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Valorization of Refinery Sulfur in Asphalt and Its Environmental and Health Implications

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Abstract: With the spread of hydrodesulfurisation in petroleum refining and increasingly strict regulations on the sulphur content of transport fuel, especially marine fuel, a global surplus of elemental sulphur has gradually appeared. There is now a surplus that will be used to improve high-volume infrastructure materials, such as asphalt binders. Sulfur-modified asphalt has the following advantages: it is less dependent on petroleum-based binders; sulfur polymerisation and inverse vulcanisation can be used to improve mechanical properties; and it is economically viable because sulfur is significantly cheaper than bitumen. Partial replacement of bitumen with sulfur can reduce binder costs and utilise the excess sulfur from the refinery productively at the same time. Meanwhile, the asphalt materials will also release various hazardous substances and other harmful factors over time. Emissions occur in binder production, mixture hauling, pavement application, and over the life of the pavement, and potential exposure routes for construction workers and nearby communities are created. Sulfur in the asphalt system can change the emission characteristics by promoting the production of sulfur-containing volatile compounds, such as sulfides and thiols, which are often highly odorous and may also be more toxic. Research has been conducted on the emissions of traditional asphalt; however, the impact of adding sulphur on the chemical structure of emissions and pathways for human health exposure remain unexplored. The three main knowledge gaps are as follows: (1) The effect of sulfur chemistry on the emission characteristics of asphalt and the generation of sulfur-containing volatile organic compounds have not been systematically studied; (2) Data on prolonged human exposure and the resulting health changes, especially neurological and respiratory problems, are scarce; and (3) How emissions from sulfur-containing asphalt are altered in the presence of environmental stress, such as heat ageing, UV degradation and oxidation, is poorly understood. At the same time, the following three new opportunities have appeared: (1) Stabilising sulphur through inverse vulcanisation and sulphur-based polymers; (2) Adding bio-derived additives and functional carbons to reduce volatile emissions; (3) Combining materials science, exposure assessment and toxicological modelling to better evaluate the health risks of sulphur-containing asphalt systems. The above deficiencies need to be rectified in order to promote the all-weather construction of roads with sulphur valorisation and safeguard the environment and public health.

Key words: Sulfur valorization; Sulfur-modified bitumen; Refinery byproducts Asphalt emissions; Occupational exposure; Health Assessment

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Introduction

Sulphur-containing compounds are among the most frequent by-products obtained from the recent refining of oil and gas. Sulfur has been produced by mining in the past, but due to increasingly strict environmental regulations on fuel emissions around the world in recent years, the structure of global sulphur supplies has changed considerably. In response to the above regulations, most refineries have introduced desulfurization technology, and hydrodesulfurization (HDS) is employed to reduce sulfur content in crude oil fractions before burning. At this time, the sulphur-containing organic compounds in petroleum are converted into hydrogen sulphide (H_2S) and then recovered and converted to elemental sulphur via a sulphur recovery unit, such as the Claus process. As a result, most of the sulfur produced around the world today comes from petroleum refining and natural gas processing rather than traditional mining [1-8]. The world's sulfur production in 2025 was estimated at approximately 84 million tonnes [2]. CRU projects nearly 3 million tonnes per year of additional global sulfur supply in 2026, with supply growth increasing from 2027 as major Middle Eastern gas projects come online; by 2030, the Middle East is projected to account for approximately 8.9 million tonnes per year of incremental global supply growth [1]. In the U.S., most of the elemental sulphur was produced at petroleum refineries, natural-gas-processing plants and coking plants in the 25 states [2]. In 2023, U.S. refiners recovered more than 10 million metric tons of sulfur, representing a 4% increase from 2022 [3].

As a direct result of the above desulfurization policies, the national monitoring data show a significant decrease in atmospheric sulfur dioxide (SO_2) concentrations, as shown in Figure 1. A decrease shows that the pollution-control measures have reduced sulphur emissions from burning. Sulfur removed

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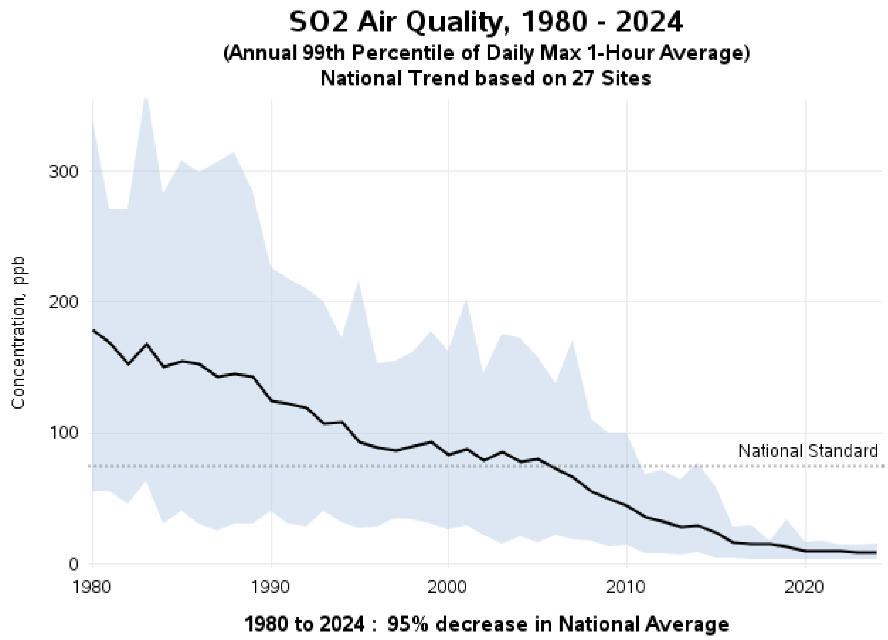

Fig. 1. National trend of sulfur dioxide (SO_2) based on measurements at 27 monitoring sites [9].

from the fuel is not gone from the system; instead, it is gradually added to the heavier-oil-fraction refinery products.

