphur, and the compounds which they produce, have stimulated and inspired people throughout the ages. Sulphur has always been associated with volcanoes, fires and smells. However, its story goes much further; sulphur is present in thousands of products of the chemical industry, which are in everyday use. These include car batteries, tyres, matches, paints, paper, textiles, food, detergents and pharmaceuticals. In Part 1 of this essay, the evolution of the role of sulphur in the history of mankind has been explained, through the lenses of etymology, geology, literature, art and chemistry. In Part 2, the role of sulphur in biochemistry and chemical technology is reviewed. In presenting these facets of the world of sulphur, a case is established, to show that sulphur is one of the most useful and interesting substances known to Man.

Keywords: sulphur, sulphuric acid, sulphur dioxide, alchemy, chemistry, technology

Introduction

The principal ideas covered in Part 1 [1] are summarised below.

Etymology - the word *sulphur* is derived from the ancient Sanskrit word *sulvari*, which means "the enemy of copper". Another term for sulphur, *brimstone*, is derived from the old English *brynstan*, or "burning stone". Although *sulphur* (Ancient Greek origin) is used as a correct spelling today, the recently (1990) adopted *sulfur* (Latin origin) is nowadays in widespread use.

Geology - sulphur is widely distributed throughout the earth's crust, both in elemental form (volcanic regions) and in combined form: e.g. sulphides (e.g. pyrites, FeS_2) and sulphates (e.g. gypsum, $CaSO_4 \cdot 2H_2O$). Significant amounts of sulphur containing compounds are found in thermal springs and in fossil fuels.

Literature and art - a wide variety of authors have made references to sulphur in a vast range of contexts: sulphur is mentioned in the Holy Bible and by renowned writers such as William Shakespeare [1564-1616], John Milton [1608-1674] and Charles Dickens [1812-1870]. Sulphur played an important role in alchemical philosophy, of which the sulphur-mercury theory of metals was most important. This underpinned the philosophy of matter for almost 1,000 years, until the 18th century. Sulphur also played a key role in the alchemical systems of Paracelsus [1493-1541] and Sendivogius [1566-1636].

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Chemistry - on account of its great reactivity, sulphur and its compounds form the basis for outstandingly interesting and educational experiments. Practical details are given for experiments which are suitable for schools and universities. They involve sulphur, sulphur dioxide, hydrogen sulphide, dilute and concentrated sulphuric acids, and thiosulphates.

Biochemistry

Sulphur in animals and plants

It has been known for a long time that sulphur is a component of substances which are found in living organisms. Some quotes from books which were published during the latter half of the 19th century illustrate the point: “Every chemist is acquainted with the disgusting smell of most organic sulphur compounds and of sulphuretted hydrogen, one of the most constant products of the decomposition of albuminous matters, and therefore the bad odour of sulphurised products of putrefaction is easily intelligible” [2]. “Sulphur… occurs in combination in white of egg, in muscle, and some other animal products” [3]. “Sulphur compounds are also found widely distributed in the vegetable and animal world, in certain organic compounds such as the volatile oils of mustard and of garlic, and in the acids occurring in the bile. Sulphur is also found in small quantities in hair and wool, whilst it is contained to the amount of about 1 per cent in all the albuminous substances which form so important a constituent of the animal body” [4]. Furthermore, it is known today, that sulphur containing compounds are responsible for the characteristic tastes of onions, horseradish, cheese and eggs.

Although sulphur’s role in living matter has been recognised for a long time, the nature of the sulphur containing compounds was not known, nor indeed were the biochemical processes in which they were involved. This knowledge only gradually became acquired, as quantitative, analytical and organic chemistry evolved during the first half of the 19th century. This enabled the formulae of compounds to be determined, and their classification into families of compounds with similar functional groups - the homologous series - to be established. As the role of organic compounds in plants and animals was investigated, so modern biochemistry was born at the beginning of the 20th century.

Today we know that proteins are natural polymers, with RMMs (relative molecular masses) ranging from 40,000 to a million, and they are the key substances to all forms of life. They are found in all living cells. In animals, they contribute to the structure and to biochemical processes which take place in cells. Hair, skin, nails, tendons, blood, muscle tissue, and ligaments are all protein based. So are enzymes, hormones and antibodies. In plants, proteins contribute to growth, structure and to various metabolic processes (where they act as enzymes) such as photosynthesis. The role of proteins in fungi is not fully understood, but they certainly provide fungi with a source of carbon and nitrogen.

The building blocks of proteins are amino acids, all of which are characterised by the presence of an amine group (-NH_2) and a carboxylic acid group (-COOH). Their structural formula is $H_2NCHRCOOH$, where R represents a functional group. In a protein, the amino acids are joined chemically by peptide links: -$CONH_2$- .

Although about 500 amino acids have been identified in nature, it has been found that these naturally occurring proteins are composed of just 20 amino acids. They are called alpha amino acids, meaning that both the -NH_2 and -COOH groups are attached to the same

carbon atom. Two of these 20 amino acids have a sulphur atom - cysteine and methionine. Their structures are shown in Figure 1, which is taken from a German textbook [5].

