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Alternative and Potential Uses for the Sulfur Byproducts Produced from Oil and Gas Fields

Saba Hanif Khan, Sara Amani, Mahmood Amani

Texas A & M University at Qatar, Doha, Qatar
Email: mahmood.amani@qatar.tamu.edu

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Abstract

Along with oil and gas operations, huge amounts of sulfur byproducts are produced. For example, in the State of Qatar which has the third largest proven reserves of natural gas, an incredible amount of sulfur is produced as byproduct from its natural gas processing facilities. The amount of produced sulfur surpasses by far the amount that can be utilized currently in the country. Hydrogen sulfide (H_2S) existing in natural gas extracted from Qatar's North Field is converted to elemental sulfur using the conventional Claus process. Managing byproduct sulfur from natural gas processing is a key aspect of economic development and environmental protection in many countries with oil and gas facilities. Therefore, new markets must be found to utilize sulfur to avoid disposal crises. Sulfur byproduct from natural gas can be utilized for various applications. This paper discusses alternative potential uses for sulfur in addition to the current practices of sulfur utilization. Some of these alternative applications of sulfur byproducts include the potential usage for medicinal uses, road construction, batteries, hydrogen production, structural additives, solar energy, waste treatment, arsenite removal, and production of maize.

Keywords

Sulfur, Sulfur Utilization, Oil and Gas Operations, Petroleum, Natural Gas

1. Introduction

Oil and gas companies recover thousands of tons of sulfur per day. In 2000, the world's total elemental sulfur production was 57.4 million tons. In January 2019, 103 KTPD (thousand tons per day) of sulfur was recovered globally, with Asia at the largest. These numbers are drastically rising as more oil and gas is extracted from the ground. For instance, Saudi Aramco, the biggest exporter of sulfur in the Middle East, exports roughly 3.5 million tons of sulfur per year. Therefore, countries like Kazakhstan are struggling to contain the decades old, "mountains of sulfur", which continue to pile up with increased petroleum production. This worries the Kazakhstan Ministry of Environment as this result in fines and can be hazardous. That is because, sulfur dust can irritate the eyes and throat, and cause blurred vision [1].

Sulfur can go through several processes converting into compounds like Sulfur Dioxide or other sulfuric substances which can lead to substantial health issues. It is flammable in powder form and the health issues include damage to immune systems, disturbance of blood circulation, neurological effects and behavioral changes, heart damage, reproductive failure, suffocation and lung embolism [2]. These issues that Kazakhstan face are universal with other countries experiencing the same problems. Therefore, with the less known uses and an already saturated market, refineries have a hard time storing the vast amount of excess sulfur.

The current main uses of sulfur depend on the sulfuric compound itself. Sulfur, as an element, is used in gunpowder, matches, fireworks, vulcanization of rubber, fungicide, insecticide, fumigant, fertilizers and in the treatment of certain skin diseases. Sulfur can be converted into sulfuric acid which is also used in fertilizers, but additionally in dyes and detergents as well. Sulfur dioxide is used in bleaching agent and refrigerants [3].

Sulfur may have many uses and can be versatile. For instance, sulfur is inert, has a moderately high boiling point of 444.6˚C, has protective properties from electromagnetic and radioactive radiation, is stable in a few forms and has anti-bacterial, anti- fungal and ketoconazole activity [4]. It is imperative that we further experiment with sulfur's properties to discover more of its benefits and explore more of its potential applications.

2. Medical Uses

1) Skin Treatments

For centuries sulfur has been used to treat a myriad of skin conditions such as acne, eczema and psoriasis. It has natural anti-bacterial, anti-fungal and anti-inflammatory properties that helps loosen up the skin layers and dry out the excess sebum that is clogged in pores. It also helps reduce extra sebum production and kills the bacteria that are sitting in the skin. People have different skin types and conditions based on their genetics and hormones, however sweat also contributes to the build-up of acne. This is why it is more prevalent among people who live in more humid climates. Given the abundance of available sulfur, pharmaceutical industries can continue to conduct research and further expand its uses of in skin products to create more affordable treatments. The two forms of sulfur which are used in those products, precipitated and colloidal, are Food and Drug Administration approved, and can be easily sold over the counter [5].