As the proportion of heavier, more sulfur-rich crude oil has increased, so too has the output of refinery-derived sulphur. Global production of sulphur has been rising steadily in recent years due to the construction of new hydrodesulphurisation plants and continuous growth in refining and natural gas processing. As the result of fuel-purification processes, sulphur recovery generally cannot be driven by fluctuations in the demand for sulphur. Therefore, large quantities of elemental sulfur are stored around refineries and other industrial areas around the world. Stockpiles can be built up over a long period of abundant sulphur supply and thus pose logistical and environmental problems [3, 10]. At the same time, the dispersion of sulphur in the refining system has shifted from the former route of atmospheric emissions to that of material-based reservoirs.

Hydrodesulfurization of sour crude oil in areas such as Western Canada has generated millions of tons of elemental sulfur each year, and large stockpiles have been built up at sites for oil sands upgrading facilities in Alberta. As the world gradually increases restrictions on sulphur in marine fuels, refinery sulphur recovery rates are also rising. Due to the excess supply, sulfur has been actively used as an additive for construction materials, especially in asphalt systems; conventional asphalt, sulfur-modified asphalt and sulfur-extended asphalt have all been prepared containing a relatively high amount of sulfur compared with traditional asphalt [10-16].

Although some necessary industries still need to use sulphur for fertiliser production and other chemical synthesis, the growth speed of these areas is not high enough to compensate for the extra demand from modern refinery supply. The resulting imbalance between the production and consumption of sulphur has led to increasing attention on exploring new large-scale applications for elemental sulphur that can be realised sustainably and economically. Therefore, the development of alternative routes for sulphur utilisation is required under the industrial waste management and resource recovery plan for the petroleum industry [10-11, 17].

One good prospect for large-scale sulphur utilisation is the asphalt pavement industry [11]. Research has shown that the amount of sulfur in transport fuel used to make bitumen has been rising steadily. As a result, the sulphur content of bitumen has risen from the typical range of less than 3% by weight to more than 20% in some places after the new fuel desulphurisation regulations, such as the International Maritime Organisation's (IMO) reduction of allowable sulphur levels in marine fuels [12]. The distribution shows that combustion-related sulphur emissions have been replaced by material-phase sulphur reservoirs. Asphaltenes, resins, aromatics and saturates are components of complex hydrocarbon materials that make up bitumen and serve as binders for asphalt mixtures. Bitumen has a certain chemical structure and is thermoplastic; therefore, elemental sulphur can be added to it to act as a partial replacement for petroleum-based binders. Historically, sulfur-extended asphalt (SEA) has been a relatively high-sulfur formulation of sulfur-modified asphalt that aims to reduce binder costs, enhance mixture stiffness and improve resistance to permanent deformation. Early studies have shown that the addition of sulphur can improve some mechanical properties of asphalt mixtures, such as rutting resistance and structural stability under heavy traffic [18]. Related studies of polymer-modified asphalt have also shown enhancements in the rheology of the binder and the performance of the mixture [19–21].

Although there are some good-performance attributes of sulfur-containing bitumen, it also has certain technical and environmental problems. Although the total amount of sulphur in the atmosphere has been decreasing, local emissions of sulphur from asphalt have been rising. The transition from combustion-driven emissions to material-phase sulfur reservoirs has introduced new exposure pathways; therefore, local emission sources and ultrafine particle generation with potentially higher toxicity risks to human health and the environment have occurred [22]. Sulfur will change the flow behaviour and ageing of bitumen, increase damage due to oxidation and UV light, and cause moisture damage over time. In addition, high-temperature conditions are used during the production and paving of asphalt, and at this time, volatile sulfur compounds such as hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) may be released; both are harmful to human health and the environment. Exposure to sulfur-containing gas has been linked to respiratory irritation and neurological problems; thus, workers in the workplace who are regularly exposed to these gases during asphalt mixing and paving work may suffer serious health damage [23-24]. Construction workers may experience repeated occupational exposure during asphalt mixing and paving operations [25].

A significant number of studies have been carried out on the mechanical and rheological properties of sulfur-modified asphalt, but relatively few have examined the wider environmental and health effects of sulfur addition in pavement materials systematically. Relocation of sulphur from fuels to infrastructure materials is a new exposure path that has not been well studied. With the increase in the world's production of sulphur due to the development of hydrocarbon processing, so too will be the demand for green and secure production models. Combining refinery-derived sulphur with asphalt binders may be a feasible route for sulphur utilisation; however, the effect on the performance, emissions and human health risks of the material must be fully verified.

Therefore, the current study will investigate the prospects of adding refinery-produced elemental sulphur to bitumen for large-scale utilisation, as well as examine the relevant material performance and possible health risks. By combining materials engineering with environmental and occupational health considerations, this paper aims to offer some support for building a safer and more environmentally friendly system for managing sulfur-byproduct emissions from modern petroleum refineries.

In recent years, many studies have been carried out on sulphur-modified asphalt and its environmental emissions or health risks. Relevant literature published in the time frame of 2000-2026 has been systematically collected from academic databases such as Scopus, Web of Science and Google Scholar. Most of the references in the paper are peer-reviewed journal articles to ensure their accuracy and scientific basis. If there were no relevant scholarly works on this subject, other reliable reports and papers from conferences and other institutions have also been referenced. Research on "sulfur-modified asphalt", "asphalt emissions", "VOC", "inverse vulcanisation" and "health risk assessment" using these keywords. Filter the collected literature to retain only the parts related to material properties, emissions, exposure paths and health risks. The selected studies were then divided into the following categories: sulphur-bitumen interaction, ageing and durability, additive effects, emission characterization, exposure assessment and mitigation strategies. Considering that a large number of studies have already been conducted on the performance characterization of sulphur-modified asphalt, we have intentionally omitted broad performance comparisons and aim to produce new knowledge in the area of emission chemistry and risk that has received relatively little attention.