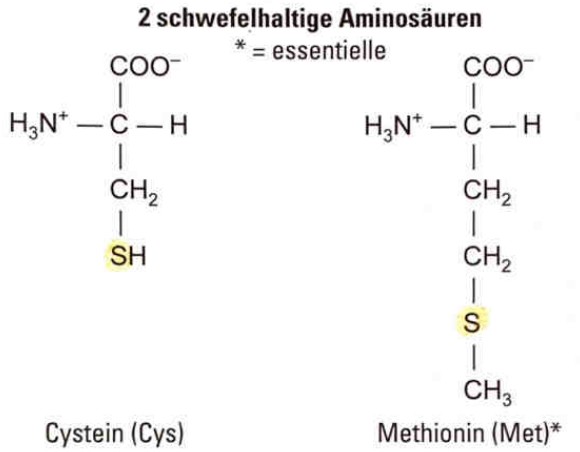

Fig. 1. Sulphur-containing amino acids [5]

In proteins, disulphide bonds (bridges) are formed from cysteine. These bonds are the key to maintaining the ordered structure of proteins, and they are formed between the thiol groups of the cysteine molecules. Cysteine is not an *essential* amino acid (EAA), whereas methionine is. Essential amino acids cannot be synthesised by animals; hence they must be present in food which the animal ingests. Methionine is necessary for its role as an antioxidant and as a stabiliser of the structure of a protein. In addition to EAAs, there are two sulphur-containing vitamins which are necessary for life - biotin and thiamine. Both of these belong to the vitamin B family, and are necessary for energy metabolism i.e. the growth, development and functioning of cells.

Sulphur is the eighth most common element in the human body, and about 140 g of it are present in a person whose weight is 70 kg. The role of sulphur in the lives of plants, animals and fungi is clearly crucial: all proteins contain sulphur, no life can exist without proteins, hence no life can exist without sulphur.

The biogeochemical sulphur cycle

In this cycle, the essence of the chemical processes involving sulphur are its redox reactions involving sulphides (oxidation number (O.N.) of sulphur = –2), elemental sulphur (O.N. = 0), sulphites and sulphur dioxide (O.N. of S = +4), thiosulphates (O.N. of S = +6 and -2) and sulphates (O.N. of S = +6).

The sulphur cycle is unlike the water, carbon and nitrogen cycles, because the atmosphere does not contain a significant fixed amount of any sulphur containing compound. Nevertheless, a consideration of how sulphur and its compounds circulate between the biosphere, geosphere and hydrosphere is of great importance in helping to understand the earth's environment and the delicate equilibria between the animate and inanimate species which exist in it. Figure 2 shows the complexity of this cycle: it shows

the interactions of sulphur containing compounds from the domains of plants, animals, microorganisms and minerals, and the earth's atmosphere and hydrosphere.

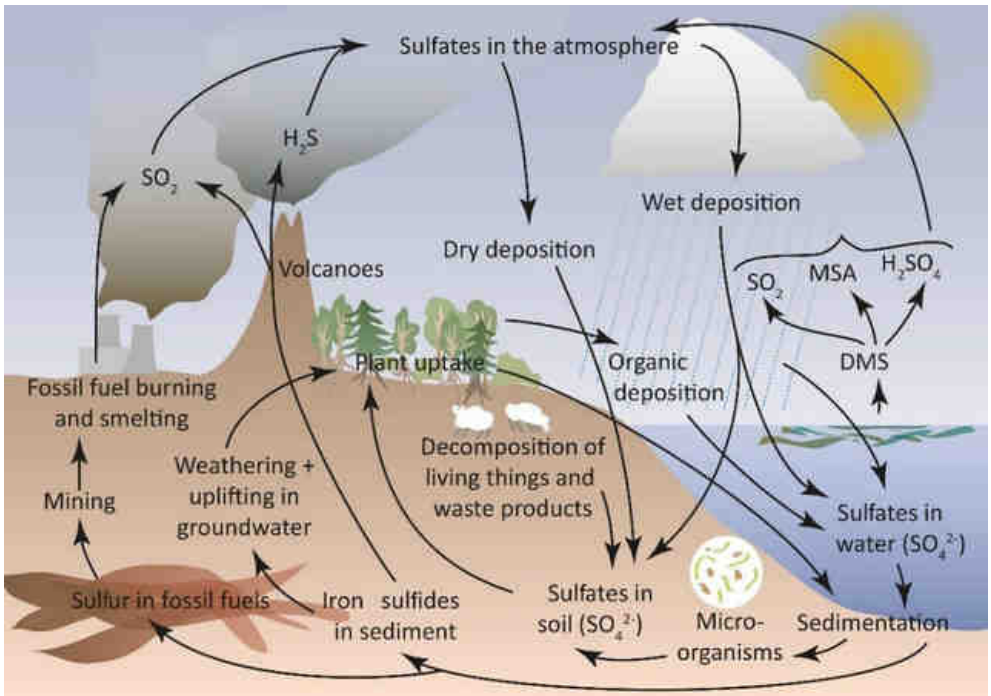

Fig. 2. Schematic figure of the sulphur cycle including human impacts from mining and burning fossil fuels [6]

The greatest store of sulphur is in the oceans and in all surface and underground waters. The main stable form of sulphur in aqueous solutions is the sulphate ion, SO_4^{2-}. Sulphides, both organic and inorganic, are released from all decaying organic matter in oceans and in other aqueous environments such as rivers and lakes. Furthermore, dissolved sulphide ions S^{2-} are present in significant concentrations near hydrothermal vents, as is hydrogen sulphide gas, and elemental sulphur.

It is in the Earth's waters that many chemical and biochemical reactions occur, which involve sulphur. Sulphur containing compounds play a significant role in the food chains of all living organisms and in their life cycles. Redox reactions involving sulphates and sulphides are important processes, in which microorganisms play a key role [7].