2) Balneotherapy

Balneotherapy is another way sulfur can be utilized. This practice is usually where a person is submerged in water or mud filled with minerals. In the case of mud, the minerals mostly consist of sulfur. It has been an excellent treatment for anti-aging and skin diseases such as acne, rosacea and eczema. This hydrotherapy is also linked with a therapy for low-grade inflammation and stress-related pathologies. It stimulates positive neuroendocrine and immunological responses in the body which not only boosts the immune system but also has anti-inflammatory, analgesic, antioxidant, chondroprotective and anabolic effects and properties [6].

This thermal treatment has been used for centuries in several countries such as France, Italy, Spain, Portugal, Slovakia, Germany, Austria, Switzerland, Egypt, Turkey, Poland, Czech Republic, Hungary, Romania, Russia, Japan. It has been clinically proven that Balneotherapy helped with many conditions related to chronic inflammation such as cardiovascular, respiratory, gastrointestinal, endocrine, neurological conditions, skin and rheumatic disorders. With further trials and studies, it has shown to help with osteoarthritis, rheumatoid arthritis, fibromyalgia [6]. The main mechanism used here is sulfur and heat, with no side effects, and helping improve the overall health, immune system, stress, stiffness, pain and fundamentally, quality of life.

Sulfur water is most commonly used for the Balneotherapy treatment. This can be found naturally in water springs or it can be produced artificially. Sulfur water is simply water exposed to hydrogen sulfide, which is easily found when it escapes through oil and gas reservoirs or through direct production: the process of treating hydrogen with elemental sulfur at 450˚C [6].

As of 2020, the country that imports the most beauty/skincare items is China, with annual imports valued at $ 13.2 billion (21.3% of total beauty/skincare imports). The next country is United States, spending $ 5.1 billion (8.2%) annually, and then Hong Kong with a $ 5 billion (8.1%) yearly expenditure on beauty/skincare imports [7]. With these statistics in mind, it will be quite beneficial to introduce Balneotherapy and other sulfur treatments to expand this industry, as it will profit the business, the patients and will allow additional uses of the sulfur byproduct.

Furthermore, due to sulfur's properties such as radical and heavy metal scavenging, antimicrobial, antioxidant, and antitumor activities, it has been an excellent non-metal for these types of issues. However, due to its insolubility with many solvents, the uses become limited. Therefore, sulfur containing salts were further studied which showed a broad-spectrum of effective antimicrobial activity with biocompatibility and little human toxicity. A new source of sulfur, Sulfur Nanoparticles (SNPs), was studied further and it exhibited stronger antimicrobial activity than elemental sulfur and sulfur-containing salt (sodium metabisulfite) against bacteria (*S. aureus* and *E. coli* O157: H7) and fungi (*A. flavus* and *C. albicans*). Field Emission Scanning Electron Microscope (FE-SEM) results showed that SNPs damaged cell membranes of microorganisms causing cell death. SNPs with high antimicrobial activity against a wide range of microorganisms are likely to be used for active food packaging and biomedical applications [8].

3. Adding Sulfur to Asphalt Used in Road Construction

Many researchers have pursued the idea of adding sulfur to the asphalt being used in the construction of roads and highways. A major advantage of this method is that sulfur can replace as much as 30% of the asphalt. It also results in improved pavement characteristics. The use of sulfur in mixing with the asphalts used in road construction is a very promising utilization of sulfur which results in significant savings of the asphalt used, as well as improved road conditions [1].

4. Batteries

Lithium batteries have been an efficient and good source of energy for electrically charged vehicles. However, the energy needed for a 40-mile electric range of a hybrid electric vehicle requires about 3 to 5 times more than what a lithium-ion can provide. Therefore, after extensive research, a lithium-sulfur (Li-S) battery was found. It is believed to be a perfect candidate due to its specific properties. For instance, Sulfur has high capacity of 1675 $mA{\cdot}g^{-1}$ based on the reaction: $16Li + S_8 \rightarrow 8Li_2S$ and the energy density of $2500Wh{\cdot}kg^{-1}$. Although, to make sure that the porosity is permanent, has large surface area, high coulombic efficiency and allows highly reversible Li-S battery, the sulfur electrode is fixed in a porous organic polymer network, known as POP [9] [10].