Sulfur in Asphalt Technology

Elemental sulphur in asphalt materials has been added for a long time to reduce the proportion of petroleum-based binders and improve some mechanical properties of the asphalt mix. As petroleum supply and price fluctuated, so too did the interest in sulfur-asphalt systems periodically, and thus research into other or supplementary pavement materials was also carried out. At the same time, developments in petroleum refining have increased the yield of elemental sulphur as a by-product, and due to its large quantity, researchers have recently begun to explore using it for construction materials. The above developments have attracted the attention of many scholars to sulfur-modified asphalt in the field of green material design, circular economy and further research on the ecological and health impact of asphalt emissions.

Elemental sulphur can partially substitute for bitumen in the asphalt mixture because it is thermoplastic and has good affinity for hydrocarbon components in bitumen. When heated during mixing, sulphur melts and can be mixed with the asphalt binder to increase the stiffness and structural strength of the pavement material [26]. Traditionally, the amount of sulfur in the formulations of old asphalt was relatively small, generally around a few per cent of the binder; however, with modern refinery processes and blending techniques, even materials labelled as conventional asphalt now contain a relatively high amount of sulfur. Therefore, the concentration of sulphur in modern binders may be as high as 10-12 wt%, due to changes in the chemistry of petroleum-derived bitumen and an increase in refinery-derived sulphur in paving materials. Conventional asphalt in this paper refers to petroleum-based binders that may contain naturally occurring sulphur from crude oil and refining processes without intentional addition of sulphur. Sulfur-modified asphalt refers to any system in which elemental sulphur is intentionally added in a specific amount to improve performance, regulate processing characteristics, or realize sulphur-utilization strategies that can reduce the use of petroleum binder and enhance material cost-efficiency through sulphur valorization. Sulfur-extended asphalt (SEA) is a high-sulfur subset in which a relatively large proportion of the petroleum binder is replaced by sulfur, and its main purpose is to extend the binder due to performance and economic reasons. Generally, these systems have a sulfur content of about 10% to 40% by weight of the binder, and they are used to extend the binding ability of the binder and modify the rheology of asphalt. The first research experiments have shown that, by adding sulphur, some mechanical properties of asphalt mixtures can be improved, such as rutting resistance and structural stability under heavy-traffic conditions [27-28]. Moisture susceptibility of sulfurized bitumen has also been linked to sulfur phase transitions and molecular interactions with water [28]. Sulfur phase transitions in bitumen have been examined separately [26], while molecular-dynamics studies have evaluated water-related adhesion at the asphalt binder–aggregate interface [29]. Sulfur will change the microstructure and phase-behavior of bitumen at the same time. Bitumen is a multi-component colloidal system that includes asphaltenes dispersed in a maltene phase, which contains saturates, aromatics and resins. Sulfur can change the interactions among these components to alter the viscosity, elasticity and heat-deflection temperature of the binder. Sulfur may also be chemically reacted with the unsaturated hydrocarbon components of bitumen in some formulations to form polysulfide links that enhance the stiffness of the binder network [30]. The above interactions can improve the high-temperature performance of asphalt mixtures, and thus sulfur-modified binders are particularly suitable for pavements in high-traffic, high-temperature environments.

Despite the above advantages, several technical problems have prevented the wide application of sulphur-modified asphalt. The first is that there is a risk of phase separation or crystallization of sulfur during storage and cooling, and this may lead to a brittle or less durable pavement. A high-sulfur content may also increase the risk of cracking in the asphalt mixture at low temperatures due to the stiff nature of sulfur crystals that form in the binder matrix [31]. Sulfur will also change the path of oxidation and alter the chemical composition of the binder to a certain extent over time.

Another problem is how to deal with and process sulphur-containing asphalt mixtures. Elemental sulphur releases gaseous byproducts such as hydrogen sulfide (H_2S) and sulphur dioxide (SO_2) during high-temperature operations in the production and paving of asphalt, which are harmful to the health and safety of workers. Therefore, many new sulfur-asphalt technologies now add stabilizers or chemical modifiers to improve sulfur stability and compatibility with bitumen. The above developments have increased attention on sulphur-modified asphalt as a potential high-volume application for surplus refinery sulphur [31-32].

With the increase in global production of elemental sulphur as a byproduct of petroleum refining, the asphalt industry is now an economically feasible target for utilisation. Optimisation of the sulphur-bitumen mixture should meet all the requirements for mechanical properties, durability, environmental protection and occupational health. Therefore, further research will need to be conducted to explore the physicochemical interaction of sulphur with bitumen in greater detail, and a formula that can maximise the advantages of adding sulphur while reducing technical and environmental risks must be developed.

Aging and Durability Effects of Sulfur-Modified Bitumen

The extension of the service life for asphalt pavement is directly related to the ageing state and durability of the bitumen binder. Bitumen ageing is caused by thermo-oxidative decomposition, loss of light-end oils and physical changes; thus, the binder becomes harder, less flexible and poorly adherent. Environmental factors, such as ultraviolet (UV) radiation, oxygen exposure and moisture infiltration, accelerate the above mechanisms to cause cracking, loss of aggregate-binder adhesion and pavement deterioration. Elemental sulphur can change the deterioration mode of aged bitumen by modifying the chemical composition, micro-structure and surface features of the binder at the same time [33-38].

Sulfur can change the rheology and surface-chemical properties of aged bitumen at the same time, as shown above. At high temperatures during the mixing and processing of asphalt, sulphur can react with unsaturated hydrocarbons in the binder to form polysulfide cross-links; therefore, both stiffness and viscoelasticity will be altered. Although such interactions can increase the rutting resistance of the high-service-temperature group, they may also promote the stiffening of the binder due to oxidative ageing and thus raise the risk of fatigue cracking and thermal cracking over time [39]. The scope of the above effects is related to the sulphur content, other chemical components of the base bitumen, and the environment where the pavement will be applied.