The significance of bacteria can be gauged by considering the number of species whose names involve sulphur related terms: *Thiobacillus* - widespread in marine and terrestrial habitats (they enable the oxidation of elemental sulphur to sulphates, which are used by plants), *Desulfovibrio desulfuricans* - common in waterlogged soils, animal stools and sewage (they enable the reduction of sulphates to hydrogen sulphide), *Thiothrix* - in sulphur springs, hot vents, deep sea hydrothermal vents and in sewage (they use reduced inorganic sulphur compounds as an energy source), *Sulfolobus* - in sulphur-rich hot springs and active volcanic regions (they enable the oxidation of sulphides to sulphur and

sulphates). Furthermore, both groups of purple and green sulphur bacteria are able to oxidise hydrogen sulphide to sulphates under anaerobic conditions, in the course of their anoxygenic photosynthesis. This process is important in the natural cycle of nutrients.

On land where organisms are born, live, die and decay, sulphur containing compounds play key roles. The bodies of dead organisms are decomposed through microbial and chemical action, and eventually go into the atmosphere as organic sulphides e.g. dimethyl sulphide, or hydrogen sulphide. Figure 3 shows a part of a biological cycle involving non-living organic matter (horse dung) and living organic matter (dung fungus, of the *Coprophylus* species).

Fig. 3. Dung fungus

Both the dung and the fungus contain sulphur bearing molecules of different kinds. Dimethyl sulphide and hydrogen sulphide are present in dung, whereas methionine is present in the fungus. Since sulphides are easily and rapidly oxidised by atmospheric oxygen, their mean residence time in the atmosphere is very short - of the order of a few hours. The oxidation products are initially sulphur dioxide, which by further reaction with oxygen and water, is converted to sulphuric acid. This may fall as a very dilute form of acid rain, which can be neutralised by soils, forming soluble sulphates which can be absorbed by plant roots.

On land which is devoid of life, especially in mountainous and volcanic regions, rainwater and oxygen from air cause chemical weathering. Minerals which contain sulphur, such as pyrites, react slowly to yield water soluble sulphates which dissolve and flow into rivers. At the vents of active volcanoes, large amounts of sulphur dioxide, hydrogen sulphide and sulphur are emitted. These go into the atmosphere, where they eventually end up as sulphuric acid, and fall as acid rain. The total amount of these emissions has now

been exceeded by anthropogenic activities. These are invariably related to the smelting of metals and the burning of fossil fuels.

The study of the sulphur cycle is by no means a closed topic. In a world of ever increasing population and of developing new technologies, new challenges confront humanity. Whilst chemical technologists have developed ingenious and economical ways of reducing SO_2 in fossil fuel emissions, (e.g. through the use of lime slurry), and also from fossil fuels (through the Claus Process), our increased understanding of the sulphur cycle, and its interaction with other natural cycles, continues to be a matter of high priority.

Chemical technology

Chemical technology of sulphur

Extraction of sulphur

Native sulphur

Sicily was the most important region for producing native sulphur, from prehistoric times until the latter half of the 19th century. Several hundred mines were in operation at various times, and thus the sulphur mining industry had a huge effect on cultural life in Sicily.

Fig. 4. I Carusi (The Boys) Onofrio Tomaselli [1866-1956] (courtesy of the Museum of Modern Art in Palermo)

The reproduction of a large painting by the Sicilian artist Tomaselli (Fig. 4), shows “carusi” (the Sicilian word for boys), who were mercilessly exploited in the Sicilian sulphur mines. They were small and hence could operate in narrow tunnels. The temperatures in the mines frequently exceeded 40 °C. For these ”carusi”, there was no hope of liberation and

the health consequences of the inhuman working conditions were lifelong. The painting is a powerful reminder how the poor have suffered at the hands of uncompromisingly selfish industrialists.

Significant deposits of sulphur have been exploited for the production of sulphur at various times in history and in various localities. The countries include: Canada, Chile, China, France, Hungary, Iceland, Indonesia, Japan, Mexico, New Zealand, Poland, Philippines, Romania, Russia, Spain, Turkey and USA. Today native sulphur is still collected by miners, working in extremely hazardous conditions, in Ijen, Indonesia, which has the largest number of active volcanoes (58) in the world. The total amount of sulphur extracted by this means accounts for about 2 % of the world's annual sulphur production today.

As a result of the increasing demand for sulphur for the manufacture of sulphuric acid during the middle half of the 19th century, and the improvement of drilling technology, which was precipitated by the demand for crude oil from the middle of the 19th century onwards, extensive underground deposits of sulphur were discovered in the cap rocks of salt domes in Louisiana, USA.

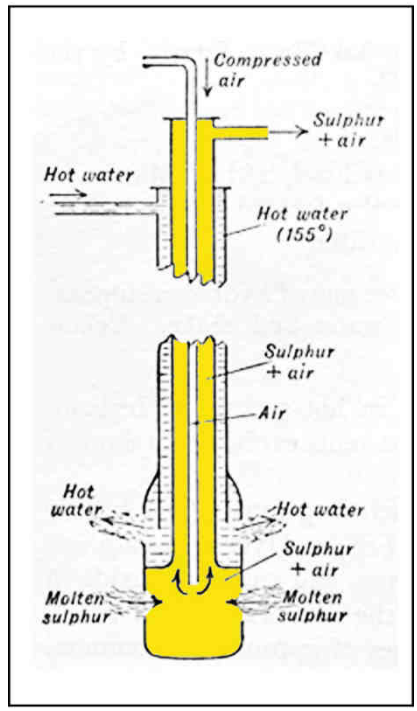

Fig. 5. Principle of the Frasch pump

In 1894, a novel process was developed by Herman Frasch [1852-1914] for extracting the sulphur. It exploited the low melting point of sulphur to liquefy it with superheated water at a temperature of about 160 °C. The liquid sulphur could then be pumped to the surface with compressed air, stored as a liquid in tanks, and transported - by pipeline, rail,

or ship. Figure 5 gives a diagrammatic representation of the arrangement of three concentric pipes, which were used to conduct compressed air, superheated water in order to melt the sulphur, and then to bring the sulphur/water mixture to the surface [8].