Using POP sulfur composite helps overpower the natural dissolution of polysulfides and its coulombic efficiency, where the charge capacity is high. As shown in **Figure 1**, the charge-discharge voltage profiles of Li-S battery is shown with the POP composite. The discharge capacity is 927 $mAh{\cdot}g^{-1}$ with a density of 200 $mA{\cdot}g^{-1}$ and the charge capacity is 898 $mAh{\cdot}g^{-1}$, which exhibits 97% coulombic efficiency. In addition, due to its large Brunauer-Emmet-Teller (BET) surface

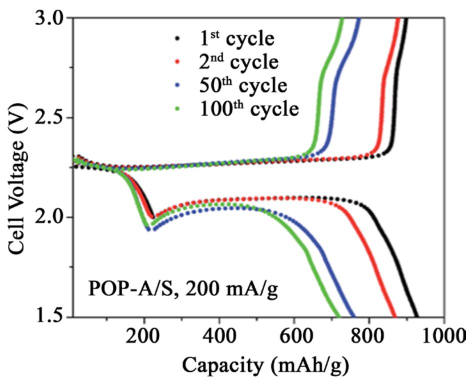

Figure 1. Li-S cells with POP-sulfur composite cathodes. In a capacity retention (Weng *et al.*, 2014b: p. 27520).

area (unlike the inorganic microporous materials such as silicas and metal organic frameworks), its work as a substrate to host the active sulfur matter for Li-S gives excellent results with high capacity and coulombic charge. These properties are particularly suited for electric vehicles as they require a high energy density [9] [10].

5. Hydrogen Production

Various environmental issues and non-renewable energy costs in the energy business are rising. Therefore, renewable energy has become increasingly more popular, and thus, extensive research has been carried out for several years. Production of hydrogen is one of the ways that does not contribute as much to Global Warming. Hydrogen is produced from electrocatalytic reduction of protons in pentafluoro thiophenol, utilizing an iron sulfur cluster. Iron clusters are used as they are heavily involved in an array of biological systems and electron transfer in catalytic, structural, and sensory roles [10].

The process of the iron sulfur cluster was conducted [11] along with cyclic voltammetry, electrolysis and gas chromatography experiments. These procedures resulted in the confirmation that the synthetic iron sulfur complex is a very powerful catalyst for reducing a proton into hydrogen as the experiment conducted without this catalyst produced no H_2. Furthermore, with the catalyst, the current efficiency was at 63% and the chemical yield present at the carbon electrode was approximately 46% [11].

6. Sulfur as Structural Additive

Using a waste product such as sulfur as an additive to construction is a way to save economic resources and address several environmental issues. The most effective plans in construction involve minimum energy consumption, sustainable development and a formulation that is optimal. Utilization of sulfur in this way may be an effective method to combat the environmental threats associated with sulfur storage. Additionally, the properties of sulfur such as its inertness and shielding properties from electromagnetic and radioactive radiation make this use very feasible [4].

Another form of structural additive using sulfur is the Polymer-Modified Sulfur. It is currently used globally when it comes to producing all kinds of materials in the building and construction industry. The process of producing this requires high temperatures and unconventional equipment is needed to keep the sulfur based polymer molten, which can be heavy on budgets. The process location would need to be near the production of the sulfur as it is difficult to transport [4].

Sulfur/Polymer Cement (SPC) is particularly useful for environmental restoration and waste-management issues, including treatment of a wide range of hazardous, radioactive, and mixed wastes. The development of SPC had many capabilities such as being able to physically encapsulate the waste (SPC microencapsulation) and has been proven to treat radioactive and mixed-waste-contaminated ash, soil, sludge and evaporator concentrates [4].

7. Storing Solar Energy

In 2017, researchers from the Karlsruhe Institute of Technology (KIT) and their European partners conducted an innovative plan to use sulfur in solar power storage. This is done through a contained sulfur-sulfuric acid cycle which produces a large-scale chemical storage of solar power. This is a renewable form of producing energy which is environmentally friendly and economically smart for the long term [12].