Recently, many studies have uncovered all sorts of functions of sulphur in surface aging. Hung et al. (2021) have studied the effect of elemental sulphur on the ageing process of rubber-modified bitumen exposed to UV light. Based on the above data, a small amount of sulphur can enhance the plasticity of the binder; however, after thermal conditioning and UV exposure, oxidised sulphur and carbon compounds accumulate at the surface of the bitumen. Oxidation increased the amount of free surface-active groups on the binder and reduced surface adhesion; thus, the rate of degradation at the binder-substrate interface was likely higher than that inferred from bulk rheology. Therefore, the binder's capacity to keep repairing cracks and adhering may decline more rapidly than shown by the traditional aging indicators [40].

Another problem of sulphur-modified bitumen with ageing is the formation of sulphur blooms; these are crystalline sulphur domains that migrate to the binder surface. Mousavi and his colleagues (2021) have discovered that sulphur in bituminous composites gradually migrates and crystallises at the surface to form millimetre-sized patches of microscale sulphur crystals. These blooms were found to be regenerative and became more frequent with the increase of oxidative ageing. The resulting sulfur crystals are relatively large and more hydrophobic; therefore, they may form a self-cleaning surface that repels water and other dirt. The authors have proposed that the idea of this regenerative surface phenomenon can extend the environmental service life of bituminous composites by reducing water absorption and surface pollution; however, its long-term structural changes have not been studied [41].

Although the hydrophobic and rough surface of sulphur bloom can increase water shedding, the formation of millimetre-scale crystalline patches may change the pavement microtexture and reduce local friction, especially in widely blooming areas. Direct measurements of the skid resistance at this time are also unavailable. Repeatedly heating and cooling may cause stress concentration at the sulphur-enriched interface, thereby increasing the risk of crack initiation at the binder-aggregate interface. Given that surface functionality and mechanical strength are likely to be in conflict, more tests need to be conducted in real traffic at different times of the year [40-41].

Elemental sulphur is hydrophobic, but the moisture-sensitivity of the sulphur-modified asphalt system is still a problem. Water molecules and sulfurised bitumen interact differently after chemical changes have occurred in the mixed and aged state. Mousavi and others (2022) have found that bitumen with a relatively high sulphur content has accumulated more strain and shows shear-thinning behaviour after a long period of water exposure. Molecular-level simulations show that at high temperatures, polysulfide chains can associate with water molecules and are therefore more easily hydrolysed. Oxidative ageing will also form sulfur-containing functional groups, such as sulfoxides, sulfonates and thiols; these are more polar than the other groups and can form hydrogen bonds with water. These chemical changes can weaken the binder-aggregate interface and increase moisture-induced damage in the asphalt mixture [28-29].

Alteration of the chemistry is a reason for the degradation of bitumen; phase changes in sulphur within the bitumen also cause damage. Sulfur may be in dissolved or crystalline forms at different temperatures and concentrations during cooling. A high-sulphur content in the binder matrix will increase stiffness and generate internal stress; therefore, the binder may become brittle and crack easily. Repeated thermal cycling during the service life of the pavement can also affect the phase transformation of sulfur, change the mechanical properties of the binder, and thus promote structural damage [39-40]. Recently, studies on photochemical and moisture-induced degradation have shown that for durable circular reuse of sulfur in asphalt, control of sulphur oxidation, interfacial weakening and aging-induced property drift under service-like environmental exposure are required [11, 39-40].

In short, there are many reasons for the changes in ageing and durability of asphalt caused by sulphur, such as all kinds of chemical reactions, microstructural changes and environmental factors. A small addition of sulfur can improve some of the performance traits and offer a way to use refinery by-products; however, high-sulfur material is more prone to oxidation, moisture absorption and structural stiffening. Therefore, these mechanisms must be better understood to improve the design of sulfur-modified asphalt and ensure that the added elemental sulfur will not harm the long-term performance of the pavement.

Effect of Sulfur on Asphalt Additives

Sulfur has many different roles in boosting the effect of many kinds of asphalt additives. The specific results of addition vary according to the type of additive and other factors during processing. Sulfur in polymer-modified asphalt systems that contain Styrene-Butadiene-Styrene (SBS) and Styrene-Butadiene-Rubber (SBR) primarily functions as a chemical crosslinking agent. This will promote the formation of a three-dimensional elastomeric network in the asphalt binder [42-46]. Cross-linking reactions are generally temperature-sensitive and occur at high-temperature mixing; thus, they increase the entanglement of polymer chains in the asphalt matrix. Thus, sulphur can enhance the compatibility of the two phases, reduce phase separation, and significantly improve storage stability [47]. Morphological analysis shows that a relatively large proportion of sulfur results in a finer dispersion of polymer domains and an interconnected structure. Thus, it has good elastic recovery and stiffness [48]. However, these advantages are very sensitive to the dose and form of sulphur. Too much sulfur can lead to over-crosslinking or gelation; polymerized sulphur may delay vulcanization and alter the viscosity during vulcanization compared with elemental sulphur [49-50].

The representative polymer-modified binder formulations have shown that the sulfur function is more effective as a low-dose cross-linking agent in SBS/SBR-modified asphalt systems rather than a bulk substitute. A representative sulfur dosage is approximately 0.15-0.20% by weight of the asphalt binder. A small amount can improve the storage stability and viscoelasticity of the polymer; otherwise, too much sulfur will lead to an uncontrolled increase in viscosity, delayed curing, or even gelation of the unsaturated polymer network [48-51]. On the other hand, other studies have explored inverse vulcanisation of sulfur to produce fully polymerised networks and thus provided an alternative route for utilising sulphur in binder systems when complete polymerisation is achieved [52-53].