This process came into commercial operation at the beginning of the 20th century, and became the principal way of obtaining sulphur, until the end of the 20th century, when it was no longer economically viable. The process was versatile, being able to operate at depths of 50 to 800 metres, and the sulphur thus obtained was very pure. Three Frasch pumps remain in operation today: in Mexico, Poland and the Ukraine.

Sulphur from minerals

It has long been known that pyrites decompose on heating to give pure sulphur and a solid black residue of iron sulphide. Pyrites, which is widely distributed, was thus used as a source of sulphur. A simplified chemical equation for their thermal decomposition is:

$$3FeS_2 \rightarrow 2S + Fe_3S_4$$

Fe_3S_4 (ferrosoferric sulphide) has its analogue in Fe_3O_4 (ferrosoferric oxide), otherwise known as magnetite, which is an important iron bearing mineral.

Fig. 6. Purification of sulphur

On account of its low melting and boiling points, sulphur could be separated and purified by the process of sublimation. This involved heating the pyrites with their involatile impurities (e.g. silicates), and condensing the sulphur vapours on a cold surface. The main difficulty of this process was the ease with which sulphur vapour could catch fire,

producing noxious fumes of sulphur dioxide. This was overcome by vessels which were sealed by luting, thus preventing access of air to the sulphur vapour.

By the 16th century, the method of purification of sulphur by this method was well established. Figure 6, which is a woodcut from one of the great classics of technical literature, shows the purification of sulphur by sublimation. It is very exact in detail [9].

Crude sulphur, in vessels A, is heated on the furnace, which has a roaring flame. Sulphur vapour passes from vessels A to B, where it condenses to a liquid. The liquid sulphur is decanted into a wooden vat, from which it is taken by ladle and cast into moulds. Eight sulphur castings can be seen on the floor. Lid C, with a handle, is for inspection purposes. In the foreground there is a pile of crude sulphur and on its left is a pile of firewood. There is a stone floor and the room is clearly well ventilated - this would have been necessary in view of the presence of smoke from the furnace, and of sulphur fumes. Both the operators would have been very skilled in this operation - not only in pouring the molten sulphur (this technique had been known to metal workers for many millennia), but also in maintaining the fire at the exact level to keep the sulphur molten, and yet not to overfill the chamber with smoke and fumes.

The Claus process

The expressions “sour gas” and “sour oil” are used today to denote crude fossil fuels. The reason for calling them “sour” is because they contain tiny amounts of sulphur, which releases small quantities of sulphur dioxide on combustion. This reacts with moisture and oxygen in air, to form sulphuric acid. Since all acids taste sour, crude fossil fuels are thus said to be sour, since they contain sulphur. The removal of sulphur from fossil fuels has become one of the greatest challenges of chemical technologists during the last century.

The Claus process was first developed by the German chemist and inventor Carl Claus [1827-1900] in 1883, and was subsequently modified by chemists from the giant German IG Farben concern in 1938. There are two basic steps: *hydrodesulphurisation*, which produces hydrogen sulphide, and *partial oxidation of hydrogen sulphide*, to produce sulphur.

The purpose of hydrodesulphurisation is to remove sulphur from the fossil fuel, and convert it to hydrogen sulphide, from which sulphur can easily be obtained. This involves the use of hydrogen, which, in the presence of a suitable catalyst and at carefully controlled conditions of temperature and pressure, combines with the sulphur atoms in the fossil fuel to produce hydrogen sulphide. An example of such a reaction is given below:

C_2H_5SH	$+ H_2$	$\rightarrow C_2H_6$	$+ H_2S$
ethanethiol	hydrogen	ethane	hydrogen sulphide

The overall process is complex, and only the briefest outline has been given. A simplified flow diagram for the hydrodesulphurisation of naphtha is given in Figure 7.

A simplified overview of the process in which sulphur is obtained from hydrogen sulphide can be described by two chemical equations:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2 \ (\Delta H = -518 \text{ kJ} \cdot \text{mol}^{-1})$$

and

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \ (\Delta H = -1166 \text{ kJ} \cdot \text{mol}^{-1})$$

They are both redox reactions, of which the first involves the complete combustion of hydrogen sulphide, and the second represents the formation of sulphur by

a disproportionation reaction, as described earlier. Both of these reactions are exothermic, and this factor has to be carefully considered in the design of industrial equipment. The efficiency of these reactions is also determined by the careful selection of catalysts, and conditions of temperature and pressure.

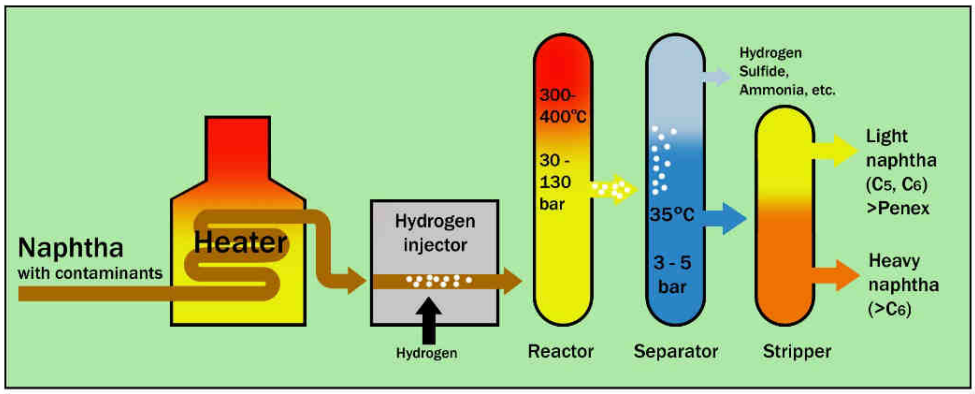

Fig. 7. Hydrodesulphurisation of naphtha

Having been relatively dormant for almost two centuries, the Claus process has made a remarkable comeback on a worldwide scale during the past two decades. Today there are over 380 Claus plants operating throughout the world, and they produce over 95 % of the world's sulphur [10]. These figures represent a truly stunning turnaround during the last 50 years. They show how chemists and technologists have adapted with remarkable efficacy to the changing needs of society - to reduce the amount of atmospheric pollution (SO_2), and simultaneously to produce a most important raw material - sulphur.