This method is performed through a solar absorber integrated with a thermochemical solar power storage system based on elemental sulfur and sulfuric acid. This modern technique helps reduce costs significantly. The technology has gone under testing with real-time conditions at the Jülich Solar Power Tower Facility (STJ) in Germany. The focused sunlight of the solar power plant supplies the process heat with the energy and temperature needed to close the sulfur cycle, converting the sulfuric acid back into sulfur dioxide, in the presence of the appropriate catalysts. Although sulfur dioxide is environmentally unfriendly, only small amounts are produced, making this process relatively more feasible than other non-renewable energy operations. As mentioned, this idea requires solar power tower facilities which are quite affordable and economically friendly because of the specific heat storage medium used. Furthermore, utilization of the stored energy in a burner makes the certain power plants generate and work on low energy. In the long term, system costs can be expected to be significantly lower than photovoltaic systems [12].

8. Chromium Waste Treatment

In countries with a large production of natural gas, such as Qatar, hydrogen sulfide gas is converted into elemental sulfur from the conventional Claus process. To prevent economic and environmental damage, it is crucial to find a way to use or dispose of the sulfur appropriately. One way of using sulfur is to treat hazardous wastes, where sulfur in cement form is coated as a primary binder and layer in Solidification/Stabilization (S/S) treatment of hazardous wastes [13]. These compounds are heavily involved in the agricultural industry (treating soils and groundwater) to combat toxicity [14] and in the process of immobilizing toxic metals in waste materials [14].

Elemental sulfur has shown to be effective in enclosing waste materials and significantly reducing their likelihood to leach contaminants. In addition, polysulfides have also been researched to be effective and efficient reagents for treating metal contamination [15] and for degradation of organic pollutants [16]. Furthermore, polysulfides can also act as agents to reductively dehalogenate halogenated organic compounds [17].

Plasticized sulfur is produced by heating elemental sulfur until it becomes a viscous fluid. At that point hydrocarbon plasticizers are added to prolong a semi-solid consistency of the sulfur as the temperature reduces gradually. Plasticized sulfur has become an alternative binding and stabilizing agent for the solidification and stabilization of hazardous, low-level radioactive and mixed wastes [18]. Plasticized sulfur has been used as a binder for solidification/stabilization of wastes contaminated with heavy metals and mercury [13].

9. Arsenite Removal

Arsenic present in Acid Mine Drainage (AMD), metallurgy industry effluents, soils, surface and ground waters is a well-recognized environmental concern, due to its high toxicity to humans and other living organisms. The World Health Organisation (WHO) provisional guideline value of arsenic is 10 μg/L [19]. Arsenite (AsIII) and Arsenate (AsV) are the most abundant arsenic species in aqueous systems, while arsenite exhibits much higher mobility and toxicity than arsenate [19]. Therefore, the removal of arsenic, especially arsenite, is critical to the treatment of the arsenic-contaminated waters.

Sulfidogenic process using Sulfate-Reducing Bacteria (SRB) has been used to remove arsenite from the arsenic-contaminated waters through the precipitation of arsenite with sulfide. However, excessive sulfide production and significant pH increase induced by sulfate reduction result in the formation of the mobile thioarsenite by-products and the inefficiency and instability of arsenite removal, especially when the arsenite level fluctuates [19].

Another study [19] uses a novel sulfidogenic process driven by sulfur reducing bacteria (S0RB) for the arsenite removal under acidic conditions. In the long-term experiment, efficient sulfide production achieved without changing the acidic condition in a sulfur reduction bio-reactor. With the acidic sulfide-containing effluents from the bio-reactor, over 99% of arsenite in the arsenic-contaminated water was precipitated without the formation of soluble thioarsenite by-products, even in the presence of excessive sulfide. Maintaining the acidic condition of the sulfide-containing effluent was essential to ensure the efficient arsenite precipitation and minimize the formation of thioarsenite by-products when the arsenite to sulfide molar ratios ranged from 0.1 to 0.46. An acid-tolerant S0RB, Desulfurella, was found to be responsible for the efficient dissimilatory sulfur reduction under acidic conditions without changing the solution pH significantly. The microbial sulfur reduction may proceed through the direct electron transfer between the S0RB and sulfur particles, and also through the indirect electron transport mediated by electron carriers. The results of this study show that the sulfidogenic process, driven by S0RB working under acidic conditions can be a promising alternative to SRB-based processes for arsenite removal from the arsenic-contaminated waters, such as Acid Mine Drainage (AMD), metallurgy industry effluents, soils, surface and ground waters, especially under the conditions with fluctuating arsenite levels and sulfide production.