Sulfur is used as a cross-linking agent in the rubber-modified asphalt system and is close to the rubber phase. Research on crumb-rubber-modified binders has shown that sulfur can increase viscoelasticity by forming additional cross-linking structures between rubber particles and in the surrounding binder matrix. Therefore, it is relatively inflexible and does not change permanently [54]. At a relatively low dose, sulphur has been shown to improve the high-temperature performance and both short-term and long-term ageing resistance by increasing the complex modulus and reducing the phase angle [55].

The combination of sulphur and the new bio-based modifiers is not as straightforward; their chemical structures are different. Sulfur can serve as a crosslinking agent to form sulfide and polysulfide bonds with the unsaturated sites of the modifier in rubberized asphalt systems that contain oil-based modifiers, and the oil phase affects rubber swelling, compatibility, storage stability and binder performance [56]. The effect of the above measures depends on the oil source, modifier composition, dosage and blending conditions. In addition, the phenolic components of biomass-derived oils can also act as activators to promote the reaction of sulfur under thermomechanical stress and thus enhance it [32]. Overall, the effectiveness of such modifiers depends on the chemical composition and molecular structure of asphalt [57].

Polymers and bio-modifiers are used to enhance rejuvenator and warm-mix additive performance and processing properties in addition to sulfur. Poly-sulphide-based rejuvenators enhance the diffusion and regeneration of aged binders and improve their rheological properties at a low concentration. However, excessive rejuvenator dosage may promote aggregation [58]. Sulfur has been found to reduce the viscosity and lower the mixing and compaction temperature of warm-mix asphalt systems containing bio-rejuvenators and polyphosphoric acid. At the same time, it increases rutting and fatigue resistance [58]. Therefore, it can be seen that sulfur enhance the performance of other additives in complex additive systems.

Therefore, the effect of sulphur on asphalt additives varies among different additives, as well as by their chemical properties, the quantity of sulphur added, and the way they are processed. Sulfur can improve the strength and stability of a material through intermolecular bonds. An excess of sulphur will cause problems such as excessive cross-linking, slow curing or instability of the mixture. To obtain the best results for sulphur-modified asphalt, an optimised formula needs to be developed, and the effect of additives in conjunction with sulphur should be studied. Table 1 summarizes the roles, representative dosages, benefits, and limitations of sulfur in common asphalt additive systems.

Emissions and Environmental Implications

Asphalt materials continuously emit various types of volatile and semi-volatile substances at all times during their

Table 1. Comparative summary of sulfur interactions with common asphalt additive systems.

Additive system	Representative sulfur role/dosage	Principal benefits	Principal considerations	Refs
Bio-oils and phenolic modifiers	Reactive co-modifier or sulfur stabilizer depending on feedstock chemistry	Improved compatibility and storage stability in selected rubber–oil systems; sulfur stabilization; reduced crystallization in selected systems	Strong dependence on bio-oil composition, catalyst choice, and curing conditions	[32, 56-57]
PPA-containing systems	Reactive co-modifier in high-sulfur binders	Can amplify stiffness and modify rheological response in sulfur-rich binders	Binder-specific response; potential over-hardening or compatibility sensitivity	[30]
SBS/SBR polymer modifiers	Low-dose crosslinker in polymer-modified binders; representative binder-level sulfur additions are about 0.15–0.20 wt % with about 4–6 wt % SBS in reported formulations	Improved storage stability, elastic recovery, stiffness, and compatibility; promotes a more continuous polymer network	Narrow dosage window; excessive sulfur may cause viscosity growth, delayed curing, or gelation in unsaturated polymer systems	[42-43, 47-51]
Crumb rubber systems	Co-network former in sulfur-crumb-rubber binders; reported systems include about 20–50 wt % sulfur with 1–6 wt % crumb rubber in sulfur-extended formulations	Greater stiffness, rutting resistance, and improved aging response	Formulation-sensitive: sulfur contents can increase stiffness and require optimization to avoid performance loss	[54-55]
Rejuvenator systems	Regenerant aid at moderate dosage (beneficial below about 8 wt % polysulfide regenerant)	Improved diffusion and regeneration of aged binders	Excessive dosage can promote aggregation and reduce effectiveness	[58]

use, from production and paving to long-term environmental exposure. Generally speaking, these emissions are volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), sulfur-containing gases and other oxidation products generated by heating and aging of the binder. Asphalt mixtures are generally produced and applied at temperatures of 140-180 °C, and thus, thermal processes may lead to the volatilization of light hydrocarbon components or generate secondary emission products through chemical reactions. Therefore, asphalt emissions have become a serious problem for the environment and the health of workers in asphalt plants and paving operations who are exposed to high levels [59-67].

Recently, some studies have shown that the emissions of asphalt do not stop after construction but continue throughout the service life of pavements due to oxidative ageing and photochemical degradation of the binder. Environmental factors such as UV radiation, changes in temperature and oxygen in the air can cause chemical changes in bitumen to occur, forming and releasing progressively more aromatic and oxidized substances over time. The above emissions may contribute to local air pollution and harm the health of nearby people in urban areas where asphalt pavements are widely used for roads, parking lots and recreational spaces [34, 68].

Recently, research on the health risks of emissions from asphalt has started to accumulate. Fini et al. (2025) examined neurological effects in biological systems exposed to asphalt emissions. Cell culture experiments, Drosophila melanogaster models and computer simulations were used in this study to show that volatile substances emitted by asphalt can alter cell metabolism and damage the nervous system. Research has also found that the toxicity of emissions changes with the ageing of asphalt, and more aromatic compounds with higher biological activity have gradually replaced aliphatic compounds. Neurologically, the study found that age increased the severity of damage in the female biological model, indicating that vulnerable groups should be considered in the health impact assessment of asphalt emissions [69].