Uses of sulphur

Five properties of sulphur have determined its multifarious uses: non-toxic, low melting point, healing properties, chemically reactive, combustible. It is also relatively light and brittle and therefore easy to mine and to transport.

The ancient world

Sicily became known throughout the Ancient world for large deposits of sulphur in its volcanic regions. In Ancient Egypt, some 4000 years ago, Sicilian sulphur was burnt in order that the fumes (SO_2) could be used to bleach linen or disinfect/purify air. Sulphur was used as a component of skin ointments and as a fungicide on vines. Its use in air purification, by killing insects, was described 2700 years ago in Homer's epic Ancient Greek poem, *The Odyssey*.

"But the king turned to devoted Eurycleia, saying, "Bring sulphur, nurse, to scour all this pollution - bring me fire too, so that I can fumigate the house…" "Fire first," the good soldier answered. "Light me a fire to purify this house." The devoted nurse snapped to his command, brought her master fire and brimstone. Odysseus purged his palace, halls and court, with cleansing fumes" [11].

Incendiaries and pyrotechnics

Sulphur has been, throughout the ages, a key component of incendiary and pyrotechnic mixtures. Greek fire and gunpowder, which have been the subject of much historical research [12], are two well-known examples. It is not known exactly how or when either of these were invented, but two facts are clear: their invention was a gradual process, lasting many centuries, and sulphur was an ingredient in both of them.

Greek fire, as it is known, was a liquid which was used primarily in naval warfare. It was discharged from siphons, which acted like flame throwers, and approached or landed on enemy ships as a burning viscous liquid which floated on water. It was probably similar to napalm, which has been used in modern warfare. The use of Greek fire was naturally subject to favourable weather conditions. It was used during the Byzantine Wars, involving Muslim-Arab dynasties and the Byzantine Empire from the 7^{th} century until the middle of the 11^{th} century and employed successfully to defend Constantinople in the siege of 673 AD.

The composition of Greek fire, which could apparently self-ignite on contact with water, remains a mystery. It would have probably contained petroleum, tree resins, sulphur and possibly quicklime (calcium oxide), which generates a great amount of heat on contact with water. Whilst Greek Fire has sunk into oblivion, and remains an historical curiosity, gunpowder has been much more successful.

It is composed of an intimate mixture of potassium nitrate (75 %), charcoal (15 %) and sulphur (10 %). It was developed about 1000 years ago in China and remains in use today, in firearms and in fireworks. Whilst both charcoal and sulphur, two non-metallic elements, had been known since antiquity, the discovery and use of potassium nitrate as an oxidant poses a much greater problem for the historian. Potassium nitrate (nitre) occurs abundantly in the soils of countries such as India and China, where animal excrements undergo chemical and biological degradation to yield ammonium compounds. These are subsequently atmospherically oxidised to nitrates in the presence of nitrifying bacteria. Nitrates react with wood ash, containing potassium and calcium carbonates, to make potassium nitrate. Upon evaporation of potassium nitrate solution in the hot climates of these countries, white crystals of the nitre are formed in soils. Exactly how these crystals became the key ingredient of gunpowder is not known, but we can speculate that glowing ashes of wood fires would have glowed much more brightly where they came into contact with the nitre crystals. Observation of this phenomenon would have prompted experimentation, which would have eventually led to the development of black powder. More detailed accounts of the discovery of gunpowder and its uses and impact on history have been well documented [13, 14].

The art of pyrotechnics, in which gunpowder plays a key role, stems from China. Fireworks displays throughout the ages have been used for a vast number of occasions and celebrations. Not the least of which was Handel's great composition of 1749: Music for the Royal Fireworks. This was written for King George II on the occasion of the ending of the war of the Austrian Succession and the signing of the Treaty of Aix la Chappelle. Figure 8 shows a pictorial representation of the orchestra playing in front of an elegant courtyard, with the audience in boats on the Thames, and fireworks being set off all around.

Fig. 8. Handel's music for the Royal Fireworks, 1749 (Alamy Images)

Moulds and castings

The history of sulphur being used for the fabrication of moulds and for creating works of art has been little studied, but surprisingly, this use of sulphur does make sense, on account of its easy fusibility.

The ability of sulphur to attract tiny pieces of straw, paper, hair and feathers was well-known ancient times. The same phenomenon of attraction had been exhibited by pieces of fossilised tree sap, known as amber. Accordingly, in the middle of the 17th century, when experimental science was being used to solve many unanswered questions concerning natural phenomena, attempts were made to investigate the seemingly magical forces that were responsible for these effects. In 1660 the German scientist and inventor Otto von Guericke [1602-1686] constructed the world's first electrostatic machine. A small sulphur sphere was turned rapidly against a dry hand, and remarkable effects were observed when small feathers could be made to dance as a result of invisible forces which the machine generated. Today we recognise these forces as electrostatic electricity. Figure 9 shows a diagram of Guericke's device [15]. This diagram provided a source of inspiration for Markus Bindhammer from Friedberg in Germany, to construct a working replica in 2023. Figure 10 shows the magnificent result of his endeavours.