10. Agriculture

Research on using sulfur in fertilisers is a topic that has become popular and is continuing to be investigated. For instance, early plant growth promotion of maize is done through different sulfur oxidising bacteria which can use different paths of thiosulfate oxidation.

If plants do not receive the sulfur they require, their growth is poor leading to great crop yield loss. Plants almost solely rely on the soil to provide the nutrient it needs to produce maximum amount of crops [20]. This is the reason why sulfur fertilisers are added to plants. It is important to note however that sulfur needs to be oxidised by bacteria and converted into sulfate for it to be absorbed by the plant [21].

In a study [21], the change in solubility of tri-calcium phosphate was tested and assessed, which was produced from the oxidation of thiosulfate and early plant growth promotion of maize when it was introduced to the thiosulfate oxidising bacteria which had the tetrathionate intermediate (S4I) and/or paracoccus sulfur oxidation (PSO) path for the thiosulfate oxidation. These thiosulfate-oxidising bacteria are known to have a minimum of 2 paths which allow for the production of sulfate from sulfur through oxidation. The results from the experiment showed that the bacteria D. thiooxydans and M. phyllosphaerae effectively promoted the early growth of maize through the S4I pathway as the solubilization in the medium used increased in the given incubation time. Furthermore, the sulfur oxidised by the bacteria into sulfates were more efficient than elemental sulfur. Therefore, the use of sulfur converted into sulfates are valuable in the agriculture industry and should be further researched and implement use of it in crops.

11. Conclusions

The more oil and gas are extracted, the more sulfur depositions in landfills or outskirts of cities are becoming a major health and environmental risk. However, through further research and development, the abundance of sulfur can be used for a myriad of issues needing to be solved or as a new additive which increases efficiency with less product. This should be not only environmentally and health friendly, but is also economically friendly.

Sulfur can be used in different forms. Sulfur as an element, is used in gunpowder, matches, fireworks, vulcanization of rubber, fungicide, insecticide, fumigant, fertilizers and in the treatment of certain skin diseases. Due to its anti-bacterial, anti-fungal and anti-inflammatory properties, skin issues like acne and rosacea can be resolved as it sinks into the multiple layers of the skin and unclogs pores. Furthermore, in its natural form, it stimulates neuroendocrine and immunological system in the bodies which boosts the immune system and produces a calming effect. This is known as balneotherapy which has been performed for decades.

Moreover, it can be also used in batteries as it is quite a good source of energy in a polymer network due to its high capacity and can be very good for storing solar energy through its sulfur-sulfuric acid reaction which is a concept still being further explored. This would be a good source renewable Energy. Another source of renewable energy is using Hydrogen, which can also be produced using a sulfur complex. In addition to that, its inertness, shielding properties and abundance allows it to be a good structural additive as well as a cheaper way to dispose hazardous substances like chromium.

Sulfidogenic process using Sulfate-Reducing Bacteria (SRB) has been researched to successfully remove arsenite and its oxidation with bacteria also makes an effective fertilizer additive which promotes the growth of crops such as maize in the agricultural industry. The use of sulfur in mixing with the asphalts used in road construction is a very promising utilization of sulfur which results in significant savings of the asphalt used, as well as improved road conditions.

Overall, it is recommended to use this profusion of sulfur for current issues and also further research this element as it has great properties on its own or is more enhanced when converted into another form.

In petroleum producing countries, tremendous amounts of sulfur is being produced as byproducts of their oil and gas operations. In many countries, the amount of sulfur being produced is by far greater than the amount of sulfur these countries can use or sell. The storage of this unwanted sulfur is becoming a great economical and environmental burden for these countries. This paper presents some alternative and potential uses for the sulfur byproducts produced from oil and gas fields. Any potential new utilization of sulfur can be a positive improvement in resolving part of this problem.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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