Sulfur-containing gases are also a problem with the use of sulfur-modified bitumen; these are not hydrocarbon emissions. Elemental sulfur gives off gases such as hydrogen sulfide (H_2S) and sulphur dioxide (SO_2) when heated and processed, and both are known air pollutants that are harmful to human health. Bitumen emissions have also been evaluated for potential cancer hazards [70]. Exposure to hydrogen sulfide can cause damage to the eyes and respiratory system, nerve injury, and is very toxic in large amounts. At a relatively low concentration, long-term exposure may also cause headaches, fatigue and impaired cognition [23-24, 71]. Therefore, the emission of sulphur-containing gases during the mixing of asphalt concrete should be monitored and controlled.

Odor-active sulfur VOCs in the sulfur-containing system, such as thiols, sulfides and other oxidized sulfur compounds, should be given particular attention because they can alter emission profiles and contribute to toxicity even at relatively low concentrations, and may cause neurological or respiratory problems. Early-stage emissions of asphalt are generally composed of light aliphatic compounds, and oxidative ageing increases the proportion of aromatic and oxygenated substances with higher biological activity. Therefore, sulfur-containing volatiles released with these aged mixtures should be regarded as toxicologically relevant co-contaminants rather than merely indicators of odour [61, 69, 72].

Asphalt emissions may adversely affect worker health. Asphalt-derived VOCs and PAHs can undergo chemical reactions in the atmosphere to form secondary organic aerosols and ground-level ozone; both pose a health risk to the public and are harmful to air quality. Runoff from the asphalt surface can carry dissolved organic matter and suspended solids, causing pollution of the adjacent soil and water environment for aquatic life [60-61]. With the increase in the scale of asphalt pavement around the world, so too have related environmental problems.

Recently, in the effort to reduce emissions from asphalt materials, research has focused on modifying binder chemistry to curb volatilization and oxidative degradation. For example, some recent studies have shown that when adding functional carbon materials such as biochar, the intermolecular forces among asphalt molecules are increased, and as a result, the migration of volatile components is reduced. Fini and others (2025) have shown that by means of free-radical stabilization and restriction of volatile compound diffusion paths, adding wood-derived biochar can reduce VOC emissions by as much as 76 per cent. Thus, the prospects for new-material design strategies to improve the durability of asphalt and reduce environmental and health impacts have been explored [69].

In short, asphalt emissions represent an important environmental and occupational-health concern. Asphalt modified with sulphur can be produced from refinery waste, but the nature and magnitude of associated pollutants and health hazards require further evaluation. Therefore, all-encompassing assessments of sulfur-containing asphalt systems should also take into account their potential environmental and toxicological effects, in addition to mechanical properties and durability. To reduce the emissions of the generation and dispersion of these substances, new asphalt materials have been developed in recent years.

Emission Characterization, Exposure Evaluation, and Mitigation

Gas chromatography–mass spectrometry (GC–MS), Fourier transform infrared spectroscopy (FTIR) and thermal desorption are generally employed to identify and quantify the various volatile and semi-volatile substances, released during the heating and ageing of asphalt, for characterization. The above research has shown that asphalt fumes are complex mixtures of hydrocarbons, including alkanes, aromatics, aldehydes and ketones, and sometimes trace amounts of sulphur-containing gases. As asphalt undergoes ageing, the composition of its emissions changes; initially, they are mainly light aliphatic compounds, but after oxidative ageing, more aromatic and oxygenated compounds with higher toxicity potential have been generated [72-73].

Temperature is another major factor controlling asphalt emissions. A high-temperature mixer will increase the release of VOCs and PAHs through volatilization and chemical reactions. Therefore, one of the ways to reduce emissions from asphalt has been to lower the production temperature.

The main routes of human exposure to asphalt emissions are inhalation of vapours and aerosols produced during mixing and paving, and dermal contact may also occur to some extent. Occupational exposure studies have reported that the concentration of PAHs and other organic compounds in the breathing zone of asphalt workers is relatively high during paving and milling. Biomonitoring studies have also found systemic exposure, and paving workers show higher urinary concentrations of PAH metabolites compared to the general population [74-77].

Exposure levels will be affected by the environment, equipment and asphalt technology. Warm mix asphalt (WMA) can reduce mixing and compaction temperatures compared with hot mix asphalt (HMA). WMA technology can reduce the production and compaction temperature by about 20-40°C; therefore, the volatilization of organic compounds during paving is also relatively low. Field and laboratory studies have shown that WMA is effective in reducing both emissions and worker exposure, thus temperature control can be realised in practice [78-81]. In recent years, some scholars have also used chemistry-based material-design strategies to reduce asphalt emissions. For example, the carbon-based additive biochar has been introduced into emission-reduction research by others [82-83]. Broader biochar literature establishes its carbon-sequestration and sorption functions [84-86]. Duan et al. (2026) showed that tannic acid-activated biochar can reduce asphalt fumes and improve the ageing-resistance of bitumen at the same time. Biochar addition reduced VOC and H_2S concentrations by as much as 58% and 96%, respectively; ozone formation potential and secondary organic aerosol (SOA) potential decreased by as much as about 69% and 66%, respectively [82]. These effects were due to an abundance of polyphenol groups, and in line with previous research that identified phenolic OH groups as the main adsorption sites through strengthened molecular interactions with aromatic compounds, further studies were conducted. This mechanism provided the basis for recognizing their combined free-radical scavenging ability [82,87]. Other research has also shown that carbonaceous and porous mineral additives can reduce asphalt VOC emissions by means of physical and chemical adsorption at the expanded pore structure, large surface area, and active adsorption sites. The above inhibitors can reduce VOC-related environmental and health risks while keeping the good performance of asphalt-mix roads [83]. Table 2 summarizes several emission mitigation strategies that are also applicable to sulfur-containing asphalt.

Most field occupational measurements only provide specific analyte concentrations or total particulate matter, not whole-fume-chamber data, and should thus be considered contextual exposure data rather than direct equivalents of controlled-chamber concentrations.