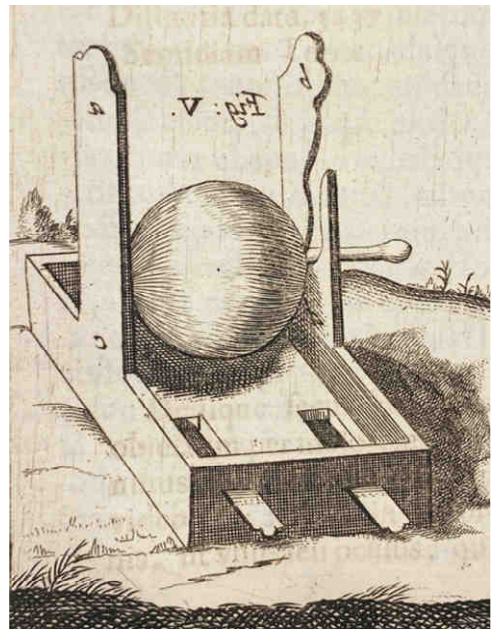

Fig 9. Guericke's sulphur ball (1660) (courtesy of the British Library)

Fig. 10. Bindhammer's sulphur ball

During the 18th century, sulphur was used to create beautiful decorative effects as an inlay for wooden cabinets [16]. During that same period, moulds started to be made from sulphur, for the production of ornate marzipan confectionery. This was made from ground almonds, sugar and honey, and lent itself particularly well for making a wide variety of shapes and figures, on account of its plasticity. Marzipan was introduced into Europe via the Hanseatic port Lubeck in the 10th century, by the Persian physician, philosopher and alchemist Rhazes [864-923], and continues to be a highly valued form of confectionery. Figure 11 shows an intricate sulphur mould in the form of a sailing ship for marzipan from 1880. It is exhibited at the Marzipan Museum at the Café Niederegger in Lübeck.

Fig. 11. Sulphur mould for marzipan

Vulcanisation

In 1840 Charles Goodyear [1800-1860] made an invention which changed the world of materials science, especially the world of transport. His invention was the process known as the vulcanisation of rubber. Latex, which is an elastic solid obtained from dried tree sap, had been known and valued for millennia by people in the Mesoamerican cultures. However, its uses (e.g. waterproof containers, shoe soles, balls) were limited, since it became too soft and sticky during hot weather, and hard and brittle in cold weather. Goodyear discovered that by adding sulphur to the hot latex, the rubber would acquire dramatically improved properties - it would become stiffer and much more tolerant to temperature changes. Thus objects made from vulcanised rubber would maintain their shape at different temperatures, and they would be hard wearing in mechanical applications.

Today it is known that sulphur is able to form cross linkages with the hydrocarbon molecules in latex, giving it a rigid polymeric structure. About 5 % of the world's annual sulphur production is used in the vulcanisation of rubber. The vast proportion of this is used in the manufacture of tyres - for cars, lorries, and aircraft.

Sulphur in today's world

Other uses of sulphur today include the manufacture of matches, insecticides, fungicides, medicinal preparations and skin creams. Furthermore it is used for the manufacture of chemicals such as carbon disulphide, which is used for viscose rayon, cellophane and certain types of synthetic rubber. Yet by far the most important use of sulphur is for the manufacture of sulphuric acid.

Chemical technology of sulphuric acid

History of its manufacture

The story of the evolution of the sulphuric acid industry is a long and complex one [17]. Three key factors were: understanding the nature of the chemical processes involved, a rapidly increasing demand for the acid and the economics of the process. Four methods have been used for the commercial manufacture of sulphuric acid, which has been known since the 13th century, and these are outlined below.

The roasting of green vitriol, which had been described by the medieval alchemists, was in use until the middle of the 17th century. The equation for the reaction is:

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$

Sulphur trioxide was dissolved in water, in a violently exothermic reaction, to give sulphuric acid. The finely powdered orange-brown residue of ferric oxide, known as colcothar, was used as a pigment and as a polishing agent known as "jeweller's rouge". This process was laborious and extremely inefficient - it took a week to produce about 2 pounds of sulphuric acid, from 6 pounds of vitriol.

A mixture of sulphur and potassium nitrate (nitre) was roasted. This reacted to form sulphur trioxide, which was released in the form of extremely acrid fumes. This was added to steam, with which it reacted violently, to form sulphuric acid in the form of a fine mist. The mist was condensed in a large ceramic bell. This process had been described by the German-Dutch chemical technologist Rudolph Glauber [1604-1670] in 1655, but the English physician and entrepreneur Joshua Ward [1685-1761] adapted it for the commercial production of the acid. The Great Vitriol Works, as they were called, were first operated in Twickenham in south west London in 1736. Figure 12 shows the arrangement of the equipment [18].

The worker is pouring a mixture of sulphur and nitre onto the fire. The rising sulphur trioxide/sulphur dioxide mixture reacts with moisture in the air and is condensed on the underside of the bell as fuming sulphuric acid. The acid drips into bottles containing water, and is subsequently distilled to increase its concentration. Needless to say, this method not only released vast quantities of acrid fumes, but it was also highly inefficient. On account of protests from local residents, it was closed in 1749.

The lead chamber process, which was much more efficient, was developed by the English industrialist and inventor John Roebuck [1718-1794]. The first plant was built in 1746, and was located in Prestonpans in Scotland. In this process, sulphur dioxide which is produced by roasting iron pyrites in air. The SO_2 is reacted with nitrogen dioxide from the reaction between potassium nitrate and sulphuric acid, and steam and air (oxygen) are added, to produce sulphuric acid. The whole process was carried out in lead lined vessels; hence it was known as the lead chamber process. The reactions in it are complex, and involve the catalytic action of nitrogen dioxide, which oxidised sulphur dioxide to sulphur

trioxide. Versions of this process were in operation until the end of the 20th century, but a serious disadvantage was that it was a batch process, meaning that the chambers had to be charged separately with sulphur and nitre on an intermittent basis [19]. Today this process is obsolete.