Health Risk Assessment

A health-risk assessment framework combines pollution source and exposure data to determine the health risks of asphalt emissions for the public. Generally speaking, the above assessments differentiate between non-carcinogenic effects, such as respiratory irritation and neurological disorders, and carcinogenic risks caused by prolonged exposure to PAHs and other harmful substances [93-97]. Epidemiological studies of asphalt workers have found associations between occupational exposure and respiratory disease, decreased lung function, and, in some studies, an elevated risk of certain cancers; however, the magnitude and duration of exposure vary among individuals [73, 98]. Recently, toxicologists have also found that asphalt emissions affect the cells' metabolism and oxidative stress pathways in the brain. Research in biology has also found that continuous exposure to a mixture of asphalt-derived VOCs alters lipid metabolism and cellular signalling pathways in neurodegenerative diseases through experiments. Based on the above results, it can be concluded that asphalt emissions may have long-term health effects besides short-term respiratory irritation [69-72].

Field measurements of sulphur-specific emissions at the production and paving sites of sulphur-modified asphalt have also been lacking in the literature. In addition, the available human exposure data mainly reflect occupational paving condi-

Table 2. Representative emission, exposure, and mitigation data relevant to sulfur-containing asphalt systems.

Context	Representative data	Exposure/mitigation	Refs
Wood-derived biochar	VOC emissions reduced by up to 76%	Promising mitigation strategy for emission suppression	[69]
Warm mix asphalt (WMA)	Production and compaction temperatures typically reduced by about 20–40°C	Lower temperatures reduce volatilization and worker exposure	[78-81]
Tannic acid-activated biochar	VOC emissions reduced; ozone formation potential and secondary organic aerosol potential reduced.	Promising targeted additive for fume suppression and improved aging resistance	[82]
Occupational PAC variability	Approximately 12-fold task-related variation; adjusted mean paver-operator PAC exposure of 5.0 μg/m^3 under low-RAP conditions and 24 μg/m^3 under high-RAP conditions	Demonstrates strong task- and process-dependent variability in worker exposure	[88]
Open-air paving particulate exposure	Full-shift total particulate concentrations generally below 1.0 mg/m^3; some highway paving means ranged from 0.075 to 0.48 mg/m^3	Provides field context for inhalation exposure under heterogeneous paving conditions	[89]
Controlled rat inhalation study	23.6 ± 3.3 mg/m^3 for 3.5 h/day over 5 days; cumulative exposure of 413.5 ± 57.7 mg-h/m^3 altered pulmonary xenobiotic metabolism without acute lung injury; no acute lung injury at 547 mg-h/m^3	Useful dose-response context when field measurements are not directly comparable	[90]
Regulatory context	EPA standards address criteria pollutants rather than asphalt fumes specifically; OSHA has no asphalt-fume-specific PEL	Highlights the need for compound-specific monitoring of sulfur-bearing VOCs	[91-92]

tions and not general urban exposures. Recently, Bej et al. (2026) have demonstrated that asphalt surfaces emit NMVOCs under ambient conditions and exhibit different day-night oxidation pathways (OH vs. NO_3) leading to ultrafine particle formation from low-volatility precursors [22]. McClean et al. reported considerable variation in inhalation exposure according to the task and reclaimed asphalt pavement (RAP) content, with adjusted mean paver-operator concentrations of 5.0 μg/m^3 in the low-RAP case and 24 μg/m^3 in the high-RAP case [88]. The National Institute for Occupational Safety and Health has also found that generally, the full-shift total particulate concentrations in open-air paving studies are below 1.0 mg/m^3, and highway paving exposures range from 0.075 to 0.48 mg/m^3 [89]. Since these measurements are heterogeneous and often analyte-specific, controlled animal inhalation studies can still be used for dose-response experiments. Exposure to asphalt fumes at 23.6 ± 3.3 mg/m^3 for 3.5 h/day over 5 days in rats altered pulmonary xenobiotic metabolism at a cumulative dose of 413.5 ± 57.7 mg·h/m^3 without acute lung injury [90]. The U.S. Environmental Protection Agency establishes standards for criteria air pollutants rather than asphalt fumes specifically; the Occupational Safety and Health Administration has not established an upper exposure limit for asphalt fumes, and compound-specific monitoring of sulfur-containing VOCs in paving environments is therefore required [91-92].

Implications for Sustainable Asphalt Design

Monitoring of emissions, assessment of exposure and health risk evaluation are all interconnected; therefore, forward-looking emission reduction measures need to be taken in asphalt technology. Lowering the production temperature with WMA technology, modifying the binder chemistry by adding functional additives, and strengthening process control in asphalt plants have all achieved reductions in emissions. Functional additives are likely to reduce emissions by more than 40% and improve both occupational health and the environment [69, 82-83]. All these research efforts on asphalt emissions have gradually revealed the necessity of an all-encompassing approach involving materials science, environmental engineering and public health. As efforts are being made to give new uses to refinery by-products, such as elemental sulphur in asphalt, careful assessments of emission characteristics and other health risks need to be conducted to ensure that these green-technology materials do not lead to new environmental or occupational hazards.

Future Research Directions

Research on sulphur-modified asphalt and its application in using refinery by-products is expanding, but some deficiencies in the current studies remain. Based on the above deficiencies, future research should aim to achieve the goals of high performance and environmental safety for sulfurisation of bitumen in a sustainable way.

First, continuous emission monitoring should be introduced to record alterations in the distribution of emissions over the entire service period of the asphalt pavement. Most of the existing studies focus on emissions during the mixing and paving stages, but the chemical composition of aged asphalt has changed due to oxidation, UV exposure and thermal cycling. Whether these altered emissions become more or less toxic over time remains unclear. Continuous monitoring in the field and aging tests in the laboratory can be carried out to learn more about the stability and long-term exposure effects of asphalt emissions.

To improve the comparability of the studies and better reflect field conditions, future work should report emissions from unaged, short-term aged, and long-term aged binders according to standardised laboratory ageing protocols. At present, most aging practices are limited to thermal conditioning and fail to consider other principal environmental stressors that cause in-service degradation, such as ultraviolet (UV) radiation and humidity. Recently, Shariati et al. (2026) have shown that both UV radiation and moisture are associated with an increase in VOC emissions and the generation of secondary pollutants; therefore, they should be added to the standard test system [34]. Therefore, the laboratory ageing sequences should be combined with chamber-based emission tests in a controlled-temperature, UV and humidity environ to improve the comparability of studies [34, 68, 72, 93].

Second, there is a large-scale development opportunity for bio-based stabilizers and modifiers to reduce sulphur volatility and suppress harmful emissions. Newer research has shown that inverse vulcanisation can be carried out to make functional polymers from elemental sulphur and other organic materials, such as biomass or waste-derived substances. Hou et al. (2023) made bitumen-like polymers by inverse vulcanisation of elemental sulphur, for instance. The resulting sulfur-containing polymers exhibited bitumen-like rheological behavior, self-healing ability, and adjustable mechanical properties and were demonstrated in applications including waterproof sealants and non-Newtonian speed bumps. Their scalable preparation and low material cost further demonstrate the potential of waste sulfur as a feedstock for functional road-related materials [99]. Similarly, Mousavi et al. (2024) introduced a biogenic catalyst derived from silver grass to facilitate sulfur polymerization, showing improved polymer elasticity, moisture resistance, and structural integrity compared with conventional catalysts. These advances suggest that biomass-derived catalysts and bio-based reactants could enable environmentally benign pathways for converting surplus sulfur into stable polymeric modifiers [52].

Inverse vulcanization provides an effective pathway for mitigating sulfur-related emissions by stabilizing elemental sulfur within polymeric networks and limiting its reversion to volatile species. In this process, sulfur radicals formed during ring-opening are chemically bound to organic crosslinkers, forming stable C–S bonds and preventing reversion to volatile sulfur species. The resulting sulfur–organic networks, particularly through allylic and olefinic reactions, enhance structural stability and improve sulfur retention, reducing the potential for volatilization during production and service. Catalyzed inverse vulcanization further improves this process by facilitating interactions between sulfur and the organic phase while suppressing undesirable byproducts, such as hydrogen sulfide (H_2S). These mechanisms highlight the potential of inverse vulcanization to reduce sulfur-carrying VOC emissions [53].

Building on these underlying mechanisms, recent studies have translated inverse-vulcanization chemistry into practical bitumen-modification strategies. Wręczycki et al. (2022) directly evaluated sulfur-organic copolymers produced through inverse vulcanization as modifiers for bitumen binders. The study evaluated polysulfides synthesized from elemental sulfur and dicyclopentadiene, as well as systems containing limonene and styrene. The modification increased the softening point by up to 7 °C, reduced penetration, improved resistance to aging and permanent deformation, and increased adhesion to glass from 25% to 87%. These findings demonstrate that inverse-vulcanized sulfur-rich copolymers can improve the high-temperature stability of bitumen binders [100].

Although inverse vulcanization can stabilize sulfur in bitumen, the extent to which aging, milling, reheating, and blending with virgin binder may cleave or rearrange C–S and S–S linkages remains unclear. Future RAP studies should therefore examine binder extraction and recovery, compatibility during re-blending, re-emission of sulfur-containing volatiles during reheating, and the retention of cracking resistance after repeated recycling cycles.

Third, advanced health impact studies remain critical for understanding the broader implications of asphalt emissions. Future research should integrate toxicological experiments, epidemiological investigations, and computational modeling to examine the long-term effects of exposure to asphalt emission mixtures. Particular attention should be given to neurological, respiratory, and metabolic outcomes, as well as differences in vulnerability among demographic groups. Combining exposure science with mechanistic toxicology and advanced modeling tools will help establish clearer links between emission chemistry and biological effects, ultimately informing safer design and regulation of asphalt materials. Collectively, these research directions highlight the importance of integrating materials innovation, environmental monitoring, and health science in the development of next-generation sulfur-modified asphalt technologies. Advances in inverse vulcanization and bio-based additives, coupled with improved emission-mitigation strategies and health-risk evaluation, offer promising pathways to transform surplus elemental sulfur into sustainable infrastructure materials.

Conclusion

The increasing accumulation of elemental sulfur from petroleum refining has motivated efforts to valorize this byproduct in asphalt materials. While sulfur incorporation and sulfur-derived polymers can improve certain performance characteristics of asphalt and reduce reliance on petroleum-based binders, their broader environmental and health implications remain insufficiently understood. Asphalt emissions consist of complex mixtures of volatile organic compounds and sulfur-containing species that can evolve during production, paving, and long-term aging. Although recent studies suggest potential neurological and cellular impacts associated with prolonged exposure to asphalt emissions, the specific role of sulfur modification in governing these risks remains largely unknown. Sulfur addition may not necessarily lead to a uniform increase or decrease in total emissions; rather, it can fundamentally alter the chemical composition, volatility distribution, and transformation pathways of emitted compounds, potentially changing their environmental persistence, atmospheric reactivity, and biological impacts. Addressing these knowledge gaps requires systematic investigation of emission factors, chemical speciation, exposure pathways, and biological responses associated with sulfur-containing asphalt materials. Advancing this understanding is essential to ensure that sulfur valorization strategies improve pavement sustainability while avoiding unintended environmental and public health impacts. Future research should focus on establishing standardized emission assessment protocols, systematically characterizing VOCs and other potentially hazardous constituents, and evaluating the recyclability, durability, and long-term performance of sulfur-modified asphalt.

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Data Availability Statement

All data used in this study have been included in the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the results of the study reported in this paper.

Use of AI statement

During the preparation of this manuscript, the authors used ChatGPT (GPT-5.6), developed by OpenAI, to assist with language editing, sentence clarity, organization, and reference-order consistency checks. After using the tool, the authors thoroughly reviewed and revised the material as needed and assume full responsibility for the final content of the publication.

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