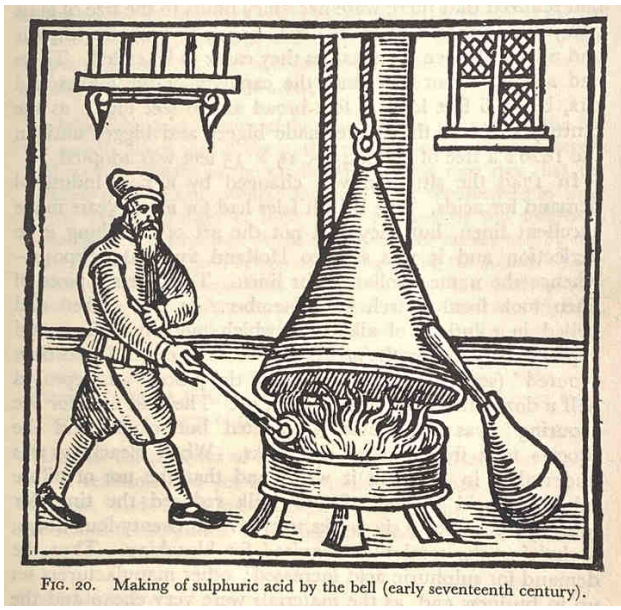

Fig. 12. Making of sulphuric acid by the bell

The Contact process for the manufacture of sulphuric acid is widely used today. The raw materials for this process are sulphur and air, with a catalyst of vanadium pentoxide. The stages of the process are briefly summarised as follows: sulphur is burnt in air to produce sulphur dioxide. This is subsequently reacted with more air (oxygen) in the presence of vanadium pentoxide catalyst, at a temperature of 450 °C and a pressure of 2 atmospheres. This forms sulphur trioxide, which is absorbed into 98 % sulphuric acid, to yield oleum, or fuming sulphuric acid. Oleum is diluted with water to yield 98.5 % (concentrated) sulphuric acid. Four chemical equations represent the main reactions which occur:

$S + O_2 \rightarrow SO_2$	Burning sulphur to make sulphur dioxide
$2SO_2 + O_2 \rightarrow 2SO_3$	Catalytic oxidation of sulphur dioxide to sulphur trioxide
$SO_3 + H_2S_2O_4 \rightarrow H_2S_2O_7$	Dissolving sulphur trioxide in sulphuric acid to make oleum
$H_2O + H_2S_2O_7 \rightarrow 2\ H_2SO_4$	Diluting oleum with water to make concentrated sulphuric acid

Figure 13 shows a diagrammatic representation of the main units in this process [20]. Unlike earlier processes, this produces fuming sulphuric acid of high purity.

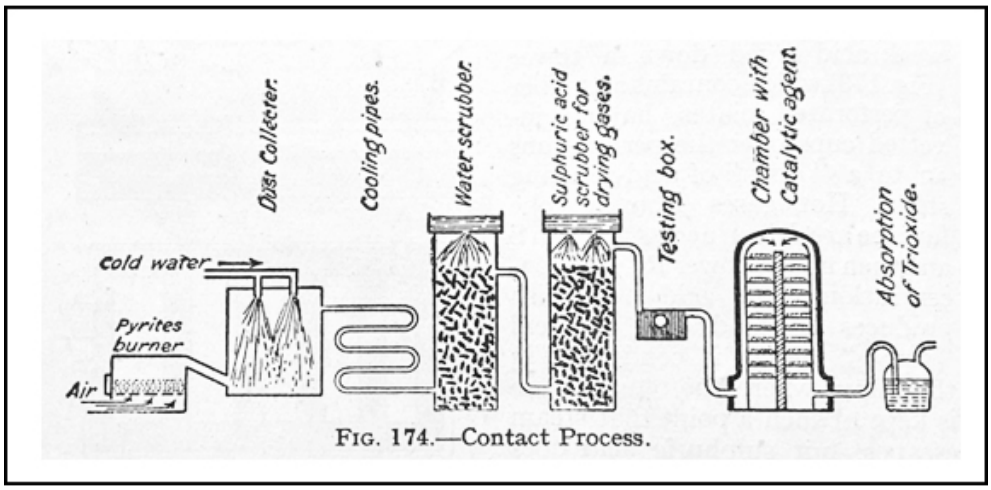

Fig. 13. The contact process

Uses of sulphuric acid

Sulphuric acid has always been the most important product of the inorganic chemicals industry. During the 18th century, it was used for making medicines e.g. Glauber's salt, *sal mirable* (sodium sulphate), which acts as a mild laxative. Furthermore, on the basis of his reading of the works of Paracelsus and others, Glauber assigned oil of vitriol to a remarkable range of cures, for almost every known disease or ailment, including fevers, apoplexy, gout, tumours and inflammation. Taken externally, it was supposed to heal scabs, ringworm, scaldings and gangrene [21]. This unrealistic list of attributes, which must have been based on false evidence or false hopes, would certainly have promoted interest in sulphuric acid.

On account of its reactivity with metal oxides, sulphides and metals, it was used by brass founders, japanners, button makers, and the refiners of precious metals. It was used for providing the acid environment which was necessary for the bleaching of linen (in this it replaced fermented buttermilk), for the manufacture of chemical bleaches (sodium hypochlorite), dyes, mordants and in calico printing [22].

At the beginning of the 19th century, the uses of sulphuric acid took a new turn. In 1800, Alessandro Volta [1745-1827] published a paper which was to revolutionise the world - he described the first electric battery. This sparked off a new era in history - the age of portable electrical energy and stored electrical energy [23]. The remarkable new energy source provided the inspiration for new inventions, such as telegraphy and electroplating of metals. By the middle of the 19th century a whole new range of electric batteries had been developed, whose aim was to satisfy the ever growing demand for new applications such as electric motors. One of the greatest challenges confronting scientists was to develop a battery that could be recharged, thus vastly increasing its efficiency. In 1859 this challenge was met.

Gaston Plante [1834-1889] was born in Orthez, in the Pyrenees Atlantique in south west France. He was educated in Paris, and from an early age he showed outstanding academic potential. When he was 16 he was awarded a PhD degree, and by the age of 19 he

had a DSc. His scientific interests were broad and included geology and meteorology. His greatest passion however, was the newly and rapidly evolving science of electricity. Thus he joined the community of scientists, whose aim was to improve battery design. After numerous trials with a variety of metals and electrolytes, in 1859 Plante invented the lead/acid accumulator, in which sulphuric acid is the electrolyte. The battery was an astounding success. Throughout his life Plante received numerous awards and distinctions, and he played a key role in the development of electrical technology in Brazil. He was a humble and generous man, giving his considerable acquired wealth to the poor [24]. Plante's lead acid battery [25], which uses sulphuric acid, continues to underpin mechanised transport throughout the world.

Today, 50% of the world's production of sulphuric acid is used for the manufacture of fertilisers. Among the myriads of other uses are included: the refining of petroleum, steel pickling and galvanising, manufacture of dyestuffs, paints, synthetic fabrics, pharmaceuticals, paper, antifreeze, insecticides, detergents and explosives. In a nutshell, we owe the vast majority of the necessities and comforts of our everyday lives, to products from the sulphuric acid industry.

Conclusion

A quote from Sendivogius summarises most aptly the content of the present article. In the context of a dialogue between an alchemist and a gaoler, in which sulphur is imprisoned, the gaoler describes the attributes of sulphur:

"Hee is the maker of a thousand things, and is the heart of all things: hee knows how to make Metalls better, and corrects Mineralls, teacheth Animalls understanding, knowes how to make all kinds of Flowers in Hearbs, and Trees, and is chief over them, corrupts the Aire, which hee amends again: hee is the maker of all Odours, and Painter of all Colours…. Friend, know that Sulphur is the vertue of all things, and is the second by birth, but yet older than all things, and more worthy, yet an obedient child." [26]

In view of this statement, and from the content of the present article, it would be truly difficult to dispute the statement that: of all substances known to Man, sulphur is the most extraordinary.

Postscript

The sulphur story has not only generated great interest in the past, but it continues to inspire scientists, novelists, artists and performers to the present day. To this effect, Jedrzej Dmochowski composed an "Ode to Sulphur" for the occasion of the author's lecture for families and children, at the Royal Institution of Great Britain, which took place in December 2023 [27].

ODE TO SULPHUR!!

In foul, four, fathoms deep,
In years now long ago
The alchemists were working where
Our darkest secrets flow -
From hydrothermal vents they drew
Their inspiration's fire

To make their dark discoveries –
Bring light to man's desire!

For science is an art - of experiments and trial,
Of utter dedication, of intelligence - and while
WE take for granted
The things we have today,
It's science which asks questions –
To light and lead the way!

Now let us shine its light upon an element of fire!
SSSSULPHUR!! burning brimstone
Now lifted from the mire
Of centuries of ignorance, of elemental need -
Its NOW we have the answers
Its NOW we can succeed
In giving explanations
As to how things work, react –
And our focus is on Sulphur
And on many brilliant facts!

It's now well known that sulphur
Creates profits and great wealth,
It contributes to economies,
To our joys and to our health –
But how did this all happen,
What is it we must learn?
Every generation must study in its turn....

Shhhhh... S U L P H U R...

Its atoms are of subtle depth –
Its molecules like stitches
Which attach themselves to other things
And create a world of riches,
Not just riches we can see
But those of thought and wonder
From the way we know volcanoes work
To lightning and thunder –

Stand back!! and light the fuse
Now burning in your mind
Which urges you to find out more
And value what you find –
Through sense and observation
We examine what we see
And mankind has done just that

Throughout all history!

The Egyptians used their sulphur
To bleach fabrics, paper, too,
And when we write our stories
We write on what they knew –

The Greeks made disinfectants
With sulphur and they staged
Their tragedies like burning flames –
Still searing through our age

The Chinese used it cannily,
For good things and for bad,
From fireworks - nice for parties –
To explosives - very sad.

In medieval times the doctors
Recommended it for worms,
And people thought they'd try it –
But regretted it - it burns!

Now in our most recent times
Sulphur touches all our days –
From rubber tyres to batteries –
It reacts in useful ways,
Fertilisers, pesticides -
In oils and fabrics too,
Sulphur bonds with many things
And burns a brightly blue.

Its melting point is fairly low,
One one five degrees,
And when it's form is acid
It sustains whole industries!
We know it is essential
To make plants and foods to grow
And it purifies petroleum
To make the traffic flow!

Even in our bodies –
It feeds our DNA,
And when it's missing from our hair
Its thickness falls away –
It's found in fish and beans and nuts,
In vegetables - such worth!
Sulphur is an element which sustains our life on earth!

Now hushhhhhhh!
Let's return to Dr Andrew,
And his science and his knowledge - - -
Don't you feel inspired
To rush off straight to college
To learn about the chemistry
Of the sulphur we adore –
Yes, let's all rush back to school my friends,
And study it some more!!

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